

**DEVELOPMENT OF A NEW COST-EFFECTIVE POLYMER
GEL FOR WATER CONTROL IN OIL AND GAS WELLS**

BY

KHALID SAAD MOHAMED ELKARSANI

A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

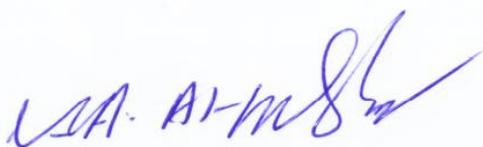
DECEMBER 2013

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **KHALID SAAD MOHAMED EL KARSANI** under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING.**



Dr. Usamah A. Al-Mubaiyedh
Department Chairman



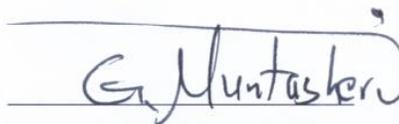
Dr. Salam A. Zummo
Dean of Graduate Studies

Date

20/1/14



Prof. Ibnelwaleed A. Hussein
(Advisor)



Dr. Ghaithan A. Al-Muntasheri
(Co-Advisor)



Dr. Muataz A. Atieh
(Member)



Dr. Mamdouh A. Al-Harathi
(Member)



Dr. Nisar Ullah
(Member)

DEDICATION

**Dedicated to my Mother (Katira Mustafa Ahmed Ali) who died before the completion of
this work**

I pray to Allah to forgive her and admit her in Jannat Al-Firdaus

Dedicated to my father (Saad Mohamed El-karsani)

I pray to Allah to keep him in a perfect health

Dedicated to my wife (Emtithal), my son (Ahmed), and my daughter (Yageen)

I pray to Allah to keep them in a perfect health

ACKNOWLEDGMENTS

In the name of Allah, the most Beneficent, the most Merciful

All praises to Allah and the peace and blessing of Allah be upon his prophet, Mohamed (S.A.W). First of all I would like to thank King Fahd University of Petroleum & Minerals for providing me the opportunity to pursue my PhD degree and great thanks to the Department of Chemical Engineering. Also, my special thanks to King Abdul Aziz City for Science and Technology (KCAST) for providing the financial fund for this research under research grant # AR-30-291. My great thanks also to Prof. Ibnelwaleed Ali Hussein my thesis advisor. In fact he was more than academic advisor. Your continuous help, support, guidance and cooperation are the main factors for completing this research. With high appreciation I would like to thank Dr. Ghaitan Ahmed Al-Muntasherri my co-advisor. His continuous help and support can not be quantified. I learned a lot from him and he introduced me to the area of polymeric gels. He was always available for me even after working hours. Dr. Abdullah Saad Sultan the chairman of the Department of Petroleum Engineering and the Director of the Center of Petroleum & Minerals helped me a lot during this research. With heartfelt appreciation, I thank all the committee members: Dr. Mamdouh Ahmed Al-Harhi, Dr. Mutaz Ali Ateih, and Dr. Nisar Ullah. A special thanks are due to Mr. Abdelrahim Mohmmadain (Department of Petroleum Engineering) for helping me with core-flooding set-up fabrication and assembly. Mr. Mohammed Arab (chemistry department) is also acknowledged for his help with the NMR tests. Last but not least, thanks are due to my wife, my son, and my daughter for their patience and support. Their continuous question “When are you going to finish?” has now found an answer.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	iv
LIST OF TABLES	x
LIST OF FIGURES	xii
THESIS ABSTRACT (ENGLISH)	xvii
THESIS ABSTRACT (ARABIC)	xix
CHAPTER ONE	1
INTRODUCTION	1
1.1 Water Production.....	1
1.2 Thesis Summary.....	2
CHAPTER TWO	6
Polymer Systems for Water Shutoff and Profile Modification: A Review over the Last Decade	6
Abstract.....	6
2.1 Introduction.....	7
2.2 Discussions	11
2.2.1 Developments in PHPA Cross-Linked with Chromium	20

2.2.2. Colloidal Dispersion Gels (CDGs)	23
2.2.3. Developments in Organically Cross-linked Gels.....	26
2.2.4. Microgels for Deep Modification of Water Injection Profiles.....	38
2.3. Environmental Issues and Toxicity.....	48
2.4. Conclusion	49
2.5 References.....	51
CHAPTER THREE	68
Abstract.....	68
3.1 Introduction.....	69
3.2 Experimental	73
3.2.1 Materials	73
3.2.2 Methods.....	74
3.3 Results and Discussion	77
3.3.1 Analysis of the NMR Spectra	77
3.3.2 Hydrolysis of Polyacrylamide.....	78
3.3.3 Effect of Salts on Cross-linking of PHPA with PEI	84
3.3.4 Insights into Retardation Mechanisms of PAM/PEI Crosslinking Reactions	90
3.3.5 Thermal stability of PAM/PEI gel	97
3.3.6 Compatibility of Salts with PAM/PEI Gel System.....	101

3.3.7 Characterization of PHPA by Fourier Transform Infra-Red (FTIR)	103
3.4 Conclusions.....	105
3.5 References.....	107
CHAPTER FOUR.....	114
Gelation of a Water Shut-off Gel at High Pressure and High Temperature: Rheological Investigation	114
Abstract.....	114
4.1 Introduction.....	115
4.2 Experimental studies.....	121
4.2.1 Materials	121
4.2.2 Procedure	123
4.2.3 Instrument	123
4.3 Results and Discussion	125
4.3.1 Effect of temperature	126
4.3.2 Effect of polymer concentration	128
4.3.3 Influence of Cross-linker Concentration.....	131
4.3.4 Effect of Salinity	134
4.3.5 Effect of Initial pH.....	136
4.3.6 Influence of Retarders.....	138

4.3.7 Gel Yield Stress and Extrusion through Fracture	143
4.4 Conclusions.....	146
4.5 References.....	147
CHAPTER FIVE	153
Gelation Kinetics of PAM/PEI System: DSC Investigation	153
Abstract.....	153
5.1 Introduction.....	154
5.2 Materials and sample preparation	158
5.3 Differential Scanning Calorimetry (DSC)	159
5.4 Results and Discussion	159
5.5 Conclusions.....	168
5.6 References.....	170
CHAPTER SIX	174
Evaluation of PAM / PEI Gel System for Water Shut-Off at High Temperature and Pressure: Laboratory Study.....	174
Abstract.....	174
6.1 Introduction.....	175

6.2 Experimental Studies	177
6.2.1 Materials	177
6.2.2 Procedure	179
6.2.3 Equipment	181
6.3 Results and Discussion	183
6.3.1 Gelation of PAM/PEI System with Retarders	183
6.3.2 Efficiency of PAM/PEI System in Porous Media.....	187
6.4 Conclusions.....	197
6.5 References.....	199
CHAPTER SEVEN.....	202
Conclusions and Future Work.....	202
7.1 General Conclusions	202
7.2 Future Work.....	206

LIST OF TABLES

Table 2.1: Lab tested and field applied classification for the various polymer systems reported in this paper.....	18
Table 2.2: Wells types where the applied polymer systems were applied.....	20
Table 2.3: Summary of developments in chromium cross-linked gels.....	21
Table 2.4: Summary of organically cross-linked gels	27
Table 2.5: Summary of field results for PDVSA-Intevep polymer gel system applied in Venezuela	28
Table 2.6: Summary of chemical retarders reported for the PAtBA/PEI system	36
Table 2.7: Microgels for deep modification of water injection profiles.....	39
Table 3.1: Chemical analysis of mixing waters used in the experiments	74
Table 3.2: PAM Hydrolysis rate constant at 120°C (248°F) at different salt concentrations	83
Table 3.3: Effect of salts (12,000 ppm) on PHPA/PEI system at 120°C (248°F).....	88
Table 3.4: Sydansk strength codes (Sydansk, 1990).....	99
Table 3.5: Bottle testing of PAM/PEI gels after 16 weeks of thermal treatment at 150°C (302°F) in different types of mixing waters	100
Table 4. 1: Summary of storage modulus data reported in literature for polymer gels	118
Table 4. 2: Chemical analysis of mixing waters	122
Table 6.1: Specifications of the cores used for polymer gel evaluation	178
Table 6.2: Elemental analysis of Berea sandstone and Indiana linstone cores.....	179
Table 6.3: Chemical analysis of the formation brine.....	180

Table 6.4: Storage modulus and gelation time for PAM/PEI (9/1) wt% gel system at 116°C
(240.8°F) after 10 hours with different retarder concentration 186

Table 6.5: Percent permeability reduction (R_k) in Berea sandstone core at 150°C (302°F) 192

Table 6.6: Percent permeability reduction (R_k) in Indiana limestone core at 150°C (302°F)..... 197

LIST OF FIGURES

Figure 2.1: Chemical structure of polyacrylamide (PAM) (Kurenkov et al., 2001).....	12
Figure 2.2: Hydrolysis of amide groups under alkaline conditions	12
Figure 2.3: Chemical structure of polyacrylamide vinylpyrrolidone (VP).....	12
Figure 2.4: Chemical structure of acrylamide / 2-acrylamido-2-methylpropane Sulfonic Acid (AMPS) Copolymer.	12
Figure 2.5: Chemical structure of PEI (Hardy et al., 1999).....	13
Figure 2.6: Chemical structure of chitosan (Reddy et al., 2003)	13
Figure 2.7: Overview of the available technologies reviewed in this paper	14
Figure 2.8: Urethane synthesis by reacting isocyanate with alcohol (Shafian et al., 2010; Petrie, 2001).....	30
Figure 2.9: Chemical structure of polyacrylamide tert-butyl Acrylate (PAtBA)	31
Figure 2.10: Cross-linking through transamidation reaction	31
Figure 2.11: Cross-linking through nucleophilic attack	31
Figure 2.12: Synthesis of microspheres from acrylamide and N, N' methylene bisacrylamide (Lei et al., 2011)	41
Figure 3.1 Viscosity evolution of the PAM / PEI, (7/0.3) wt% system at 150°C (302°F).....	71
Figure 3.2 Hydrolysis of amide groups under alkaline conditions	72
Figure 3.3: 13C NMR spectrum of neat sample of PAM	78
Figure 3.4: Hydrolysis of neat PAM at 120°C (248°F) & pH 10.....	79
Figure 3.5: Effect of high salts concentration (30,000 ppm) on DH of PAM at 120°C (248°F) ..	81
Figure 3.6: Effect of salts concentration (0.0114 moles) on D _H of PAM at 120°C (248°F).....	82

Figure 3.7: Effect of number of moles of NaCl on DH of PAM at 120°C (248°F), 20 wt% PAM	84
Figure 3.8: Effect of salts on cross-linking of PHPA (7 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)	85
Figure 3.9: Effect of salts on cross-linking of PHPA (11.83 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)	86
Figure 3.10: Effect of salts on cross-linking of PHPA (16.92 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)	87
Figure 3.11: Effect of salts on cross-linking of PHPA (57.8 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)	89
Figure 3.12: Effect of degree of hydrolysis on gel strength at 120°C (248°F)	90
Figure 3.13: Effect of salt type on PAM viscosity at 10 s ⁻¹ after ageing at 120°C (248°F) for 7 days for a salt concentration of 7,500 ppm	92
Figure 3.14: PAM cross-linked with different PEI concentrations & 1,200 ppm NH ₄ Cl	93
Figure 3.15: Effect of distilled, field, and sea water on D _H of PAM at 120°C (248°F), 20 wt% PAM	94
Figure 3.16: Effect of NH ₄ Cl on PAM hydrolysis (DSC scan)	95
Figure 3.17: Effect of salts on onset gelation temperature for PAM/PEI (9/1) wt%	96
Figure 3.18: Effect of salts on heat of gelation for PAM/PEI (9/1) wt%	97
Figure 3.19: A sample of PAM/PEI, (9/1) wt% in distilled water, (a) 0 day, (b) 1 day	98
Figure 3.20: Sample of PAM/PEI, (9/0.3) wt% aged for 49 days at 150°C (302°F)	99
Figure 3.21: Sample of PAM/ PEI, (7/1) wt% with 30,000 ppm retarders: (a) NaCl,.....	103

Figure 3.22: FTIR spectrum of PAM with, 7,500 mg/l aged at 120°C (248°F) for 3 days.....	104
Figure 3.23: FTIR spectrum of PAM with 30,000 mg/l aged at 120°C (248°F) for 3 days (a) neat PAM (b) NaCl (c) NH ₄ Cl.....	105
Figure 4.1: Effect of pressure on dynamic shear measurement	124
Figure 4.2: Strain sweep of PAM / PEI (7/0.) wt% at 130°C (266°F) and 1 Hz.....	125
Figure 4.3: Effect of temperature on elastic modulus.....	128
Figure 4.4: Elastic modulus of PAM/PEI with different polymer concentrations.....	130
Figure 4.5: Equilibrium elastic modulus as a function of polymer concentration.....	131
Figure 4.6: Effect of cross-linker concentration on elastic modulus	133
Figure 4.7: Equilibrium elastic modulus as a function of cross-linker concentration	134
Figure 4.8: Effect of salinity of mixing water on equilibrium elastic modulus	136
Figure 4.9: Effect of initial pH value on equilibrium elastic modulus	137
Figure 4.10: Effect of NaCl concentration on elastic modulus.....	139
Figure 4.11: Effect of NH ₄ Cl on elastic modulus with different polymer concentration	140
Figure 4.12: Effect of NH ₄ Cl concentration on elastic modulus	141
Figure 4.13: Effect of salts (12,000 mg/l) on elastic modulus in distilled water.....	142
Figure 4.14: Effect of salts (12,000 mg/l of NaCl and NH ₄ Cl) on elastic modulus in field water	143
Figure 4.15: Frequency sweeps for gel samples with different PAM concentrations	145
Figure 4.16: Yield Stress determination of PAM/PEI at 130°C (266°F)	145

Figure 5.1: Dynamic DSC scan of PAM/PEI system (9/1) mass ratio and final heating temperature of 120°C (a) Heat flow vs. temperature, (b) Heat flow vs. time	161
Figure 5.2: Alkaline hydrolysis of PAM groups (Al-Muntasheri et al. 2007; El-karsani et al, submitted for publication)	162
Figure 5.3: Dynamic DSC scan of PAM up to 120°C (20 mass % activity)	162
Figure 5.4: Experimental data versus predicted data (Rate model) for PAM/PEI (9/1) mass ratio and heating temperature up to 120°C in (a) distilled water, (b) sea water	164
Figure 5.5: Fractional conversion as a function of time for the gelation of PAM/PEI (9/1) mass ratio at different salinities	166
Figure 5.6: Effect of salts (1.2 g/L) on fractional gelation of PAM/PEI (9/1 mass ratio) for a final temperature of 120°C.....	167
Figure 5.7: Avrami plots for PAM/PEI at different temperatures for the non-isothermal regime	168
Figure 6.1: A schematic diagram of core-flooding apparatus.....	182
Figure 6.2: Effect of retarders on gelation time and storage modulus of PAM/PEI (9/1) wt% gel system	185
Figure 6.3: Effect of retarders on gelation time and storage modulus of PAM/PEI (9/1) wt% gel system at different salt concentration	186
Figure 6.4: Viscosity vs. shear rate for the 9/1 PAM/PEI gelant at 25°C.....	187
Figure 6.5: Pressure drop as a function of pore volumes in a core-flow experiment	189
Figure 6.6: Pressure drop as a function of time during gelant placement in Berea sandstone core	190

Figure 6.7: Sample from Berea sandstone core effluents ((PAM/PEI) 9/1 wt% with
6,000 mg/l NH₄Cl) aged beside the core-holder for 5 days 191

Figure 6.8: Pressure data as a function of pore volumes injected in Indiana limestone core
with initial permeability to brine of 2.98 mD 194

Figure 6.9: Pressure data vs. time during gelant placement in Indiana limestone core
(with initial permeability to brine of 2.98 mD 195

Figure 6.10: Pressure data as a function of pore volumes injected in Indiana limestone core
with initial permeability to brine of 2.98 mD 196

THESIS ABSTRACT (ENGLISH)

Name : KHALID SAAD MOHAMED ELKARSANI
Title : DEVELOPMENT OF A NEW COST-EFFECTIVE POLYMER GEL
FOR WATER CONTROL IN OIL AND GAS WELLS
Major Field : CHEMICAL ENGINEERING
Date of degree : DECEMBER, 2013

Excessive water production from petroleum reservoirs has been a serious problem. Polymer gel is one of the common successful treatments. In this study, cheap polyacrylamide (PAM) polyethylenimine (PEI) gel system was developed for use at high temperature applications. The effect of salts on PAM degree of hydrolysis was studied by using NaCl and NH₄Cl. These salts showed good compatibility with field mixing water whereas, NaCO₃ (a high effective retarder) was observed to form a white precipitate with PAM / PEI at high temperatures. ¹³C NMR and DSC revealed that NH₄Cl increased PAM degree of hydrolysis more compared to NaCl. Rheological measurements showed that NH₄Cl decrease the viscosity of the hydrolyzed PAM. The cross-linking retardation was concluded to be due to charge shielding effect rather than decreased PAM hydrolysis. The strength of PAM / PEI was examined through dynamic measurements taking into account different parameters like temperature, polymer and cross-linker concentrations, initial pH, salinity, salt (retarder) effect. The gelation kinetics was studied by DSC and modeled using rate-based processes. The developed PAM / PEI gel system was evaluated in sandstone and carbonate cores at high temperature (150°C) and pressure (1000 psi). A reduction in permeability of about 94% was obtained in sandstone core. In the carbonate core, about 99.8% permeability reduction was achieved by PAM / PEI at the same conditions. The

proposed PAM/PEI system proved to provide satisfactory gel strength at high temperature using field water.

DOCTOR OF PHILOSOPHY
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

THESIS ABSTRACT (ARABIC)

الاسم : خالد سعد محمد الكرسي

عنوان الرسالة : تطوير مادة هلامية جديدة قليلة التكلفة للتحكم بإنتاج المياه من ابار النفط والغاز

تاريخ التخرج : ديسمبر 2013

ان انتاج المياه الذائد من المكامن البترولية يعتبر من المشاكل الكبرى في حقول النفط. يعتبر استخدام الهلام البولمري من الطرق الاكثر شيوعا و نجاحا. في هذا البحث تم تطوير هلام بولمري يتكون من البولي اكريل اميد و البولي ايثيلين امين لاستخدامه في التطبيقات ذات درجات الحرارة العالية. تم ايضا دراسة اثر الاملاح (مثبطات تكون الهلام البولمري) على درجة تحلل البولي اكريل اميد. تم استخدام ملح كلوريد الصوديوم و كلوريد الامونيوم و التي اظهرت ملائمه جيده مع مياه الحقول المالحة بينما وجد ان كربونات الصوديوم و التي تعتبر مادة فعالة في تأخير تكون الهلام البولمري غير ملائمه حيث كونت راسب ابيض مع الهلام البولمري. باستخدام تقنيات طيف الرنين النووي المغنطيسي و قياس فرق الحرارة وجد ان كلوريد الامونيوم يذيد من درجة تحلل البولي اكريل اميد اكثر من كلوريد الصوديوم. باستخدام تقنية الريولوجيا لوحظ ان كلوريد الامونيوم يقلل من لزوجة البولي اكريل اميد المتحلل. استنتج من ذلك ان ميكانيكية تأخير تكون الهلام البولمري هي عن طريق حجب الشحنات السالبة في البولي اكريل اميد المتحلل و ليس خلال تقليل درجة تحلل البولي اكريل اميد. تم ايضا دراسة قوة الهلام البولمري المتكون من البولي اكريل اميد و البولي ايثيلين امين من خلال اثر عدة عوامل مثل درجة الحرارة , تركيز البولي اكريل اميد و البولي ايثيلين امين, الرقم الهيدروجيني الابتدائي, الملوحة, و الاملاح (مثبطات تكون الهلام البولمري). تمت دراسة حركية تفاعل تكون الهلام البولمري باستخدام تقنية قياس فرق الحرارة و تم ايضا محاكاة معدل تكون الهلام البولمري. تم تقييم الهلام البولمري لحجب المياه في درجات الحرارة العالية و الضغط العالي. وجد ان الهلام البولمري المطور قادر على تقليل نفاذية الصخور الرملية للمياه بنسبة 94% تقريبا, بينما اظهر نسبة تقليل للنفاذيه 99.8% في الصخور الكرونية. ان الهلام البولمري المقترح اثبت قوة معتبره عند درجات الحرارة العالية باستخدام مياه الحقول المالحة.

جامعة الملك فهد للبترول و المعادن

قسم الهندسة الكيميائية

CHAPTER ONE

INTRODUCTION

1.1 Water Production

When an oil or gas field matured, there are more volumes of water produced compared to oil. The large production of water causes severe operational problems as well as an environmental impacts. The problems that associated with water production include for example corrosion and scale (Donham, 1991; Nasr-El-Din, 2003; Merdhah and Yassin, 2009; Al-Tolaihy and Bukhari, 2010). In addition, there is a loss of oil and gas with excess water, and there is a need to construct larger gas oil separation plants (Bailey et al., 2000) which is not preferable from economic point of view. The produced water may contain mercury, arsenic, and other salts (Hibbeler and Rae, 2005), so that will lead to an environmental impact if this water is disposed.

In oil industry, there are different methods used to describe the production of water. These methods include: using submersible pump which will give an indication about the water cut (water cut is defined as the volume fraction of water in the produced liquid hydrocarbon), production plots in terms of time, reservoir simulation analysis. The most quantitative method used in the oil field to estimate the water production is the water to oil ratio (WOR) which is flow rate of water to the flow rate of oil in barrels/day. In 2000, it has been reported that the universal WOR is 3 (Bailey et al., 2000).

Different mechanical and chemical methods can be used to deal with the produced water. The mechanical methods include the application of specific completion tools, casing replacement or water separation by using particular plants. Some remediate chemical treatments were designed and implemented in the oil field to reduce or totally shutoff water. One of these is to

use silicate (Grattoni et al., 2001; Nasr-El-Din and Taylor, 2005; Elewaut et al., 2006; Al-Dhafeeri et al., 2008; Boye et al., 2011), resins (Seright et al., 2003), cements and polymer gels (Seright et al., 2003; Sydansk 2007; Lightford et al., 2008; Al-Muntasheri et al., 2010). In-situ polymerization was also used in the past to shut off water produced through perforations (Saltel et al., 1999). Some reasons make polymer gels the most common extensively applied in oil field. This is because for their low cost compared to other methods, the ease of pumping, and the penetration into the rock matrix. Polymer gels is prepared by cross-linking a polymer with a cross-linker such as PAtBA with PEI. Recent research revealed that some low cost polymers can be used such as polyacrylamide (PAM) instead of the existing one (PAtBA). In addition, PAtBA showed some compatibility problems with the mixing brines of some reservoirs. This research aims at developing a new cost-effective polymer gel by using PAM. Also, the cross-linking needs to be delayed to give the adequate time for field operators to place the system safely in the target zones without prior gel formation in the tubings. So, this project will also develop a cost effective retarders that are compatible with the high saline mixing brines.

1.2 Thesis Summary

This section gives general outline of this manuscript-based thesis.

CHAPTER TWO

This chapter reviewed the polymer systems that were studied in the last ten years. For high temperature applications, valuable informations were collected for the professions working in the oil field in the area of water shutoff by using polymer systems. The literature revealed that the polymer systems developed during the past decade can be categorized into two groups. First, polymer gels for water shutoff near wellbore area in which a polymer is cross-linked with

organic or inorganic cross-linkers. The second group is concerned with deep treatment of water injection wells diverting fluids away from high permeability zones (thief zones). These thief zones take most of the injected water, which results in leaving a lot of oil unrecovered. For the two groups, different systems were reviewed giving the chemistry as well as the available field application data.

CHAPTER THREE

This chapter discussed the thermal stability of the organically cross-linked polymeric gels at high temperature for about four months. Also, the effect of salts on the polymer hydrolysis was investigated through ^{13}C NMR since these salts are used to delay the cross-linking reaction. The compatibility of these salts with the polymer gel system was also examined. It was found that sodium chloride and ammonium chloride are compatible with PAM/PEI gel system, but sodium carbonate formed a white precipitate, hence, it is incompatible and was ruled out as a retarder. Other techniques were used to confirm the ^{13}C NMR data such as FT-IR, steady shear viscosity, and DSC. In addition, the effect of retarders on cross-linking of partially hydrolyzed polyacrylamide (PHPA) with PEI was investigated. It was observed that these retarders are also effective in increasing the gelation time in case of a hydrolyzed polymer.

CHAPTER FOUR

In this chapter, the strength of PAM/PEI gel system was studied extensively by using dynamic rheology. Different parameters were examined such as polymer and cross-linker concentrations, temperature, mixing water, pH, and the effect of retarders. The elastic modulus was found to increase with temperature from 120 to 130°C (248 to 266°F), but no more appreciable increase

was observed above 130°C. Also, the elastic modulus increased with the increase in polymer and cross-linker concentrations. Salinity of mixing water has a negative impact on elastic modulus. Moreover, the alkaline and acidic media produced stronger gel compared to neutral media. However, the gelation time is higher in neutral media. The effect of retarders (NaCl & NH₄Cl) which are used for gelation time delay was also examined. These retarders were observed to decrease the elastic modulus of the polymer gel. NH₄Cl was found to decrease the elastic modulus more compared with NaCl which showed negligible effect. However, from the aspect of gelation time, NH₄Cl is very effective in increasing the gelation time even at high polymer concentrations.

CHAPTER FIVE

The gelation kinetics was studied by the use of differential scanning calorimeter (DSC) over the temperature range 80° to 120°C. The DSC dynamic scan showed two consecutive peaks. An endothermic peak was observed at low temperature due to PAM alkaline hydrolysis. Another exotherm was observed at ~ 70°C which corresponds to the onset of cross-linking of PAM and PEI. It was found that high temperatures lead to high release of heat due to gelation. The effect of salts on the cross-linking was also examined. More delay in cross-linking was observed in the case of NH₄Cl compared to NaCl. The gelation kinetics was modeled using a rate process model that relates fractional gelation with time. Further, Avrami model, usually used to study crystallization kinetics, was also used to model the gelation process. Kinetic parameters were obtained from the two different models and the results showed good agreement with experimental data.

CHAPTER SIX

PAM / PEI gel system was evaluated through core-flooding system. The injectivity of the PAM/PEI in high temperature formations required the use of a retarder to elongate the gelation time of the subject gel in order to achieve a successful placement. NaCl and NH₄Cl were evaluated for gelation time delay at different concentrations. Dynamic oscillatory measurements were conducted by using these retarders to find an accepted gelation time with a higher strength. NH₄Cl was found to be a good candidate for application to be used with PAM/PEI system. The injectivity of PAM/PEI was tested in Berea sandstone core with initial permeability of ~ 45 mD. The post treatment of the system showed a permeability reduction of ~ 94%. Moreover, Indiana limestone core was used to examine the efficiency in tight carbonate lithology. More retardation was required for gelant placement in Indiana limestone cores. The developed polymer gel reduced the permeability to brine by 99.8%.

CHAPTER SEVEN

Brief conclusions as well as suggested future work for the area of water control is presented in this chapter.

CHAPTER TWO

Polymer Systems for Water Shutoff and Profile Modification: A Review over the Last Decade

Khalid M. El-Karsani¹, Ghaiathan A. Al-Muntasheri^{2} & Ibbelwaleed A. Hussein³*

*^{1&3}Chemical Engineering Department, King Fahd University of Petroleum & Minerals; Dhahran
31261, PO BOX 5050, Saudi Arabia*

²EXPEC Advanced Research Center, Saudi Aramco, Dhahran 31311, PO Box 62, Saudi Arabia

**[This chapter had been published online on May,7, 2013 in Society of Petroleum Engineers
Journal (SPEJ); DOI : <http://dx.doi.org/10.2118/163100-PA>]**

Abstract

Unwanted water production is a serious issue in oil and gas producing wells. It causes corrosion, scale and loss of productivity. One method to treat this problem is to chemically reduce unwanted water. This paper discusses the use of polymer systems for this purpose where a thorough review of available literature over the last decade is presented. In this paper, field application data using various polymer systems are summarized over the range: 40 to 150°C (104 to 302°F). These applications cover a wide range of permeabilities from 20 to 2,720 mD in sandstone and carbonate reservoirs around the globe. Moreover, the review revealed that the last decade developments can be categorized into two major types. First, polymer gels for total water shutoff in the near wellbore area where a polymer is cross-linked either with an organic or an inorganic cross-linker. The second type is concerned with deep treatment of water injection wells diverting fluids away from high permeability zones (thief zones). These thief zones take most of the injected water, which results in leaving a lot of oil unrecovered. For the total blocking gels,

various systems were identified such as: polyurethane resins, chromium (Cr^{+3}) cross-linking terpolymers, Cr^{+3} cross-linking foamed partially hydrolyzed polyacrylamide (PHPA) and nanoparticle polyelectrolyte complexes (PECs) sequestering Cr^{+3} for elongation of its gelation time with PHPA. In addition, polyethyleneimine (PEI) was identified to cross-link various polyacrylamide (PAM)-based polymers. The PDVSA Research & Development Center developed a PAM-based thermally stable polymer and an organic cross-linker. The system is applicable for a wide temperature range from 50 to 160°C (130 to 320°F).

For the deep modification of water injection profiles in water injection wells, two systems were identified. Namely, microspheres prepared from PAM monomers cross-linked with N, N' methylene bisacrylamide, and microspheres produced by cross-linking 2-acrylamido-2-methylpropane sulfonic acid (AMPS) with diacrylamides and methacrylamides of diamines (Bright Water technology). This paper highlights all major developments in these areas.

***Corresponding author:**

Email: Ghaithan.muntasheri@aramco.com

2.1 Introduction

Whenever water production exceeds economic limits of a given oil or gas field, the need arises for a process by which produced water is reduced. Approximately, U.S \$40 billion is spent annually to deal with the excessive water produced from oil and gas reservoirs (Bailey et al., 2000; Seright et al., 2003). More recent publications indicate that this number has increased to U.S \$45 billion in the year 2002 (Mercado et al., 2009; Boye et al., 2011). Costs data on more recent years is lacking. Data is available on the amount of produced water. The production of water was reported to be 210 million barrels per day (210,000,000 BD) globally in the year 1999 (Veil et al., 2004). Bailey et al. (2000) reported the same figure for the year 2000. This amount

increased to 249, 000,000 BD in the year 2005 (Khatib, 2007). The disposal of produced water affects the environment seriously especially if the produced water contains mercury, arsenic, and other salts (Hibbeler and Rae, 2005). Water is also responsible for most of the corrosion and scale problems in the oilfield (Donham, 1991; Nasr-El-Din, 2003; Merdhah and Yassin, 2009; Al-Tolaihy and Bukhari, 2010). There are mechanical and chemical methods to deal with excessive water production. The mechanical methods include the application of particular completion tools, casing replacement or separation of produced water by use of hydro-cyclones (Vega et al., 2012). Chemical methods include silicate (Grattoni et al., 2001; Nasr-El-Din and Taylor, 2005; Elewaut et al., 2006; Al-Dhafeeri et al., 2008; Boye et al., 2011), resins (Seright et al., 2003), cements and polymer gels (Seright et al., 2003; Sydansk 2007; Lightford et al., 2008; Al-Muntasheri et al., 2010). In-situ polymerization was also used in the past to shut off water produced through perforations (Saltel et al., 1999). In this technology, an inflatable setting element (ISE) is used to carry a composite sleeve to the specified perforations zone into the well. The composite sleeve is soft and deformable since it is made of thermo-setting resins and carbon fiber. When the tool is set in, heat is supplied to polymerize the resins and the ISE is deflated and removed. The composite sleeve is left as a hard material inside the casing. Some problems and limitations were encountered during the application of this technology (Leighton et al., 2001). No new advancements were captured during the last decade for in-situ polymerization.

Among these chemical methods, polymer gels are considered to be one of the most commonly applied types. This is because of their relatively low cost, ease of pumping and penetration ability into the reservoir. Treatments utilizing polymer gels are generally referred to as Conformance Improvement Treatments (CITs) (Sydansk et al., 2005). This technology is based on the use of a flowable mixture of polymer, cross-linker and water. This mixture of

relatively low viscosity (around 20 cP) is injected into the reservoir. Then, with time and temperature, it forms a physical barrier hindering water production. Yet, these treatments do not differentiate oil and gas zones from those producing water. Thus, it is extremely important that the water source is identified properly before selecting the treatment method (Bailey et al., 2000; Botermans et al., 2001; Seright et al., 2003; Sydansk, 2007; Sydansk and Seright, 2007). In many field cases, water producing zones still produce significant amounts of hydrocarbons. As such, shutting off these zones completely may not be the right option. In these cases, other polymer technologies exist where a polymer is used to decrease the permeability to water more than that to oil (Zaitoun and Kohler, 1988; Sydansk and Seright, 2007). This process is referred to as the disproportionate permeability reduction effect (DPR) (Liang et al., 1993; Liang et al., 1995; Botermans 2001; Stavland et al., 2006). Polymer gels can also be applied in injection wells to improve the reservoir sweep efficiency. This is needed when oil is bypassed by the water in cases where the injected water flows through high permeability channels or fractures. Deep treatment systems can also be used for improvement of reservoir sweep efficiency. In these systems, microgels are suspended in water and then injected into the reservoir where they swell in the presence of water deep inside the reservoir (Chang et al., 2002; Lei et al., 2011).

Important Factors for Successful CITs

The identification of the water source is a key factor for successful CITs. The characterization of water production can be done through different methods. A submersible pump can give an observation for the increase in water cut. Any increase in WORs is a clear indication about excess water production. Also, the production plots as a function of time can be used to assess

the WORs. The water production can also be estimated from reservoir simulation analysis (Seright et al., 2003).

Seright et al. (2003) gives comprehensive strategies for addressing excess water production and suitable treatments. For the problems with flow behind pipes, cement alone could not solve the problem. This is due to its limited penetration into the rock matrix. Thus, to treat excess water production in unfractured wells with cross-flow; cement, sand plugs, carbonate squeezes, and gels can be used. Although gel treatments showed a wide success in treating water production, but there are some difficult and complicated water problems in which gels will not be successful. These problems include three dimensional coning, cusping, and channeling through layers (unfractured) with cross-flow.

In addition to identifying the source of water in a certain oil or gas producing well, there are other important factors to be considered while designing these treatments. First, the gel must be thermally stable where it maintains a reasonable physical structure over extended periods of time (from 6 months to two years) (Moradi-Araghi, 2000). Gelation time is also an important factor. In matrix treatments, it must be long enough so that the gel can penetrate into the reservoir to ensure sufficiently deep placement. Various factors affect gelation time such as: temperature, salinity of mixing water, concentrations of polymer, cross-linker and pH value of the mixed fluid. Hence, proper lab testing must include all of these factors into consideration where tests are done using representative samples of mixing waters from the concerned fields.

Moradi-Araghi (2000) gives a comprehensive review on gels chemistry for water control. Kabir (2001) also gives another review on chemical systems for water and gas shutoff systems. Jaripatke and Dalrymple (2010) discussed the diagnosis of water problems as well as the developments in the technologies used to solve those problems. These reviews did not give

detailed field application data or chemistry information for the treatments reviewed. Sydansk and Romero-zeron (2011) gives abroad review about gel treatments, but some advancements were not captured. To the best of the authors' knowledge, since the year 2000, no article has provided a thorough review on the development of polymer systems for water shutoff and their chemical properties. This is despite the fact that there is a good number of publications that was devoted for various technologies of water shutoff over the last decade. Thus, the objectives of this paper are to (1) provide a thorough review on available polymer systems for total water shutoff and modification of water injection profiles, (2) highlight advantages and shortcomings of these technologies and (3) summarize the field experience with these systems.

2.2 Discussions

Polyacrylamide has been extensively used in preparing polymeric gels (**Figure. 2.1**). It is a cost-effective polymer, which costs about 2 to 4 \$/kg (Morel et al., 2007). Under high temperatures, polyacrylamide undergoes hydrolysis that produces partially hydrolyzed polyacrylamide (PHPA) and ammonia (NH_3) as shown in **Figure. 2.2** (Moradi-Araghi and Doe, 1987; Moradi-Araghi, 2000; Kurenkov et al., 2001). This reaction is responsible for the thermal instability of the produced gel. To enhance the thermal stability of PAM, other groups are incorporated into the polymer backbone such as: vinyl pyrrolidone (VP) (**Figure. 2.3**) and methylpropane sulfonic acid (MPSA) (**Figure. 2.4**). One more way of addressing thermal stability is the use of higher polymer loading (up to 5 wt%) (Sydansk and Southwell, 2000). Cross-linkers can be: inorganic such as Cr^{+3} (Sydansk, 1990) or organic such as polyethyleneimine (Hardy, 1998) (**Figure. 2.5**) or natural such as chitosan (Reddy, 2003) (**Figure. 2. 6**).

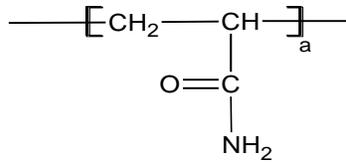


Figure 2. 1:Chemical structure of polyacrylamide (PAM) (Kurenkov et al., 2001)

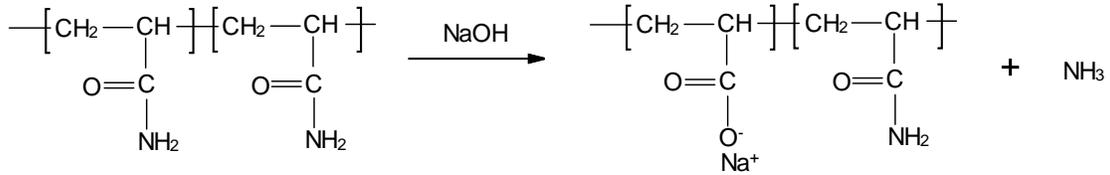


Figure 2. 2: Hydrolysis of amide groups under alkaline conditions

(Moradi-Araghi and Doe, 1987; Moradi-Araghi, 2000; Kurenkov et al., 2001)

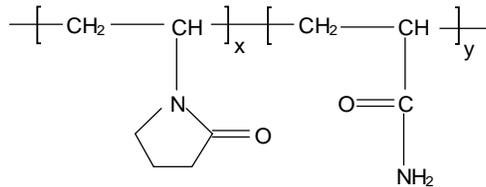


Figure 2. 3: Chemical structure of polyacrylamide vinylpyrrolidone (VP)

(Moradi-Araghi, 2000)

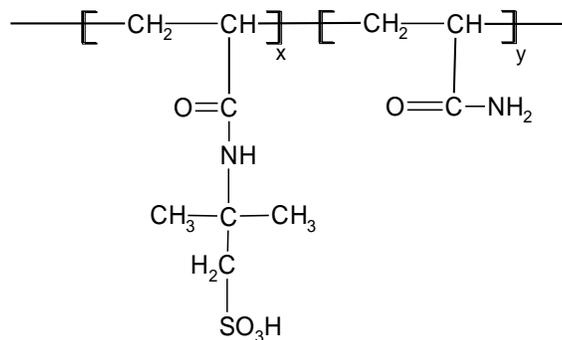


Figure 2. 4: Chemical structure of acrylamide / 2-acrylamido-2-methylpropane Sulfonic Acid

(AMPS) Copolymer.

(Al-Muntasheri et al., 2008)

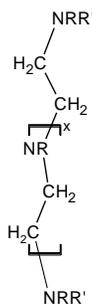


Figure 2. 5: Chemical structure of PEI (Hardy et al., 1999)

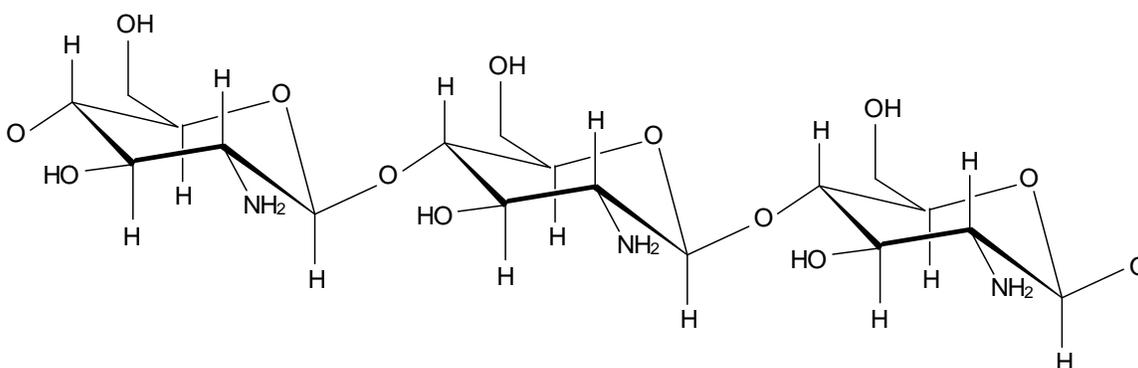


Figure 2. 6: Chemical structure of chitosan (Reddy et al., 2003)

During the last decade, various new chemical properties were introduced as well as modifications of existing products by adding strengthening components. Two types of polymer systems were reviewed in this paper; systems for treating water problems near wellbore area and systems for deep profile modification. **Figure 2.7** gives an overview of the technologies reviewed in this paper.

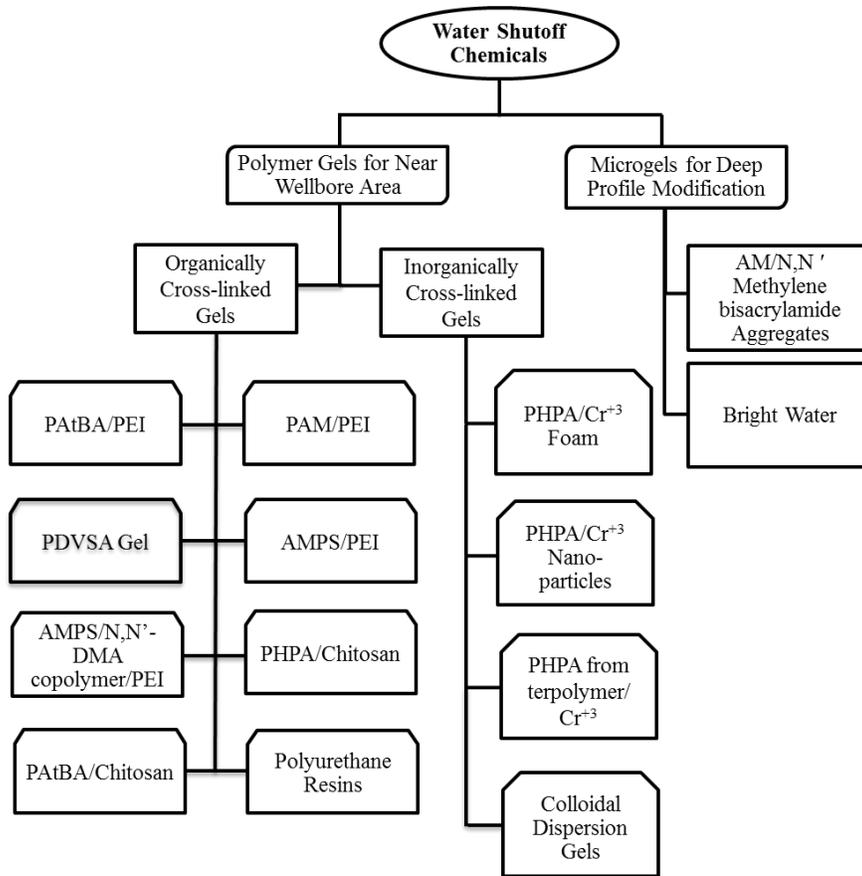


Figure 2. 7: Overview of the available technologies reviewed in this paper

For inorganically cross-linked gels, foam was combined with PHPA/Cr⁺³ gels to treat deep wormholes in Canada (Asghari et al., 2005). Advances in nanotechnologies were used to elongate the gelation time of PHPA/Cr⁺³ gels by sequestering the chromium (Cordova et al., 2008). Moreover, PHPA produced from PAM terpolymers were tested for cross-linking with chromium (Prada et al., 2000). Colloidal Dispersion Gels (CDGs) are based on PHPA cross-linked by aluminum citrate (Al-Assi et al., 2009). Chromium triacetate was also used as a cross-linker to form CDGs in many applications in Argentina (Diaz et al., 2008). The formulated CDGs are suspended in solution as colloids. The gel structure requires low polymer concentration and longer time to be formed compared to bulk gels. CDGs were reported for use in modification of

water injection profiles. There has been a controversy on the propagation of CDGs deep into the rock matrix. In a field pilot study by Chang et al. (2006), it was reported that the injection of CDGs resulted in increasing the residual resistance factor. It was explained that CDGs created a resistance deep in the reservoir without any plugging in the near wellbore area. The authors did not provide legitimate evidence for this claim. Spildo et al. (2009) hypothesized that the increased in oil recovery by CDGs is caused by an increase in microscopic diversion due to the blocking of pore throats by those aggregates. Al-Assi et al. (2009) studied the propagation of CDGs in sandpacks with a permeability of 10 D. The penetration of CDGs was found to be limited to a short distance due to the retention of these particles. More studies of CDGs propagation showed that once the cross-linking occurs, the PHPA/Al⁺³ complexes (i.e., those larger than pore throats) will not propagate through porous rock (Seright, 2007). For this reason, we are reporting CDGs under the treatments of near wellbore area. The paper will discuss these advances in chromium cross-linked gels as well as CDGs (PHPA/Al⁺³).

For the organically cross-linked gels, several systems were identified in this review. Polyurethane resins produced from isocyanate/alcohol reactions were tested for application in PETRONAS fields in Malaysia (Shafian et al., 2010). The system has a controllable gelation time due to the use of blocking materials that do not expose the isocyanate to the reaction with alcohol until a certain temperature is reached. The PDVSA Research & Development Center developed a gel system, which was based on a PAM polymer that is thermally stable and an organic cross-linker. Different versions of this system were formulated depending on the temperature of the target zone. The polyacrylamide tert-butyl acrylate (PAAtBA) cross-linked with polyethyleneimine (PEI) was modified by adding strengthening materials such as: cement, silica flour and rigid setting materials. Reddy et al. (2003) reported that according to European

environmental regulations, PEI was planned to phase-out from the Norwegian sector of the North Sea. Thus, alternatives to PEI were sought. Chitosan was found to be a good alternative for PEI as it contains amino groups to react with acrylamide-based polymers in the same way of PEI. At the same time, it is a bio product with no environmental concerns. Similar to cross-linkers, research was devoted to look into polymer chemical properties. More research was dedicated to use simple PAM homopolymers to replace PAtBA. There was no technical reason for this trend other than the cost of PAM being less compared to that of PAtBA. High temperature applications enforced the use of chemical retarders to elongate the gelation time of these gels. An overview of these retardation chemicals will be given in this paper.

For the deep modification of water injection profiles, the paper identified two systems. Namely, Bright Water, and microgel nanospheres. Bright Water is a micro particles-based system that can be injected with water. It also has a similar density to water and therefore has minimum gravity segregation in the reservoir during its propagation (Pritchett et al., 2003). These particles will expand with temperature and time to block the high permeability zones (thief zones). Since the swelling of micro particles needs to be activated by high temperature, the working mechanism of Bright Water in the reservoir could be explained by the concept of thermal front (Seright et al., 2011). Thermal front is created by injecting cold water into hot or warm reservoir. The micro particles should be injected thereby swell first in the high permeability zones after passing the thermal front. This result in diverting the injected water to less swept zones (low permeability zones) and thus additional oil could be recovered (Chang et al., 2002; Ohms et al., 2010). Aggregate gels that are based on the cross-linking of acrylamide monomers with N, N'-methylene bisacrylamide cross-linker were also introduced in the past decade for deep modification of water injection profiles (Lei et al., 2011). These authors reported

that these aggregates have small size (5 to 25 μm) with large storage and loss moduli. As such, their propagation was attributed to the elasticity of these aggregates where the authors reported that these aggregates deform and recover their shapes when passing through the pore throats. However, the measured elasticity moduli were not compared with other systems. All of these systems along with their available field application data will be discussed in the next sections. Some of these systems were applied in the field while others were only lab tested (**Table 2.1**). Moreover, some systems were applied in production wells for water shutoff, while others were designed for in-depth profile modification in water injection wells (**Table 2.2**).

Table 2. 1: Lab tested and field applied classification for the various polymer systems reported in this paper

System	Lab Tested	Field Proven
PDVSA-Intevep polymer gel system	Yes	Yes
Polyurethane resins from isocyanate fluids	Yes	No
Polyacrylamide t-butylacrylate (PAtBA)/ Polyethyleneimine (PEI)	Yes	Yes
PAtBA/PEI, with cement	Yes	Yes
PAtBA/PEI, with silica flour	Yes	Yes
PAtBA/PEI, with rigid setting material	Yes	Yes
Acrylamide / 2-Acrylamido-2-methylpropane sulfonic acid (AMPS)/PEI	Yes	No
Mixtures of acrylamide/AMPS and N, N-dimethyl acrylamide/PEI	Yes	No
Polyacrylamide (PAM)/PEI	Yes	No
Partially hydrolyzed polyacrylamide (PHPA)/chitosan	Yes	No

Table 2.1 (Continued): Lab tested and field applied classification for the various polymer systems reported in this paper

System	Lab Tested	Field Proven
PDVSA-Intevep polymer gel system	Yes	Yes
PAtBA/chitosan	Yes	No
PHPA/Sequestered Cr ⁺³ by polyelectrolyte nanoparticles	Yes	No
Foam PHPA/Cr ⁺³	Yes	No
Terpolymer of acrylamide, acrylate and AMPS/Cr ⁺³	Yes	No
Acrylamide monomers crosslinking N, N' methylene bisacrylamide	Yes	No
Acrylamide monomers crosslinking N, N' methylene bisacrylamide Preformed Particle Gel (PPG)	Yes	Yes
Thermally activated microparticles (Bright Water)	Yes	Yes
Colloidal Dispersion Gels (CDGs)	Yes	Yes

Table 2. 2: Wells types where the applied polymer systems were applied

Polymer System	Well Type
Colloidal Dispersion Gels (CDGs)	Injection
PDVSA-Intevep polymer gel system	Production
Polyacrylamide t-butylacrylate (PAtBA)/Polyethylenimine (PEI)	Production
PAtBA/PEI, with cement and silica floor	Production
PAtBA/PEI, with rigid Setting material	Production
PAtBA / PEI with, chemical Retarder	Production
Acrylamide monomers cross-linking N,N' methylene bisacrylamide	Injection
Thermally activated microparticles (Bright Water)	injection

2.2.1 Developments in PHPA Cross-Linked with Chromium

Partially hydrolyzed polyacrylamide (PHPA) cross-linked with chromium (Cr^{+3}) was first introduced in 1990 (Sydansk, 1990). The gel is based on coordination covalent bonding between

chromium and the negatively charged carboxylate groups on the PHPA (Sydansk, 2007). PHPA structure is shown in **Figure. 2.2** as a product of the hydrolysis reaction. To improve the thermal stability of this gel, Sydansk suggested the use of higher polymer loadings (5 wt%) and a low molecular weight PHPA (around 270,000) with a low degree of hydrolysis. More literature reports are available to discuss PHPA thermal stability (Moradi-Araghi et al., 1987; Lockhart, 1991; Albonico et al., 1994). Over the past decade, this system had three new advancements available in the literature and they will be discussed in the below subsections. These advancements include lab tests only and were not applied in the field yet. **Table 2.3** provides a summary of the developments in this section for chromium cross-linked gels.

Table 2. 3: Summary of developments in chromium cross-linked gels

System	Temperature Range for Lab Tests, °C	Reference
PHPA/Sequestered Cr ⁺³ by polyelectrolyte nanoparticles	40-80	Cordova et al. (2008) & Johnson et al (2010)
Foam PHPA/Cr ⁺³	30	Asghari et al. (2005)
Terpolymer of acrylamide, acrylate and AMPS/Cr ⁺³	60-121.1	Prada et al. (2000)

Nano Particles for Retardation

To increase the gelation time, nanoparticle polyelectrolyte complexes (PECs) were introduced by Cordova et al. (2008) and Berkland et al. (2010). The system was based on PHPA, Cr^{+3} , PEI and dextran sulfate (DS). PEI and DS form a particle, which has a diameter ranging from 100 to 200 nanometer (nm). This particle sequesters the Cr^{+3} . At these conditions, the gelant will be a stable colloid. The sequestration of Cr^{+3} in these particles delay the gelation reaction. Johnson et al. (2010) studied the effect of divalent cations like Ca^{+2} and Mg^{+2} , as well as seawater and field water on gelation time when using PEI/DS/ Cr^{+3} PECs nanoparticles. In distilled water, the gelation time was less than 30 minutes at 40°C (104°F). Upon the addition of nanoparticles, the gelation time increased to 7 days under the same conditions. It should be noted that the authors observed precipitation of salts upon the use of high concentrations of Mg^{+2} and Ca^{+2} . Mg^{+2} was found to delay the gelation time further compared to Ca^{+2} . The authors observed a gelation time of about 9 hours at 40°C (104°F) and 0.08 mol/kg divalent cations. It increased to about 18 days after increasing the divalent cations concentration to 0.18 mol/kg. This system is newly introduced and it is yet to be applied in the field.

Foam Gel

Foam-gel was also developed to block wormholes in the Lloydminster region of Canada (Asghari et al., 2005). These wormholes were the result of producing sand through the process of Cold Heavy Oil Production with Sand (CHOPS). The wormholes resulted in excessive water production in the subject field. The authors proposed the use of foam gel. It is based on cross-linking PHPA with chromium along with a surfactant. Nitrogen gas is added to produce the foam. The advantage of this foam system over conventional gel treatments is using less amounts of gelant and thus reducing the treatment costs significantly. To provide adequate foam stability

in this high permeability application, the authors used two surfactants (main and a co-surfactant). A setup was used for testing the performance of the system for reducing the brine permeability. The setup had a high permeability wormhole in between two sand layers. Wormholes had different sizes. Injecting 1 ml/min of the gel system in a wormhole with 0.7 cm thickness reduced the permeability to brine from 777 D to 1.67 D. When increasing the size of the wormhole to 3.7 cm, the brine permeability was reduced from 92 D to 0.215 D by using the same flow rate. This foam gel technology is still in the research phase and has not been tested in the field.

PHPA from Terpolymers

Prada et al. (2000) studied a polymer system based on a terpolymer of acrylamide, acrylate, and AMPS (about 3 to 5 million Daltons) cross-linked with chromium. The temperature limit for this system as reported by the authors is 140 to 250°F (60°C to 121.1°C). However, a core flooding test was only done at a low temperature of 140°F (60°C) by using two cores having water permeabilities of 2,720 and 1,145 mD. The final permeabilities were observed to be 450 and 10 mD, respectively. The resulting gel had a moderately deformable nonflowing structure. The authors did not report gelation time data for this system.

2.2.2. Colloidal Dispersion Gels (CDGs)

In heterogeneous reservoirs, where the permeability variations cover a wide area, it required to inject large volumes of gels for in-depth permeability correction. Injection of gel as bulk was found to have some drawbacks. Producing strong bulk gels required high polymer and cross-linker concentrations, which are unfavorable from economic point of view. Also, fast cross-linking makes in-depth placement difficult to achieve. On the other hand, it is difficult to control the gelation if the polymer and cross-linker are injected separately (sequential injection).

Colloidal dispersion gels (CDGs) were claimed to overcome those drawbacks. CDGs are based on PHPA cross-linked with aluminum citrate. The gel formed is suspended in solution as separate bundles or colloids and this gives the name CDG. Comparing to bulk gels, which require high polymer concentration (around 5000 ppm), lower polymer concentrations (around 100-1000 ppm) are needed to form the gel network in CDGs (Spildo et al., 2009). Increasing the molecular weight and concentration of PHPA was found to increase the size of CDGs (Li et al., 2004). At the same time, the intra-molecular cross-linking in CDGs is dominant over the inter-molecular cross-linking. Moreover, the time needed to complete the CDGs formation was found to be higher than that required for bulk gels. The reaction time was observed to be 7 days at 40°C (104°F) (Li et al., 2004). Bjørsvik et al. (2008) studied the formation of CDGs. The particle size of the CDGs was found to be about 50 nm. In another study, the size of the suspended polymer molecules was reported to be within the range from 1 to 100 nm (Spildo et al., 2009). The propagation of CDGs into rock matrix has been in controversy up to date. Chang et al. (2006) speculated that CDGs propagates a long way into a reservoir and provides a resistance factor greater than a polymer without a cross-linker. All legitimate available studies proof that once the cross-linking takes place, the PHPA/Al⁺³ complex, which has larger size than pore throats will not propagate through porous media (Seright, 2007). Spildo et al. (2009) studied the propagation of CDGs in real cores from a North Sea sandstone oilfield. The permeability of the cores is within the range from 100 mD to 1 D. The coreflooding tests were done at 85°C (185°F). After injecting the CDGs, a decrease in residual oil saturation was noticed. Unlike the earlier studies on CDGs at low temperature and salinities (around 5,000 ppm), the study by Spildo et al. (2009) revealed that CDGs could be prepared at high temperature of 85°C (185°F) and high salinity

(around 35,000 ppm). It should be noted that using low salinity waters for CDGs preparations leads to faster cross-linking and higher strength (Chang et al., 2006).

The first field application data by using CDGs was first reported by Mack and Smith (1994). The incremental oil recoveries were ranged from 1.3 to 18.2%. Chang et al. (2006) reported about a more recent application of CDGs in Daqing oilfield, China. The reservoir is sandstone with low salinity (5,000 to 7,000 ppm) and a temperature around 45°C (113°F). The average water cut prior to the injection of CDGs was 95.2%. The post-treatment data showed that the maximum decrease in water cut was 19.8%. The incremental oil recovery was found to be 10.5%, which was above the planned value (9.0%). A trial was made to inject CDGs in a well with a watered-out zone. The water cut was reduced from 98 to 91% only and the oil production increased from 1 to 3 tons per Day (tons/D). The authors used this finding to conclude that CDGs are not operative in fully watered-out zones. CDG was also applied in Grupo Neuquen Formation, Argentina (Diaz et al., 2008). The reservoir is heterogeneous multilayered sandstone with a temperature of 45°C (113°F) and a permeability ranging from 20 to 1,000 mD. Chromium triacetate was used as a cross-linker instead of aluminum citrate. The injection of 186,000 barrels of CDGs resulted in an incremental oil recovery of about 21,194 m³ (133,292 barrels), which represents 2.9% of the original oil in place (OOIP).

There has been a long-standing controversy about the propagation of CDGs and their effectiveness over uncross-linked polymer. Some questions were raised and still wait for answers. Specifically, why should the CDGs not enter and plug low permeability zones as well as high permeability zones? How will the CDGs propagate deep into the reservoir?. Generally, a legitimate scientific and engineering basis for the propagation of CDG has not been established till today.

2.2.3. Developments in Organically Cross-linked Gels

The literature review revealed that there are several new advancements in the area of organically cross-linked gels. The following subsections will give an overview of these developments. **Table 2.4** gives a summary of the information presented in this section.

PDVSA-Intevap Gel System

The PDVSA Research & Development Center has developed a polymeric gel to meet the high temperature conditions of Venezuelan fields. This polymer gel has been developed in different formulations depending on the target zone temperature from 130 to 320°F (50 to 160°C). The system is based on a thermally stable water soluble polymer and an organic cross-linker. The elasticity and gelation time of this system can be highly controlled which makes it applicable as an RPM or a total blocking gel at high temperature applications. There is no data supporting their claim about using the system as an RPM. Perdomo et al. (2007)

Table 2. 4: Summary of organically cross-linked gels

System	Temperature Range, °C	Field Application	Reference
PDVSA-Intevep polymer gel system	54-160	Reduced water cut up to zero in some cases	Perdomo et al. (2007)
Polyurethane resins from isocyanate fluids	95-120	No field application	Shafian et el. (2010)
Polyacrylamide t-butylacrylate (PAtBA)/ Polyethyleneimine (PEI)	Up to 176	Reduced water cut up to zero in some applications	Vasquez & Eoff (2010)
PAtBA/PEI, with cement	118-144	Reduced water cut from 63 to 25 %	Van Eijden et al. (2004)
PAtBA/PEI, with silica flour	Up to 150	Total sealing	Van Eijden et al. (2005) & Dalrymple et al. (2008)
PAtBA/PEI, with rigid setting material	204	Total sealing	Deolarte et al. (2009)
Acrylamide / 2-Acrylamido-2-methylpropane sulfonic acid (AMPS)/PEI	132-177	No field application	Vasquez et al. (2003)
Mixtures of acrylamide/AMPS and N, N-dimethyl acrylamide/PEI	Up to 135	No field application	Vasquez et al. (2005)
Polyacrylamide (PAM)/PEI	130	No field application	Allison & Purkale (1988); Al-Muntasheri et al. (2008)
Partially hydrolyzed polyacrylamide (PHPA)/chitosan	Up to 65.5	No field application	Reddy et al. (2003)
PAtBA/chitosan	65.5-121.1	No field application	Reddy et al. (2003)

reported that this system was able to withstand 5,000 psi of differential pressure. The chemistry of this system was not published in any patent or paper (Hernandez, 2012).

The system was implemented in different fields in Venezuela. Different water production problems were treated by this system like high permeability channels and flow behind casing. The system was applied in a sandstone reservoir with a permeability ranging from 20 to 3,000 mD and a temperature from 190°F to 310°F (90°C to 150°C). **Table 2.5** shows a detailed description about the field results in different parts of Venezuela.

Table 2. 5: Summary of field results for PDVSA-Intevep polymer gel system applied in Venezuela

Field Location	Water Production Mechanism	Application Results	Reference
Southern Venezuela	High permeability channels	WOR reduced from 16 to 0.11 Oil production increased from 170 to 450 BOPD	Prado et al. (2005)
Maracaibo Lake Basin	Channeling and flow behind casing	WOR reduced from 4 to 0.05 (channeling), and from 6.4 to 1 (flow behind casing) Oil production increased by more than 100%	Der Sarkissian et al. (2005)
North Mongas (El Furrial field)	Channeling through formation	WOR reduced from 0.639 to zero Oil production increased by more than 100%	Perdomo et al. (2007)

Polyurethane Resins from Blocked Isocyanate Fluids

Polyurethane is used as a coating material for offshore equipment to protect them against corrosion (Son et al., 2010; Park et al., 2009). It is a strong polymeric material with good adhesion properties. Shafian et al. (2010) reported on the use of polyurethane for water shutoff. The system was designed for use in PETRONAS fields as a sealant. The application of this system may face some environmental regulations since isocyanate is toxic and explosive and needs special handling. The chemistry of this system is based on isocyanate group ($-\text{N}=\text{C}=\text{O}$), which has a blocking material making it unreactive. This is because isocyanate reaction with alcohol cannot be controlled to provide adequate gelation delay. Then, as the temperature increases to 90°C (194°F) and above, the isocyanate group becomes active and it reacts with polyalcohol groups to form polyurethane (Shafian et al., 2010; Petrie, 2001). This reaction is illustrated in **Fig. 2.8**. Coreflood tests were carried out to evaluate the injectivity of this system into Berea cores at three different temperatures, 80, 95 and 120°C (176, 203, and 248°F). Their results indicated that the injectivity at 80°C (176°F) is easier than at 95 and 120°C (203 and 248°F). When the gel was cured for 36 hours at 80°C (176°F), no water breakthrough was noticed after applying 900 psi differential pressure across 6 inch cores. The same results were noticed at 95 and 120°C (203, and 248°F) under the same conditions. An aging test was conducted at 95°C (203°F) for a long period of time (ranged from one week to 3 months), and the system showed good shutoff with low water breakthrough. In fact, the system was able to reduce the permeability in Berea cores from 30.5 to 0.11 mD showing 99.6% reduction when aged for one month, while this reduction dropped to 81% after 3 months. The authors did not provide reasons for the decreasing trend in water shutoff efficiency. This system has not been applied in the field yet. Data is only available as lab tests.

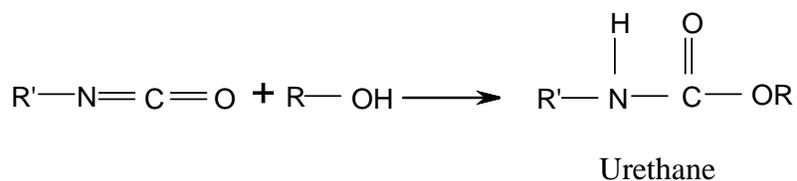


Figure 2. 8: Urethane synthesis by reacting isocyanate with alcohol (Shafian et al., 2010; Petrie, 2001)

Advances in the System of PAtBA Cross-Linked with PEI

The System of PAtBA Cross-Linked with PEI

The PAtBA/PEI gel system was introduced before 2000 by several researchers (Morgan, 1997; Hardy et al., 1998; Urlwin-Smith, 1998 & 2001) as a sealant for water in petroleum reservoir. The chemical structures of PEI and PAtBA are shown in **Figures. 2.5 & 2.9**, respectively. PAtBA has 4.7 mol% of tBA groups and this is referred to as the degree of esterification of the PAtBA. Two mechanisms were proposed for this reaction including a nucleophilic attack on the carbonyl carbon of the tBA part by an imine nitrogen and a transamidation reaction at the amide nitrogen of the PAM part. These mechanisms are shown in **Figure. 2.10** and **Figure. 2.11**, respectively. Al-Muntasheri et al. (2006) provided a detailed investigation of the mechanisms of the PAtBA and PEI. This system was applied widely in various parts of the world (Uddin et al., 2003; Polo et al., 2004; Eoff et al., 2006; Vasquez et al., 2006; Junesompitsiri et al., 2009; Vasquez and Eoff, 2010).

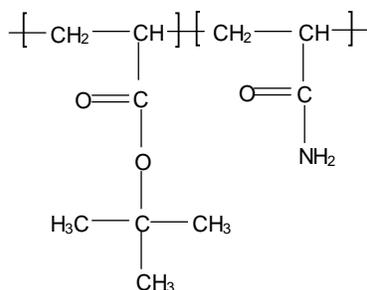


Figure 2. 9: Chemical structure of polyacrylamide tert-butyl Acrylate (PATBA)

(Al-Muntasheri et al., 2009)

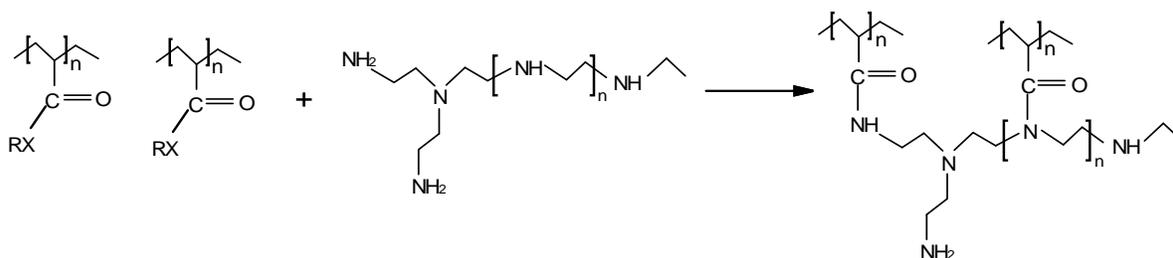


Figure 2. 10: Cross-linking through transamidation reaction

(X=O, N; R=NH₂, N(CH₃)₂)

(Hardy et al., 1999; Vasquez et al., 2005)

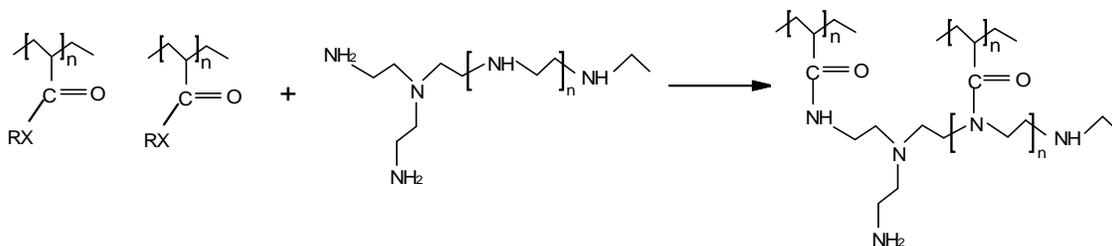


Figure 2. 11: Cross-linking through nucleophilic attack

(X=O, N, R=C(CH₃)₃, C(CH₃)₃, CH₂SO₃H)

(Hardy et al., 1999; Vasquez et al., 2005)

Gel Strength Enhancement by the Use of Cement and Silica Flour

To enhance the strength of PAtBA/PEI system, other materials were added to the gelling recipe. Van Eijden et al. (2004) investigated the use of cement as an additive to the PAtBA/PEI system. The objective was to use the modified gel with the extra strength to seal the lower perforations of oil producers. This option was more cost-effective compared to using a work-over rig as a mechanical solution, which requires casing replacement. The addition of cement can give a robust perforation shutoff, while the gel will be responsible for the rock matrix shutoff. This modified version of PAtBA/PEI was applied in two oil producing wells having bottom hole temperatures of 118 and 144°C (244 and 291°F), respectively. In the first well with 118°C (244°F), the well was producing a total of 3,000 BOD at a water cut of 63%. After the treatment, the increase in oil rate ranged from 4,000 to 4,500 BOD. At the same time, the water cut was reduced to 25%. However, the water cut increased from 25 to 55% over a period of one year. The treatment for the second well was not successful. Van Eijden et al. (2005) developed another system, which is an extension of the gel-cement system. This was developed to meet the high temperature condition of wells in Syrian fields (150°C or 302°F). This because using retarders with the gel in the cement-gel system did not elongate the gelation time, as cement interacted chemically with the retarders. The chemical nature of these interactions was not known. At 10 wt% of cement, interactions were not noted. Thus, the authors used a maximum of 10 wt% of cement to provide more strength while the rest of the solid material was silica flour. Silica flour was selected due to its availability, cost-effectiveness and inert behavior to the gel chemistry. Note that the total amount of solids in the gelant was 51 wt% (including 10 wt% cement). The field tests indicated that the system without cement was washed out using coiled tubing. The gel was squeezed into a long perforation interval of 186 m and provided a total sealing capability.

The authors did not report final oil and water rates after this treatment. In a more recent publication, Dalrymple et al. (2008) reported gelation time measurements of the PAtBA/PEI system with and without silica flour; the two measurements gave approximately the same time and the authors used that finding as a confirmation of the inert behavior of silica flour to the gelation reaction.

PAtBA/PEI with Rigid Setting Material

Deolarte et al. (2009) reported the application of PAtBA/PEI along with another additive referred to as: Rigid Setting Material (RSM). This system was developed as a sealing gel to treat water coning problems in the Cantarell field in Mexico. The PAtBA/PEI was proposed to treat the formation matrix. In such a scenario, the near wellbore area will be left untreated as the gelant will penetrate deep into the reservoir before it forms the three dimensional structure. Hence, water finds its way quickly into the wellbore. This water entry was the experience in the subject field until the RSM was introduced to overcome this challenge. The RSM is a metal oxychloride-type of cement that is thermally stable up to 400°F (204°C) (Barclay et al., 2006). Although this material is designed to give a low viscosity fluid, its setting time into a solid is very short. Thus, it seals the near wellbore area immediately. The technology was applied in various wells in the subject field. We will give two examples. The candidate well in the Cantarell field had a permeability of 1,710 mD. It was completed in a carbonate reservoir with a bottom hole temperature of 225°F (107°C). After the treatment, the well produced an extra 1,325 BOPD for a period of one year. Another candidate well was treated with the same technology. It had a permeability of 2,512 mD with a bottom hole temperature of 222°F (105°C). The gel-RSM system was used to seal the lower interval and the old perforations. Then, an upper interval in the

same formation was perforated to produce dry oil. After the treatment, the well produced 12,800 BOPD at a zero water cut.

Chemical Retardation Systems for the PAtBA/PEI Gel

High temperature reservoirs require the use of a method to elongate the gelation time of the gelant. This is to avoid pre-mature gelation and to ensure deep penetration of the gelant. One method is to use pre-flush to cool down the near wellbore area. This method can drop the temperature by around 30°C (54°F) (Al-Muntasheri et al., 2010). In several cases, it might be unacceptable to inject more amounts of water into oil zones. Besides, in some reservoirs the injection of small amounts of water can alter the effective permeability to oil significantly (Morgan et al., 1997). Another method to elongate the gelation time is to alter the cross-linker chemistry to reduce its activity during injection. Also, a chemical retarder can be used. The retarder affects the chemistry of the gelation reaction and elongates the time it takes the gel to form. Various retardation chemicals were introduced in the literature over the past several years. In this section, we will shed light on these technologies.

Vasquez et al. (2005) reported on a different form of PEI to elongate gelation time. In this form, the amine groups have been converted into amides. This is referred to as derivatized PEI (Hardy et al., 2001). As a result, these groups will take time to be converted into active sites for cross-linking. Another retarder for the PAtBA/PEI system was a polyamino acid. The working mechanism for this retarder is believed to be by forming a complex with the cross-linker (PEI). As a result, this complex will hinder the imine groups attack on the polymer. This will in turn increase the gelation time.

Sodium carbonate was also reported as a retarder for the PAtBA/PEI system. The mechanism for elongating gelation time by sodium carbonate is believed to be an interaction between the positively charged sodium ion with the carboxylate groups resulting from the hydrolysis of PAtBA, thus reducing the sites available for cross-linking and consequently increasing the gelation time. Eoff et al. (2007) extended the working temperature of the PAtBA/PEI system to 350°F (176.7°C) by the use of this retarder. After doing a sand pack flow test, the authors concluded that the addition of this salt as a retarder can raise the working temperature without affecting the gel strength and its subsequent ability to stop fluid flow.

Sodium carbonate has disadvantages when used with high salinity brines. A recent study of PAtBA/PEI gel was reported where the gel was considered for a high temperature reservoir in a horizontal well with a bottom hole temperature of 300°F (149°C) in Saudi Arabia (Al-Muntasheri et al., 2010). Sodium carbonate was found to be incompatible with the formation and mixing brines of the subject field. The authors attempted the use of sodium chloride but its retardation effectiveness was below expectations. Thus, it drove further research to look for a new retarder, which was cost-effective, efficient, and compatible with the available mixing brines. The retarder (ammonium chloride) gave a gelation time of 1.5 hours at 150°C (302°F). The treatment was performed on a dead gas well. After the treatment, the well showed a 46 % water cut reduction and produced 17 times more gas. The chemistry of this retarder is reported by Al-Muntasheri et al., 2011. **Table 2.6** gives a summary of the retarders available for the PAtBA/PEI system.

Table 2. 6: Summary of chemical retarders reported for the PAtBA/PEI system

Retarder Type	Maximum Temperature, °C	Reference
Derivatized PEI	Up to 177	Hardy et al. (2001); Vasquez et al. (2005)
Polyamino acid	Up to 135	Vasquez et al. (2005)
Sodium carbonate	Up to 177	Eoff et al. (2006)
Sodium chloride	127	Al-Muntasheri et al. (2010)
Ammonium Chloride	Up to 150	Al-Muntasheri et al. (2011)

New Polymers Cross-Linked with PEI

The Acrylamide / 2-Acrylamido-2-Methylpropane Sulfonic Acid (AMPS) Copolymer

Cross-Linked with PEI

Another polymer system, which was based on acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (AMPS) cross-linked with PEI was introduced (Vasquez et al., 2003). The AMPS was developed to address challenges associated with high temperatures and to avoid the use of retarders and pre-flush fluids. In this case, the cross-linking is believed to be delayed due to the steric hindrance provided by the bulky groups on the polymer (**Figure. 2.4**). These groups are methylpropane and sulfonic acid. The gelation time was measured for this system through visual observation in a laboratory test by using sealed tubes. The results showed a gelation time ranging from 2 to 20 hours over the temperature range: 270 to 350°F (132.2 to 176.7°C) by varying the concentration of the polymer and cross-linker. There are no literature reports highlighting a field application with this system.

Mixtures of Acrylamide/2-Acrylamido-2-Methylpropane Sulfonic Acid and N, N-dimethyl Acrylamide Cross-Linked with PEI

Further efforts were continued to develop new polymer chemical properties for very high temperature applications. A mixture of acrylamide, 2-acrylamido-2-methylpropane sulfonic acid and N, N-dimethyl acrylamide (A/AMPSA/N, N-DMA) cross-linked with PEI was studied by Vasquez et al. (2005). This system was reported to be stable up to a temperature of 350°F (177°C). The gelation time at 275°F (135°C) was found to be 23 hours at a PEI concentration of 1 wt% using this mixture. Moreover, an increase in gelation time up to 41 hours was noticed at the same temperature by using a polymer concentration of 5 wt%. This system achieved a 97% reduction in water permeability for one year. However, no field application data was reported to verify its performance in the reservoir.

Polyacrylamide (PAM) Cross-Linked with Polyethyleneimine (PEI)

The first study of PAM cross-linked with PEI was reported by Allison and Purkale (1988). These authors observed aqueous gels upon the cross-linking of PAM with PEI at room temperature. Al-Muntasheri et al. (2006) investigated the gelation mechanisms of PAtBA/PEI and the authors concluded that cross-linking can still take place at the amide groups of the PAtBA. Thus, eliminating the need for the ester groups. Al-Muntasheri et al. (2008) investigated the gelation kinetics and thermal stability of the PAM/PEI system. The system showed rigid stable gels for 8 weeks at 130°C (266°F) using polymer and PEI concentrations of 7 and 1 wt%, respectively. The authors investigated the effect of salts and found out that sodium chloride increased the gelation time from 0.67 hour (in distilled water) to 4.4, and 6.8 hours by adding 30,000 and 50,000 mg/l, respectively. Note that 30,000 ppm corresponds to 250 lb/1000 gal in

field units, which is not too much to use in a field application for a retarder (Al-Muntasheri et al., 2010). In terms of performance in porous media, in Berea cores, the gel reduced the permeability of the core from 47 to zero mD at 90°C (194°F). The gel was not aged for more than a week in those tests. Yet, its strength was investigated in high pressure experiments where the gel withstood yielding pressures of 1,000 psi (Al-Muntasheri and Zitha, 2009) at room temperature. The development in this system was only lab prototypes and there is no field data available for this system.

Chitosan Cross-Linked Gels

PEI was phased out from the Norwegian section of the North Sea. Reddy et al. (2003) studied a replacement to PEI. The gel system was based on a cross-linker that can be extracted from natural resources, chitosan (**Figure. 2.6**), which can cross-link a variety of acrylamide-based polymers. Cross-linking PHPA with chitosan gave lipping gels over the temperature range: 150 to 190°F (65 to 88°C) for a weight ratio of 14. The system showed fast gelation at 190°F (3 hours) for different formulations. AMPS/AA showed long gelation time (48 hours) at 250°F (121°C) at the same weight ratio. No field application data is available for this system. The cross-linking of PAtBA cross-linked with chitosan was also studied by Reddy et al. (2003). The authors reported that the data showing a ratio of 14 (PAtBA/PEI) resulted in ringing gel at 190°F (88°C) and 5.5 hours gelation time. Chitosan precipitates at a pH of 6. And this prevented further developments of this cross-linker and the subsequent field applications.

2.2.4. Microgels for Deep Modification of Water Injection Profiles

Although microgel systems were developed as RPMs to reduce water production (Chauveteau et al., 2000, 2001, 2003 & 2004; Feng et al., 2003; Rousseau et al., 2005; Zaitoun et al., 2007;

Cozic et al., 2009), other systems, based on suspensions with various chemical properties, were developed for total water shutoff and deep modification of water injection profiles. The following two subsections will provide an overview of two technologies. These two technologies provide a deep water shutoff application in high permeability zones that are responsible for taking most of the injected water resulting in poor reservoir sweep. Thus, the injected microgels block the high permeability zones and direct water to less swept zones and help recover additional oil. **Table 2.7** gives an overview of the technologies reported in this section.

Table 2. 7: Microgels for deep modification of water injection profiles

System	Temperature for Lab Tests, °C	Particle Diameter, micron	Reference
Acrylamide monomers crosslinking N, N' methylene bisacrylamide	55	0.05	Wang et al. (2010)
Acrylamide monomers crosslinking N, N' methylene bisacrylamide Preformed Particle Gel (PPG)	87.8	10-30	Lei et al. (2011)
Thermally activated microparticles (Bright Water)	95	~ 0.5	Frampton et al. (2004)

Acrylamide (PAM)/N, N' Methylene Bisacrylamide Aggregates

Pre-formed gel aggregates (microspheres) were introduced to provide total water shutoff with deep penetration into the reservoir. These materials are injected in the suspension form with their

diameters ranging from 10 to 30 micrometers (microns). Lei et al. (2011) reported on the lab testing of a microgel cross-linked organically. In addition to the controlled size of the produced microspheres, this system is thought to provide a short cross-linking time (2 hours). This compares to a cross-linking time of one week for Colloidal Dispersion Gels (CDGs) that are based on cross-linking of PHPA with aluminum citrate (Spildo et al., 2009). These microspheres also swell in the presence of water and this is thought to provide a deep reservoir treatment to allow a better sweep efficiency by improving the injection profiles in water injection wells. The system is prepared by mixing acrylamide monomer, N, N'-methylene bisacrylamide (organic cross-linker) and ammonium persulfate (initiator) in water. The solution is then sprayed slowly over heated oil maintained at 60 to 80°C (140 to 180°F). The reaction mechanism of this chemical system is shown in **Figure. 2.12**. After 30 minutes, the mixture is cooled and the oil is separated and removed. Then, the microspheres are collected. Note that the sprayer has different sizes allowing different sizes of the produced microspheres. These microspheres can expand up to 5 times their original size in 5 days when mixed in distilled water. This expansion process is a function of time and salinity where expansion decreases with increasing salinity. For example, in 20,000 ppm NaCl brine, the microspheres expanded to only 2 times their original size after 5 days at 175°F (78.8°C).

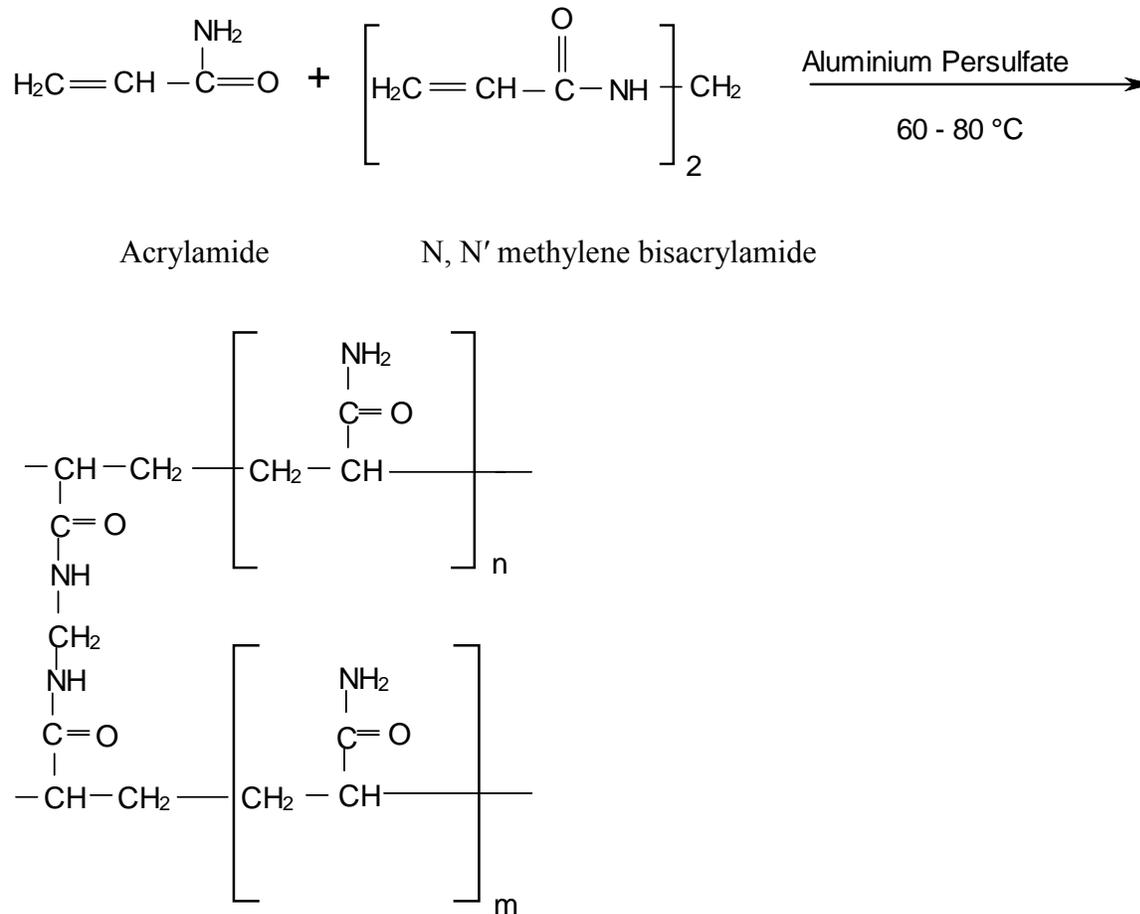


Figure 2. 12: Synthesis of microspheres from acrylamide and N, N' methylene bisacrylamide

(Lei et al., 2011)

The microspheres were reported to have large elastic (storage) and viscous (loss) moduli. However, no comparisons were made with the elasticity of other systems. The elasticity of the microspheres was used to explain the propagation of these materials. It was stated that the microspheres deform and recover their shapes when passing through pore throats. Moreover, a long sandpacks (1400 cm) with 5 pressure taps was used to study the propagation of these microspheres. The brine permeability of this sandpacks was 3,852 mD. It was found that the pressure increased in tape 1 first, then, followed by an increase in the other taps. The authors used this finding as an indication to the propagation of the microspheres through the sandpacks.

It was stated that the microspheres can be dispersed broadly in the pores when injected with water in sandstone reservoir. However, in case of stratified reservoirs with crossflow, the propagation of these particles into less-permeable strata was ignored which may lead to blocking of pores and results in adversative effect. Moreover, higher salinity (more than 20,000 ppm NaCl) may limit the application since it was found that the expansion of microspheres is decreasing with increasing salts content. Although particles could be produced with the same size, but pores are not all the same size. So, particles may enter all or most pores. The reader should realize that particles for in-depth profile modification should be designed small enough to flow freely into high permeability zones, and at the same time, large enough not to enter low permeability zones. Also, the particles should be immobile to divert water into unswept oil zones.

This chemical system was applied in Jidong, Dagang and Shengli oilfield formations in China. The authors reported the field application data for a water injector in Lizuan area. Injection pressure increased after the treatment by 1 to 5 MPa indicating plugging of the water injection layers. Moreover, the water injection profile was improved in the well where the water started flowing into 7 layers instead of only 2 layers before the treatment (from water distribution results). The authors reported that there is a decrease in the water cut from 55 vol% to a minimum value of 26 vol% in the producing wells. Overall, a total of 6,467 tons of incremental oil were recovered after 7 months as a result of this treatment. Wang et al. (2010) studied this system for profile modification in sandstone cores with a smaller size. The authors were able to produce microgels (nanospheres) that are 50 nm in size. In the coreflood experiments, injection of 0.5 PV of microgel solution containing 1 wt% polymer produced small amount of oil. Then, the core was immersed in water for 15 hours at 55°C (131°F). This was done to allow the

nanospheres to swell and absorb water. Then, the formation brine injection was resumed. A 20 % incremental recovery of oil was realized due to the blockage of the water paths of low resistance by the nanospheres.

Another version of acrylamide monomer/ N, N'-methylene bisacrylamide system was developed in the past decade. Specifically, this system was designed for oilfields in China. These oilfields exhibited high permeability variations and extreme channels (Coste et al., 2000). This system is referred to as preformed particle gel (PPG). PPGs have many advantages over other polymer systems (Bai et al., 2007a). Synthesis of PPGs at surface facilities can avoid some drawbacks, which may exist with the in-situ gelation systems such as controlling the gelation time and effect of shear on gelation. The size (from microns to centimeters) and strength of PPGs are both controllable. Due to their size, PPGs were developed for treating fractured reservoirs only. PPGs are thermally stable up to 120°C (250°F) and can resist salinities up to 300,000 ppm. The produced water can be used to prepare PPGs instead of using fresh water; and this will lead to lower the cost of the treatment as well as protecting the environment.

These aggregates were considered as superabsorbent cross-linked polymers, which can swell in formation water within the range from 30 to 200 times their original size (Bai et al., 2008). The system is prepared by mixing acrylamide monomer, N, N'-methylene bisacrylamide (organic cross-linker), initiator (peroxydisulfate), and some other additives (Bai et al., 2007b). The mixture is heated to 60°C (140°F) to initiate the reaction, which will complete in 30 minutes, then aged for an extra 3 hours at room temperature. The produced PPG is cut into pieces and dried at 70°C (160°F). The final step is to grind the particles mechanically before use. Bai et al. (2007b) studied some factors, which can affect the swelling and the strength of the PPGs.

PPGs have a limitation to be applied for conformance control. PPGs are developed to be used in reservoirs with small fractures or high permeability channels, but none at all for treating matrix. However, the reader should note that in very severe open channels or super-high permeability fractures, PPGs cannot be used. This is because PPGs may be flushed out from the producers. The propagation of PPGs through porous media was studied by Bai et al. (2007a) in a sandpack model. Macroscopically, it was found that PPGs are following three arrangements. After the injection of the PPGs suspension, it was observed that the particles will pass first, and then they will be broken and pass, and finally, the particles will plug the pores.

The injectivity of PPG was investigated in a pilot test performed at Shengli oilfield, East of China (Coste et al., 2000). Two injection wells were selected at Shangdian reservoir. The lithology of this reservoir is sandstone with a high layer permeability ranges from 2 to 6 D and low layer permeability ranges from 0.04 to 0.5 D. The water cut of the producers of the subject wells was above 90%. The post-treatment data after 8 months showed a decrease in water cut as well as an increase in incremental oil by a total of 2,278 tons. The benefit from the treatment in terms of cost was reported to be about U.S \$180,000. Bai et al. (2007b) reported about two field application cases using PPGs. The first case was in Zhongyuan oilfield, China. The reservoir is sandstone with an average permeability of 121 mD, a temperature of 107°C (225°F), and high formation water salinity (15×10^4 ppm). The treatment resulted in a decrease in water cut from about 80 to 70% and an increase in oil production from 40 to 60 tons/D. The second case was in Xingbei oilfield located in Daqing, China. The reservoir is heterogeneous with thick oil layers. The reservoir permeability ranges from milli darcies to 1,200 mD with temperature and salinity of about 45°C (113°F) and 4,500 ppm, respectively. The water cut prior to treatment was more than 90%. The post-treatment results showed 8% reduction in water cut as well as 2,400 tons

more incremental oil. Bai et al. (2008) reported another case study in Lamadian reservoir located in Daqing oilfield, China. The reservoir is heterogeneous sandstone with temperature and salinity of about 40°C (104°F) and 4,000 ppm, respectively. The initial average water cut was 95.4% prior to treatment. The post-treatment showed a decrease of 0.94% in average water cut, and the oil production increased by 34.8 tons/D.

Bright Water Technology

A system for modification of injection profile known as Bright Water has been introduced within the last decade, which can be injected with water for in-depth waterflood sweep control (Chang et al., 2002). It is a thermally activated particle system, which was developed as a collaboration effort between Chevron, BP, and Nalco in 1997. The Bright Water is based on polyacrylamide-based particles cross-linked with an organic cross-linker - referred to as a nonlabile cross-linker - which controls the size of the particle. The formulation also comprises another type of cross-linker, which is labile. The labile cross-linker degrades as a function of time and temperature, allowing the particle to be exposed to the surrounding water, and then the particle expands in size (Ohms et al., 2010). The particles will tend to block pore throats of water and prevent further fluid flow through the rock. Consequently, injected water will be diverted into less swept zones, which enables more oil recovery. The particles of this technology are around 0.5 microns in diameter (Roussennac and Toschi, 2010). They are produced in light mineral oil with 30% activity. Then, an emulsion is made by adding a surfactant to disperse the particles and emulsify the carrier oil. Specific amount of shear is needed to accomplish the mixing. Detailed chemistry is reported by Chang et al. (2002) and hence we provide an overview of the chemical components here. The polymer is based on AMPS while the labile cross-linker (reversible) is

comprised of diacrylamides and methacrylamides of diamines. The stable (nonlabile) cross-linker is based on methylene bisacrylamide.

Frampton et al. (2004) evaluated the performance of the Bright Water in long sand packs (66 ft long) divided into five sections with different permeabilities. At the first 50 ft, the pressure difference was noticed to be low indicating that the particles penetrate the sand packs with no swelling. At the last section of the sand packs, the pressure drop increased after about 100 days indicating that it is the beginning of the expansion process. The authors referred to this process as the popping process. Scanning Electron Microscopy (SEM) showed that the particles enlarged to 2-4 microns from the original size, which ranged from 0.1 to 3 microns. The authors also reported on the viscosity change of the system as a measure of its expansion. This viscosity change occurred because when the system swells water that reduces the volume fraction of the continuous phase. This reduction translates into an increase in viscosity. The data indicated that the viscosity of the system increased with temperature and time. For example, at 210°F (98.89°C), the viscosity increased by a factor of 17 after 45 days. Pritchett et al. (2003) reported the operating limits for the application of the Bright Water. The applicable temperature ranges from 50°C (122°F) to 150°C (302°F), the permeability in the thief zone must be greater than 100 mD, and the salinity of the injected water should be below 70,000 ppm. It is worth mentioning that lab tests can be used to select the optimum formulation of the particles as they are available in different commercial grades with different chemical properties covering a wide range of temperatures (Mustoni et al., 2010). Also, the type of labile cross-linker to be used is a function of the temperature of the targeted reservoir.

The Bright Water process has a legitimate basis for in-depth profile modification, but there are rigid requirements for placement and applicability. As it was mentioned before, the

expansion of the micro particles requires enough time and elevated temperature during their propagation through the rock matrix. So, this technology has been developed to be applied in hot or warm reservoir where cold water has been injected (Seright et al., 2011). The injection of cold water creates what is called thermal front. The micro particles should be injected thereby swell first in the high permeability zones after passing the thermal front. This result in diverting the injected water to less swept zones (low permeability zones) and thus additional oil could be recovered (Chang et al., 2002; Ohms et al., 2010). If the micro particles flow into the low permeability zones, they will not be in adequate concentration to form a block (Ohms et al., 2010). There are some limitations for the application of Bright Water. First, the swelled micro particles will not help in improving the sweep efficiency much beyond the maximum depth of micro particles propagation. The sweep efficiency in the reservoir before the treatment is supposed to be very poor for the process to work well. The resistance factor of the particles should not exceed that for water, and should not increase during micro particles placement.

The first application of Bright Water technology was conducted in the Minas field located on the island of Sumatra in Indonesia in 2001 as reported by Pritchett et al. (2003). It was reported that there was very little incremental oil after that treatment. The Bright Water technology was also implemented in San Jorge Basin (SJB) (sandstone reservoir) located in Argentina (Mustoni et al., 2010). The irregular reservoir sweep was reported to be due to the presence of thief zones with permeabilities ranging from 500 to 1,000 mD. A total of six treatments were executed in two fields of the SJB (Koluel Kaike and Piedra Clavada fields). The post-treatment results showed a decrease in WOR from 55 to 39 (30% reduction), and at the same time, oil production increased by 40%. The system was also applied in Alaska with positive results as reported by Ohms et al. (2010). A total of 60,000 barrels were produced over a

period of four years. This compares to a 10-years target of 50,000 to 250,000 barrels. In another attempt, the Bright Water technology was tested in Salema field located in the Campos Basin, Brazil (Roussennac and Toschi, 2010). The thief zones of the reservoir had permeabilities ranging from 100 mD to multi darcies, and the temperature is 88°C (190.4°F). The incremental oil gain was under evaluation by the authors at the time of their paper publication.

2.3. Environmental Issues and Toxicity

An important factor to be considered for the selection of a certain chemical for water control is the toxicity level of its components. Therefore, in this section we shed light on some toxicity levels of some chemicals reported in this paper. One way to measure toxicity of chemicals is the median lethal dose (LD₅₀) which measures the required amount of the material required to kill 50% of the given test population (mice for example). For inorganic cross-linkers, chromium is well-known to have toxicity issues. The toxicity of chromium compounds depends on the oxidation state. As such, Cr⁺⁶ is more toxic than the trivalent state (Cr⁺³). In addition, Cr⁺⁶ is easier to be absorbed either by inhalation or oral routes. The LD₅₀ value for Cr⁺⁶ is 29 mg per kg body weight in rats, whereas the LD₅₀ value for Cr⁺³ is 11300 mg per kg body weight in rats (Assem and Zhu, 2007). On the other hand, PEI is greatly less toxic compared to Cr⁺⁶. The LD₅₀ value for PEI is 2,200 mg per kg body weight in rats. Due to the European environmental regulations, PEI was planned to phase-out from the Norwegian sector of the North Sea (Reddy et al., 2003). As such, chitosan is attempted for use as a replacement of PEI. It is nontoxic and biodegradable. A value of LD₅₀ was reported to be 16,000 mg per kg body weight in mice (Reddy et al., 2003).

Isocyanates are very interactive with bases, acids, and alcohols, thereby; should not be stored near these chemicals. Moreover, isocyanates should be stored in closed containers away

from water as isocyanate-water reaction can generate enough pressure to rupture containers. Isocyanates are very toxic materials (Patnaik, 2007). For example, the LD₅₀ value for methyl isocyanate is 69 mg per kg body weight in rats. For deep profile modification, the N, N'-methylene bisacrylamide is used as a cross-linker. Its LD₅₀ was reported to be 380 mg per kg body weight in mice.

2.4. Conclusion

In this paper, a thorough review on the development of polymer systems for water shutoff over the last ten years is summarized. Various polymer systems were identified. These include organically and inorganically cross-linked polymer gels, resins, micro and nanosphere gels. These systems were applied in oil and gas producing wells as well as water injection wells.

For inorganically cross-linked gels, nanotechnology was introduced to extend the gelation time of PHPA/Cr⁺³ systems. Chromium is sequestered by the particles formed by PEI and DS. Moreover, PHPA/Cr⁺³ is mixed with foam to block deep wormholes. Copolymers of PAM were also examined for cross-linking with Cr⁺³. Colloidal dispersion gels were developed for in-depth blockage of high permeability zones in heterogeneous reservoirs. It was claimed that these aggregates propagate a long way into the reservoir and provide higher resistance factors compared to the polymer without cross-linker. Other experimental studies showed that these systems do not have a deep propagation to support this claim.

For the organically cross-linked gels, a system was developed by PDVSA Research & Development Center, which can be used at temperatures up to 320°F (160°C). Another organically cross-linked gel system for near wellbore treatments is the PAtBA/PEI gel system, which was used in fields with temperatures up to 320°F (160°C). Other materials were used along with PAtBA/PEI to increase its strength like cement, silica flour and rigid setting

materials. The elongation of gelation time was achieved by adding retarders, use of a derivatized form of PEI and the addition of polyamino acid to PEI. The chemistry of the polymer was also altered to elongate the gelation time. This alteration was done through incorporating some bulky groups (such as AMPS) to the polymer backbone.

Two systems were identified for deep modification of water injection profiles. The first one is a microgel system formulated by cross-linking acrylamide monomers with N, N' methylene bisacrylamide to produce elastic microspheres with controllable size. The other is Bright Water which was designed to treat deep water injection wells to modify their injection profiles and help in improving the reservoir sweep efficiency. One advantage of these new particles is that it has a density similar to water enabling them to penetrate deeper into the reservoir.

In the future, we do believe that the area of chemical methods for water shutoff can make use of advances in nanotechnology and address water production problems in deep reservoirs. There is a need for particles that can swell much more than an order of magnitude to block fractures with very high permeabilities. Moreover, organic cross-linkers for high temperature that are accepted in offshore environments are lacking. This should drive research toward more environmentally friendly cross-linkers, such as those from naturally occurring materials. There is a need to investigate the effect of the retarders on the final gel strength in many of the available systems.

2.5 References

Al-Assi, A.A., Willhite, G.P., Green, D.W., and McCool, C.S. 2009. Formation and Propagation of Gel Aggregates Using Partially Hydrolyzed Polyacrylamide and Aluminum Citrate. *SPEJ* **14**(3): 450-461. SPE-100049-PA.

Albonico, P., Bartosek, M., and Lockhart, T.P. 1994. New Polymer Gels for Reducing Water Production in High-Temperature Reservoirs. Paper SPE 27609 presented at the SPE European Production Operations Conference and Exhibition, Aberdeen, 15-17 March. DOI: <http://dx.doi.org/10.2118/27609-MS>.

Al-Dhafeeri, A.M., Nasr-El-Din, H.A., and Al-Harith, A.M. 2008. Evaluation of Rigless Water Shutoff Treatments to be Used in Arab-C Carbonate Reservoir in Saudi Arabia. Paper SPE 114331 presented at the CIPC/SPE Gas Technology Symposium Joint Conference, Calgary, 16-19 June.

Allison, J.D. and Purkapple, J.D. 1988. Reducing Permeability of Highly Permeable Zones in Underground Formations. US Patent No. 4,773,481.

Al-Muntasheri, G.A. 2008. Polymer Gels for Water Control: NMR and CT Scan Studies. PhD thesis, Delft University of Technology, Delft, The Netherlands (September 2008).

Al-Muntasheri, G.A. and Zitha, P.L.J. 2009. Gel Under Dynamic Stress in Porous Media: New Insights Using Computed Tomography. Paper SPE 126068 presented at the SPE Saudi Arabia Section Technical Symposium and Exhibition, AlKhobar, 9-11 May. DOI: <http://dx.doi.org/10.2118/126068-MS>.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha, P.L.J. 2006. Gelation Kinetics of an Organically Cross-linked Gel at High Temperature and Pressure. Paper SPE 104071 presented at the First International Oil Conference and Exhibition, Cancun, 31 August-2 September. DOI: <http://dx.doi.org/10.2118/104071-MS>.

Al-Muntasheri, G.A., Sierra, L., and Bakhtiyarov, A. 2011. Ammonium Halide as Gelation Retarder for Cross-linkable Polymer Compositions. U.S. Patent Application WO 2011/ 107744.

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. 2010. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Al-Tolaihy, M. and Bukhari, D.O. 2010. Study on the Optimization of De-Scaling Operations in Saudi Arabian Khuff Gas Wells. Paper NACE 10271 presented at the NACE International Corrosion Conference, San Antonio, 14-18 March.

Asghari, K., Taabbodi, L., and Dong, M. 2005. A New Gel-Foam System for Water Shut-off Purposes in Wormhole Reservoirs. Paper SPE 97765 presented at the SPE/PS-CIM/CHOA International Thermal Operations and Heavy Oil Symposium, Calgary, 1-3 November. DOI: <http://dx.doi.org/10.2118/97765-MS>.

Assem, I., and Zhu, H. 2007. Chromium-Toxicological Overview. Institute of Environment and Health. Version. http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1194947362170.

Bai, B., Hung, F., Liu, Y., Seright, R.S., and Wang, Y. 2008. Case Study on Preformed Particle Gel for In-Depth Fluid Diversion. Paper SPE 113997 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19-23 April.

Bai, B., Li, L., Liu, Y., Liu, H., Wang, Z., and You, C. 2007b. Preformed Particle Gel for Conformance Control: Factors Affecting Its Properties and Applications. *SPE Res Eval & Eng* **10**(4): 415-422. DOI: <http://dx.doi.org/10.2118/89389-PA>.

Bai, B., Liu, Y., Coste, J.-P., and Li, L. 2007a. Preformed Particle Gel for Conformance Control: Transport Mechanism Through Porous Media. *SPE Res Eval & Eng* **10**(2): 176-184. DOI: <http://dx.doi.org/10.2118/89468-PA>.

Baily, B., Crabtree, M., Tyrie, J., et al. 2000. Water Control. *Oilfield Review* **12** (1): 30-51.

Barclay, D.A., Lawson, K., Mullins, B., and Cardno, B. 2006. Stand-Alone Coiled-Tubing Water Shutoff Operations Reinstate Well on a Normally Unattended Installation. Paper SPE 100132 presented at the SPE/ICoTA Coiled Tubing and Well Intervention Conference and Exhibition, The Woodlands, 4-5 April. DOI: <http://dx.doi.org/10.2118/100132-MS>.

Berkland, C., Cordova, M., Liang, J.T., and Willhite, P. 2010. Polyelectrolyte Complexes as Delayed Gelling Agents for Oil and Gas Applications. US Patent No. 7,644,764.

Bjørsvik, M., Høiland, H., and Skauge, A. 2008. Formation of colloidal dispersion gels from aqueous polyacrylamide solutions. *Colloids and Surfaces A: Physicochem. Eng. Aspect* **317** (2008) 504-511.

Botermans, C.W., Dalrymple, E.D., Dahl, J., and Smith, D. 2001. Chemical Systems for Water and Gas Control: Terminology, Evaluation Methods, Candidate Selection, and Expectations. Paper SPE 65415 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 13-16 February. DOI: <http://dx.doi.org/10.2118/65415-MS>.

Boye, B., Rygg, A., Jodal, C., and Klungland, I. 2011. Development and Evaluation of a New Environmentally Acceptable Conformance Sealant. Paper SPE 142417 presented at the SPE European Formation Damage Conference, Noordwijk, 7-10 June. DOI: <http://dx.doi.org/10.2118/142417-MS>.

Chang, H.L., Sui, X., Xiao, L., Guo, Z., Yao, Y., Xiao, Y., Chen, G., Song, K., and Mack, J.C. 2006. Successful Field Pilot of In-Depth Colloidal Dispersion Gel (CDG) Technology in Daqing Oil Field. *SPE Res Eval & Eng* **9**(6): 664-673. SPE-89460-PA.

Chang, K.T., Frampton, H., and Morgan, J.C. 2002. Composition and Method for Recovering Hydrocarbon Fluids from A Subterranean Reservoir. US Patent No. 6,454,003.

Chauveteau, G., Omari, A., Tabary, R., Renard, M., and Rose, J. 2000. Controlling Gelation Time and Microgel Size for Water Shutoff. Paper SPE 59317 presented at the 2000 SPE/DOE Improved Oil Recovery symposium, Tulsa, 3-5 April.

Chauveteau, G., Omari, A., Tabary, R., Renard, M., Veerapen, J., and Rose, J. 2001. New Size-Controlled Microgels for Oil Production. Paper SPE 64988 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, 13-16 February.

Chauveteau, G., Tabary, R., Blin, N., Renard, M., Rousseau, D., and Faber, R. 2004. Disproportionate Permeability Reduction by Soft Preformed Microgels. Paper SPE 89390

presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil recovery, Tulsa, 17-21 April.

Chauveteau, G., Tabary, R., Bon, C.L., Renard, M., Feng, Y., and Omari, A. 2003. In-Depth Permeability Control by Adsorption of Soft Size-Controlled Microgels. Paper SPE 82228 presented at the SPE European Formation Damage, The Hauge, 13-14 May.

Cordova, M., Cheng, M., Trejo, J., Johnson, S.J., Willhite, G.P., Liang, J.T., and Berkland, C. 2008. Delayed HPAM Gelation via Transient Sequestration of Chromium in Polyelectrolyte Complex Nanoparticles. *Macromolecules J* **41**: 4398-4404.

Coste, J.-P., Liu, Y., Bai, B., LI, Y., Shen, P., Wang, Z., and Zhu, G. 2000. In-Depth Fluid Diversion by Pre-Gelled Particles. Laboratory Study and Pilot Plant. Paper SPE 59362 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April.

Cozic, C., Rousseau, D., and Tabary, R. 2009. Novel Insight Into Microgel System for Water Control. *SPE Prod & Opera* **24**(4): 590-601. SPE-115974-PA.

Dalrymple, D., Eoff, L., Vasquez, J., and Van Eijden, J. 2008. Shallow Penetration Particle-Gel System for Water and Gas Shutoff Applications. Paper SPE 114886 presented at the SPE Russian Oil & Gas Technical Conference and Exhibition, Moscow, 28-30 October. DOI: <http://dx.doi.org/10.2118/114886-MS>.

Deolarte, C., Vasquez, J., Soriano, E., and Santillan, A. 2009. Successful Combination of an Organically Cross-linked Polymer System and a Rigid-Setting Material for Conformance Control in Mexico. *SPE Prod & Opera* **24**(4): 522-529. DOI: <http://dx.doi.org/10.2118/112411-PA>.

Der Sarkissian, J., Prado, M., and Rauseo, O. 2005. Lessons Learned From Four Selective Water-Shutoff Treatments in Mature Reservoirs in Maracaibo Lake. 2005. Paper SPE 96528 presented at Offshore Europe 2005, Aberdeen, 6-9 September.

Diaz, D., Somaruga, C., Norman, C, and Romero, J. 2008. Colloidal Dispersion Gels Improve Oil Recovery in a Heterogeneous Argentina Waterflood. Paper SPE 113320 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19-23 April.

Donham, J.E. 1991. Offshore Water Injection System: Problems and Solutions. Paper OTC 6782 presented at the 23rd Annual OTC, Houston, 6-9 May. DOI: <http://dx.doi.org/10.4043/6782-MS>.

Elewaut, K., Stavland, A., Zaitoun, A., Krilov, Z., and Zitha, P.L.J. 2006. Investigation of a Novel Chemical for Bullhead Water Shutoff Treatments. Paper SPE 94660 presented at the SPE European Formation Damage Conference, Scheveningen, 25-27 May.

Eoff, L., Dalrymple, D., and Everett, D. 2006. Global Field Results of a Polymeric Gel System in Conformance Applications. Paper SPE 101822 presented at the SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, 3-6 October.

Eoff, L.S., Dalrymple, E.D., Everett, D., and Vasquez, J. 2007. Worldwide Field Applications of a Polymeric Gel System for Conformance Applications. *SPE Prod & Oper* **22** (2): 231-235. SPE-98119-PA. DOI: <http://dx.doi.org/10.2118/98119-PA>.

Feng, Y., Tabary, R., Renard, M., Bon, C.L., Omari, A., and Chauveteau, G. 2003. Characteristics of Microgels Designed for Water Shutoff and Profile Control. Paper SPE 80203 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 5-7 February.

Frampton, H., Morgan, J.C., Cheung, S.K., Munson, L., Chang, K.T., and Williams, D. 2004. Development of a Novel Waterflood Conformance Control System. Paper SPE 89391 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery, Tulsa, 17-21 April.

Grattoni, C.A., Jing, X.D., and Zimmerman, R.W. 2001. Disproportionate Permeability Reduction When a Silicate Gel is Formed In-Situ to Control Water Production. Paper SPE 69534 presented at SPE Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, 25-28 March.

Hardy, M.B. 2001. Methods and Compositions for Reducing the Permeabilities of Subterranean Zones. US Patent No. 6,196,317.

Hardy, M.B., Botermans, C.W., and Smith, P. 1998. New Organically Cross-linked Polymer System Provides Competent Propagation at High Temperatures in Conformance Treatments. Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19-22 April.

Hardy, M.B., Botermans, W., Hamouda, A., Valdal, J., and Warren, J. 1999. The First Carbonate Field Application of a New Organically Cross-linked Water Shut-off Polymer System. Paper SPE 50738 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 16-19 February.

Hernandez, M.I. 2012. Private Communication. March.

Hibbeler, J. and Rae, P. 2005. The Environmental Benefits of Reducing Water Production. Paper SPE 96582 presented at the SPE Asia Pacific Health, Safety, and Environment Conference and Exhibition, Kuala Lumpur, 19-20 September. DOI: <http://dx.doi.org/10.2118/96582-MS>.

Jaripatke, O. and Dalrymple, D. 2010. Water-Control Management Technologies: A Review of Successful Chemical Technologies in the Last Two Decades. Paper SPE 127806 presented at the 2010 SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, 10-12 February.

Johnson, S., Trejo, J., Veisi, M., Willhite, G.P., Liang, J.T., and Berkland, C. 2010. Effects of Divalent Cations, Seawater, and Formation Brine on Positively Charged Polyethyleneimine/Dextran Sulfate/Chromium (III) Polyelectrolyte Complexes and Partially Hydrolyzed Polyacrylamide/Chromium (III) Gelation. *J of Applied polymer Science* **115**: 1008-1014.

Junesompitsiri, C., Berel, A., Curtice, R., Riyanto, L., Thouvenin, E., and Cheneviere, P. 2009. Selective Water Shutoff in Gas Well Turns a Liability into an Asset: A Successful Case History from East Kalimantan, Indonesia. Paper SPE 121182 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, 4-6 August. DOI: <http://dx.doi.org/10.2118/121182-MS>.

Kabir, A.H. 2001. Chemical Water & Gas Shutoff Technology-An Overview. Paper SPE 72119 presented at the SPE Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, 8-9 October.

Khatib, Z. 2007. Produced Water Management: Is it a Future Legacy or a Business Opportunity for Field Development. Paper IPTC 11624 presented at the International Petroleum Technology Conference, Dubai, 4-6 December.

Kurenkov, V.F., Hartan, H.G., and Lobanov, F.I. 2001. Alkaline Hydrolysis of Polyacrylamide. *Russian Journal of Applied Chemistry* **74** (4): 543-554.

Leighton, J., Saltel, J.L., Morrison, J., Welch, R., and Pilla, J. 2001. Water Shutoff Using Inflatable Composite Sleeve Polymerized In-Situ: A Case History on Forties Delta. *SPE Prod & Fac* **16** (2): 97-105. SPE-72051-PA.

Lei, G., Li, L., and Nasr-El-Din, H.A. 2011. New Gel Aggregates To Improve Sweep Efficiency During Waterflooding. 2011. *SPE Res Eng* **14**(1): 120-128. SPE-129960-PA.

Li, M.Y., Dong, Z.X., Lin, M.Q, and Wu, Z.L. 2004. A study on Size and Conformation of Linked Polymers Coils. *Journal of Petroleum Science and Engineering* **41**(1-3): 213-219.

Liang, J., Lee, R.L. and Seright, R.S. 1993. Gel Placement in Production Wells. *SPE Prod & Fac* **8** (1): 276-284. SPE-20211-PA.

Liang, J.T, Sun, H. and Seright, R.S. 1995. Why Do Gels Reduce Water Permeability More Than Oil Permeability? *SPE Res Eng* **10** (4): 282-286. SPE-27859-PA.

Lightford, S., Pitoni, E., Burrafato, G., and Serapiglia, C.P. 2008. Solving Excessive Water Production in a Prolific Long Horizontal Open Hole Drilled in a Naturally Fractured Carbonate Reservoir. Paper SPE 113700 presented at the SPE/ICoTA Coiled Tubing and well Intervention Conference and Exhibition, The Woodlands, 1-2 April. DOI: <http://dx.doi.org/10.2118/113700-MS>.

Lockhart, T.P. 1991. Chemical and Structural Studies on Cr^{+3} /Polyacrylamide Gels. Paper SPE 20998 presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, 20-22 February.

Mack, J.C. and Smith, J.E. 1994. In-Depth Colloidal Dispersion Gels Improve Oil Recovery Efficiency. Paper SPE 27780 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 17-20 April. DOI: <http://dx.doi.org/10.2118/27780-MS>.

Mercado, M., Acuna, J.C., Caballero, C., Vasquez, J., and Soriano, E. 2009. Successful Field Application of a High-Temperature Conformance Polymer in Mexico. Paper SPE 120966 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, 20-22 April. DOI: <http://dx.doi.org/10.2118/120966-MS>.

Merdhah, A.B. and Yassin, A.M. 2009. Scale Formation Due to Water Injection in Malaysian Sandstone Cores. *American J. of Applied Science* **6** (8): 1531-1538.

Moradi-Araghi, A. 2000. A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production. *Journal of Petroleum Science and Engineering* **26** (1-4): 1-10.

Moradi-Araghi, A. and Doe, P. 1987. Hydrolysis and Precipitation of Polyacrylamide in Hard Brines at Elevated Temperatures. *SPE Res Eng* **2** (2): 189-198. SPE-13033-PA.

Moradi-Araghi, A., Cleveland, D.H., and Westerman, I.J. 1987. Development and Evaluation of EOR Polymers Suitable for Hostile Environments-Part II: Copolymers of Acrylamide and Sodium AMPS. Paper SPE 16273 presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, 4-6 February. DOI: <http://dx.doi.org/10.2118/16273-MS>.

Morel, D., Labastie, A., Jouenne, S., and Nahas, E. 2007. Feasibility Study for EOR by Polymer Injection in Deep Offshore Fields. Paper IPTC 11800 presented at the International Petroleum Technology Conference, Dubai, 4-6 December.

Morgan, J.C., Smith, P.L., and Stevens, D.G. 1997. Chemical Adaptation and Deployment Strategies for Water and Gas Shut-off Gel Systems. Paper presented at the 1997 Royal Chemistry Society's Chemistry in the Oil Industry International Symposium, Ambleside, April 14-17.

Mustoni, J.L., Norman, C.A., and Denyer, P. 2010. Deep Conformance Control by a Novel Thermally Activated Particle System to Improve Sweep Efficiency in Mature Waterfloods of the San Jorge Basin. Paper SPE 129732 presented at the 2010 SPE Improved Oil Recovery Symposium, Tulsa, 24-28 April.

Nasr-El-Din, H.A. 2003. New Mechanisms of Formation Damage: lab Studies and Case Histories. Paper SPE 82253 presented at the SPE European Formation Damage Conference, The Hauge, 13-14 May.

Nasr-El-Din, H.A. and Taylor, K.C. 2005. Evaluation of sodium silicate / urea gels used for water shut-off treatments. *Journal of Petroleum Science and Engineering* **48** (3-4): 141- 160.

Ohm, D., McLeod, J.D., Graff, C.J., Frampton, H., Morgan, J.C., Cheung, S.K., and Chang, K.T. 2010. Incremental-Oil Success From Waterflood Sweep Improvement in Alaska. *SPE Prod & Opera* **25**(2): 247-254. <http://dx.doi.org/10.2118/121761-PA>.

Park, C.S., Lee, H.I., Son, S.M., Chung, M.K., Baek, K.K., and Chung, E.S. 2009. Premature Coating Disbonding on Ships and Offshore Structures. Paper NACE 09015 presented at the NACE International Corrosion 2009 Conference & EXPO, Atlanta, 22-26 March.

Patnaik, P. 2007. A Comprehensive Guide to the hazardous Properties of Chemical Substances. 3ed Edition. ISBN-13: 978-0-471-71458-3.

Perdomo, L., Rodriguez, H., Liamedo, M., Oliveros, L., Gonzalez, E., and Molina O. 2007. Successful Experiences for Water and Gas Shutoff Treatments in North Monagas, Venezuela. Paper SPE 106564 presented at the Latin American & Caribbean Petroleum Engineering Conference, Buenos Aires, 15-18 April.

Petrie, E.M. 2001. Adhesives Families/Handbook of Adhesives and Sealant. Page 383.

Polo, R.P.O., Monroy, R.R., Toledo, N., Dalrymple, E.D., Eoff, L., and Everett, D. 2004. Field Applications of Low Molecular-Weight Polymer Activated with an Organic Cross-linker for Water Conformance in South Mexico. Paper SPE 90449 presented at the SPE Annual Technical Conference and Exhibition, Houston, 26-29 September. DOI: <http://dx.doi.org/10.2118/90449-MS>.

Prada, A., Civan, F., and Dalrymple E.D. 2000. Evaluation of Gelation Systems for Conformance Control. Paper SPE 59322 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April. DOI: <http://dx.doi.org/10.2118/59322-MS>.

Prado, M., Palencia, J., Reyna, M., Fernandez, I., Espinoza, J., and Rauseo, O. 2005. Two Different Water Shutoff Applications in a Poorly Consolidated Sandstone Reservoir with Strong

Water drive. Paper SPE 93060 presented at the 2005 SPE International Symposium on Oilfield Chemistry, Houston, 2-4 February.

Pritchett, J., Frampton, H., Brinkman, J., Cheung, S., Morgan, J., Chang, K.T., Williams, D., and Goodgame, J. 2003. Field Application of a New In-Depth Waterflood Conformance Improvement Tool. Paper SPE 84897 presented at the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, 20-21 October.

Reddy, B.R., Eoff, L., Dalrymple, E.D., Black, K., Brown, D., and Rietjens, M. 2003. A Natural Polymer-Based Cross-linker System for Conformance Gel Systems. *SPEJ* **8** (2): 99-106. SPE-84937-PA. DOI: <http://dx.doi.org/10.2118/84937-PA>.

Rousseau, D., Chauveteau, G., Renard, M., Tabary, R., Zaitoun, A., Mallo, P., Braun, O., and Omari, A. 2005. Rheology and Transport in Porous Media of New Water Shutoff /Conformance Control Microgel. Paper SPE 93254 presented at the 2005 SPE International Symposium on Oilfield Chemistry, Houston, 2-4 February.

Roussennac, B. and Toschi, C. 2010. Bright Water Trial in Salema Field (Campos Basin, Brazil). Paper SPE 131299 presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition, Barcelona, 14-17 June.

Saltel, J.L., Leighton, J.R.N., Faure, A.M., and Baaijens, T. 1999. In-Situ Polymerization of Inflatable Composite Sleeve To Reline Damaged Tubing and Shut Off Perforations. *SPE Drill & Comp* **14**(2): 115-122. SPE-56867-PA.

Seright, R.S. 2007. Are Colloidal Dispersion Gels Really a Viable Technology? New Mexico Petroleum Recovery Research Center. DOI: <http://baervan.nmt.edu/randy>.

Seright, R.S., Lane, R.H., and Sydansk, R.D. 2003. A Strategy for Attacking Excess Water Production. *SPE Prod & Fac* **18** (3): 158-169. SPE-84966-PA.

Seright, R.S., Zhang, G., Akanni, O.O., and Wang, D. 2011. A Comparison of Polymer Flooding With In-Depth Profile Modification. Paper CSUG/SPE 146087 presented at the Canadian Unconventional Resources Conference, Calgary, 15-17 November.

Shafian, S.R.M., Hassan, A.A., Ismail, S., Teng, L.K., and Irawan, S. 2010. Blocked Isocyanate Fluid System for Water Shut Off Application. Paper IADC/SPE 132813 presented at the IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition, Ho Chi Minh City, 1-3 November.

Son, S.M., Chung, M.K., Shin, C.S., and Kim, K.H. 2010. Feasibility Study of Rapid Cure Anti-Corrosive Coatings for Marine Environments. Paper NACE 10016 presented at the NACE International 2010 Corrosion Conference & EXPO, San Antonio, 14-18 March.

Spildo, K, Skauge, A, Aarra, M.G., and Tweheyo, M.T. 2009. A New Polymer Application for North Sea Reservoirs. *SPE Res Evaluation & Eng* **12**(3): 427-432. SPE-113460-PA.

Stavland, A., Andersen, K.I., Sandoy, B., Tjomsland, T., and Mebratu, A.A. 2006. How To Apply a Blocking Gel System for Bullhead Selective Water Shutoff: From laboratory to Field. Paper SPE 99729 presented at the SPE/DOE Symposium on Improved Oil Recovery Tulsa, April 22-26 April. DOI: <http://dx.doi.org/10.2118/99729-MS>.

Sydansk, R.D. 1990. A Newly Developed Chromium (III) Gel Technology. *SPE Res Eng* **5** (3): 346-352. SPE-19308-PA.

Sydansk, R.D. 2007. Polymers, Gels, Foams, and Resins. Petroleum Engineering Handbook (2nd edition), L. W. Lake (ed.), Society of Petroleum Engineers, Richardson, Texas, Volume V (Reservoir Engineering and Petrophysics), Chapter 13: 1149-1260.

Sydansk, R.D. and Romero-zeron, L. 2011. Reservoir Conformance Improvement. Society of Petroleum Engineers. ISBN-10:1555633021.

Sydansk, R.D. and Seright, R.S. 2007. When and Where Relative Permeability Modification Water-Shutoff Treatments Can Be Successfully Applied. *SPE Prod & Oper* **22** (2): 236-247. SPE-99371-PA.

Sydansk, R.D. and Southwell, G.P. 2000. More than 12 Years Experience with a Successful Conformance-Control Polymer-Gel Technology. *SPE Prod & Fac* **15** (4): 270-278. SPE-55668-PA.

Sydansk, R.D., Xiong, Y., Al-Dhafeeri, A.M., Schrader, R.J., and Seright, R.S. 2005. Characterization of Partially Formed Polymer Gels for Application to Fractured Production Wells for Water-Shutoff Purposes. *SPE Prod & Fac* **20** (3): 240-249. SPE-89401-PA.

Uddin, S., Dolan, J.D., Chona, R.A., Gazi, N.H., Monteiro, K., Al-Rubaiyea, J.A., and Al-Sharqawi, A. 2003. Lessons Learned from the First Openhole Horizontal Well Water Shutoff Job Using Two New Polymer Systems-A Case History from Wafra Ratawi Field, Kuwait. Paper SPE 81447 presented at the SPE Middle East Oil Show, Bahrain, 9-12 June.

Urlwin-Smith, P.L. 1998. Oil and Gas Field Chemicals. US Patent No. 5, 836, 392.

Urlwin-Smith, P.L. 2001. Blocking Composition for Use in Subterranean Formation. US Patent No. 6, 192, 986.

Van Eijden, J., Arkesteijn, F., Akil, I., Vliet, J., van, Batenburg, D., and McGinn, P. 2004 Gel-Cement, a Water Shut-Off System: Qualification in a Syrian Field. Paper SPE 88765 presented at the International Petroleum Exhibition and Conference, Abu Dhabi, 10-13 October.

Van Eijden, J., Arkesteijn, F., Van Batenburg, D., and Van Vliet, J. 2005. Development and Field Application of a Shallow Perforation Shutoff System for HP/HT Oil Wells. Paper SPE 94518 presented at the SPE European Formation Damage Conference, Sheveningen, 25-27 May. DOI: <http://dx.doi.org/10.2118/94518-MS>.

Vasquez, J. and Eoff, L. 2010. Laboratory Development and Successful Field Application of a Conformance Polymer System for Low, Medium, and High-Temperature Applications. Paper SPE 139308 presented at the SPE Latin American & Caribbean Petroleum Engineering Conference, Lima, 1-3 December. DOI: <http://dx.doi.org/10.2118/139308-MS>.

Vasquez, J., Civan, F., Shaw, T.M., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Brown, D. 2003. Laboratory Evaluation of High-Temperature Conformance Polymer Systems. Paper SPE 80904 presented at the SPE Production and Operations Symposium, Oklahoma City, 22-25 March. DOI: <http://dx.doi.org/10.2118/80904-MS>.

Vasquez, J., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Civan, F. 2005. Development and Evaluation of High Temperature Conformance Polymer Systems. Paper SPE 93156 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, 2-4 February. DOI: <http://dx.doi.org/10.2118/93156-MS>.

Vasquez, J., Jurado, I., Santillan, A., and Hernandez, R. 2006. Organically Cross-linked Polymer System for Water Reduction Treatments in Mexico. Paper SPE 104134 presented at the First International Oil Conference and Exhibition, Cancun, 31 August-2 September. DOI: <http://dx.doi.org/10.2118/104134-MS>.

Vega, I., Morris, W., Robles, J., Peacock, H., and Marin, A. 2010. Water Shut-off Polymer Systems: Design and Efficiency Evaluation based on Experimental Studies. Paper SPE 129940 presented at the 2010 SPE Improved Oil Recovery Symposium, Tulsa, 24-28 April.

Veil, J.A., Puder, M.G., Elcock, D., and Redweik, R.J. 2004. Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. United States Department of Energy, National Energy Technology laboratory, Under Contract W-31-109-Eng-38, 2004.

Wang, L., Zhang, G.C., Ge, J.J., Li, G.H., Zhang, J.Q., and Ding, B.D. 2010. Preparation of Microgel Nanospheres and Their Application in EOR. Paper SPE 130357 presented at the CPS/SPE International Oil & Gas Conference and Exhibition, Beijing, 8-10 June.

Zaitoun, A. and Kohler, N. 1988. Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. Paper SPE 18085 presented at the SPE Annual Technical Conference and Exhibition, Houston, 2-5 October.

Zaitoun, A., Tabary, R., Rousseau, D., Pichery, T., Nouyoux, S., Mallo, P., and Braun, O. 2007. Using Microgels To Shut Off Water in a Gas Storage. Paper SPE 106042 presented at the 2007 SPE International Symposium on Oilfield Chemistry, Houston, 28 February-2 March.

CHAPTER THREE

Retardation of Polyacrylamide Crosslinking with Polythethyleneimine: New Insights using ^{13}C NMR, DSC and Rheology

Khalid S.M. El-Karsani¹, Ghaithan A. Al-Muntasheri^{2}, Abdullah S. Sultan³ & Ibbelwaleed A. Hussein⁴*

^{1&4}Chemical Engineering Department, King Fahd University of Petroleum & Minerals; Dhahran 31261, PO BOX 5050, Saudi Arabia

²Production Technology Team, EXPEC Advanced Research Center, Dhahran 31311, Saudi Aramco, Saudi Arabia

³Petroleum Engineering Department, and Center for Petroleum & Minerals (CPM), King Fahd University of Petroleum & Minerals; Dhahran 31261, Saudi Arabia

Abstract

Polyacrylamide (PAM) and its derivatives are the most commonly used polymers to prepare polymeric gels for water control in petroleum reservoirs. This study involves polyethylenimine (PEI) as a cross-linker for PAM. This paper investigates PAM alkaline hydrolysis at high temperatures. Salts are used as retarders to elongate the gelation time of PAM/PEI system. The effect of salts on the degree of hydrolysis of PAM was investigated. The data obtained from ^{13}C Nuclear Magnetic Resonance Spectroscopy (NMR) was used to understand the retardation mechanisms by salts. NH_4Cl was found to accelerate the extent of hydrolysis more in comparison with NaCl . FTIR was used to characterize the hydrolysis and confirm the NMR results. Moreover, the apparent viscosity of the hydrolyzed samples was measured. Despite their higher degree of hydrolysis, samples hydrolyzed in the presence of NH_4Cl were found to have lower viscosity as opposed to NaCl . This indicates that NH_4Cl is more effective in shielding negative charges on the carboxylate groups of the PAM chain. The thermal stability of the

PAM/PEI polymeric gels was examined in bulk at 150°C (302°F) for about 16 weeks using freshwater (1,200 ppm) and seawater (45,000 ppm). Samples prepared in sea water showed more stability compared to distilled and field water samples. In a compatibility test, NaCl and NH₄Cl were found to be compatible with PAM/PEI system, but Na₂CO₃ showed a white precipitate. In addition, high temperature/high pressure elastic modulus data is reported for the first time for this system. Differential Scanning Calorimetry (DSC) was coupled with rheology to explain PAM/PEI crosslinking in the presence of salts.

Keywords: Polyacrylamide, hydrolysis, Polymeric gel, organic cross-linking, thermal stability, Gel strength

***Corresponding Author: ihussein@kfupm.edu.sa; Tel/fax: +966 13 860 2235/4234**

3.1 Introduction

Polyacrylamide (PAM) is one of the most commonly used water-soluble polymers in oilfield processes. These processes comprise drilling, polymer flooding and other Enhanced Oil Recovery (EOR) methods such as alkaline and alkaline-surfactant-polymer (ASP) flooding. In Improved Oil Recovery (IOR), PAM is used in water control (Seright et al. 2003), friction reduction (Gaillard et al. 2013) and more recently as a fracturing fluid (Holtsclaw & Funkhouser 2010).

Literature reports that PAM can be cross-linked with different types of cross-linkers to produce polymeric gels for water control in conformance improvement treatments (CITs). This includes inorganic cross-linkers such as chromium (Prud'homme et al. 1983; Sydansk. 1988& 1990; Lockhart. 1991& 1994; Sydansk and Southwell. 2000; te Nijenhuis et al. 2003; Al-Assi et al. 2006) and organic cross-linkers like phenol and formaldehyde (Albonico and Lockort. 1993)

or polyethylenimine (Morgan et al. 1997; Hardy et al. 1998; Urlwin-Smith. 1998 & 2001). Chitosan which is a natural cross-linker was also used to form polymeric gels (Reddy et al. 2003). Organically cross-linked gels are more preferable than inorganic cross-linked gels. This is due to their stability at high temperature.

In organically cross-linked gels, the gelation time was found to be short at high temperatures. In **Fig. 3.1**, PAM was cross-linked with PEI at a concentration ratio of (PAM/PEI) 7/0.3 wt% at 150°C (302°F), the gelation time (defined as the inflection point in the viscosity vs. time plot) was less than half an hour. This gelation time is too short for successful placement of the gel in reservoirs at high temperatures (300°F). The gel may form inside the tubings before reaching the desired zone which may lead to severe plugging problems. A practical gelation time should be more than 55 minutes. This is based on studies in local fields (Al-Muntasheri et al. 2010). Thus, there is a need for increasing the gelation time to an optimum value. Different options were implemented to overcome this issue. This includes cooling the near wellbore area using a pre-flush, cross-linker modification, and adding some retarders (salts). The injection of large amounts of water is not an acceptable option in oilfield. Besides, it was reported that the permeability to oil could be altered by injecting small amount of water (Morgan et al. 1997). Different literature reports discussed the modification of the cross-linker. Specifically, the PEI was modified to derivatized PEI (Hardy 2001; Vasquez et al. 2005) and polyamino acid (Vasquez et al. 2005). Different retarders (salts) were reported to elongate the gelation time for polyacrylamide tert-butyl acrylate (PAtBA) / PEI. This includes sodium carbonate (Na_2CO_3), sodium chloride (NaCl), and ammonium chloride (NH_4Cl). Although Na_2CO_3 was found to have a good retardation effect for PAtBA / PEI system (Eoff et al. 2006), but it showed some compatibility problems with high salinity brines (Al-Muntasheri et al. 2010). NaCl and NH_4Cl

were chosen to be alternatives for Na_2CO_3 to increase the gelation time of PAtBA/PEI system in high temperature applications. NaCl did not give an acceptable increase in gelation time (Al-Muntasheri et al. 2010), whereas, NH_4Cl extend the gelation time to 1.5 hours at 150°C (302°F).

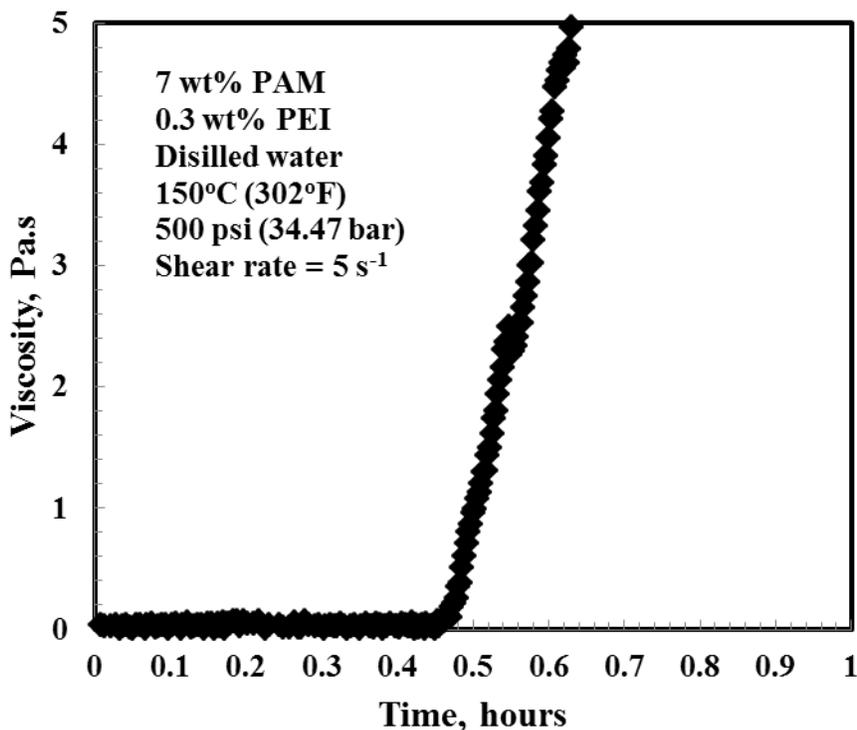


Figure 3. 1 Viscosity evolution of the PAM / PEI, (7/0.3) wt% system at 150°C (302°F)

The mechanism by which salts elongate the crosslinking reaction of PAM-based polymers with PEI was a subject of discussion over the past several years. It was hypothesized that salts affect hydrolysis of PAM where they reduce its hydrolysis extent. Moreover, it has been thought that salts do affect the hydrodynamic volume of the polymer and thus reduce the number of accessible sites on the polymer. PAM undergoes alkaline hydrolysis under high temperature to produce partially hydrolyzed polyacrylamide (PHPA) (contains carboxylate groups) and ammonia (Moradi-Araghi and Doe 1987; Moradi-Araghi, 2000; Kurenkov et al., 2001). This chemical reaction is shown in **Fig. 3.2**.

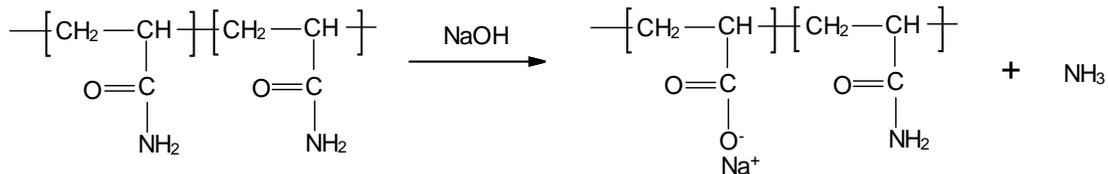


Figure 3. 2 Hydrolysis of amide groups under alkaline conditions

(Moradi-Araghi and Doe, 1987; Moradi-Araghi, 2000; Kurenkov et al., 2001)

The formation of PHPA through the hydrolysis reaction turns the polymer into a polyelectrolyte carrying negative charges on the carboxylate groups. This may lead to strong interactions with cations depending on the degree of hydrolysis. The degree of hydrolysis is an important factor which plays a major role in polymer instability as well as in determining the charge density of the polymer backbone. The use of salts can also be negative if compatibility with the field mixing brines was not examined.

The first study of PAM/PEI polymeric gel system was reported by Allison and Purkapple (1988). The authors observed a formation of aqueous gels at room temperature. The PAM/PEI gel system was found to be rigid and stable in distilled water for 8 weeks at 130°C by using a polymer and cross-linker concentrations of 7 and 1 wt%, respectively (Al-Muntasheri et al. 2008). There is a need to investigate the stability of this system at higher temperatures because some reservoirs exhibited temperatures above 130°C (266°F). Also, using representative field water in laboratory studies is a key factor for the success of the system in field applications. The degree of hydrolysis plays an important role in cross-linking reactions.

Hence, the objectives of this paper are to: investigate the effect of salts on the degree of hydrolysis through 13C NMR; utilize various analytical techniques such as Differential Scanning

Calorimetry (DSC), Fourier Transform Infrared (FTIR) and oscillatory rheological measurements to contribute to the understanding of the salts retardation mechanisms of PAM/PEI gels and study the stability of PAM/PEI polymer gel system in bulk at 150°C (302°F) using different salinities (distilled, field, and sea water).

3.2 Experimental

3.2.1 Materials

The polyacrylamide (PAM) used in this study was supplied by SNF Floerger as an aqueous solution with 20% activity and it was used as provided. The molecular weight as disclosed by the supplier ranges from 250 to 500 kg/gmol. The pH value of PAM is around 4.0. The cross-linker was polyethylenimine (PEI) and has a pH value of about 11.7. The molecular weight and the activity of PEI are 70 kg/gmol and 30%, respectively (as disclosed by the supplier). Sodium chloride (NaCl), ammonium chloride (NH₄Cl), and sodium carbonate (Na₂CO₃) were used. All of these salts were ACS grade. The pH of the solutions was adjusted to 10 by adding NaOH (1M). The HQ40D pH meter was used to measure the pH of the polymer solution. All samples were purged with nitrogen before heating to remove oxygen. This is because at high temperatures, oxygen could lead to a negative impact on polymer thermal stability (Shupe. 1981; Ryles. 1983). Field water was collected from a close field, whereas, sea water was obtained from the Arabian Gulf. The pH values of field and sea water were 8.02 and 7.75, respectively. The chemical analysis of these waters is given in **Table 3.1**.

Table 3. 1 Chemical analysis of mixing waters used in the experiments

Ion, ppm	Water type	
	Field	Sea
Na	175	17,085
Mg	46	2,200
Ca	112	1,040
Cl	377	31,267
SO ₄	266	4,308
HCO ₃	146	140
Total Dissolved Solids (TDS)*	1,122	56,040

* TDS were determined by addition.

3.2.2 Methods

The thermal stability was assessed through bulk testing and a wide range of concentrations was used for PAM and PEI. The gelling solutions were prepared at room temperature. PAM was added to water first and stirred for about one minute, then PEI was added and the mixture was stirred for 10 more minutes. The polymer solutions which are referred to as gelants were transferred into the Screw-Thread GL 18 Schott-type high thermal resistance glass tubes. Nitrogen gas was circulated through the gelling solutions. Finally, all samples were put in an oven at 150°C (302°F).

To determine the degree of hydrolysis, various techniques were reported in literature. These include: conductometric titration, nitrogen content, potentiometric titration, IR & UV spectroscopy, thermogravimetric analysis, ¹³C Nuclear Magnetic Resonance Spectroscopy (NMR) and calorimetry (Taylor and Nasr-El-Din 1994). Due to its accuracy and availability, ¹³C NMR spectroscopy was used in this work for the measurement of the degree of hydrolysis of

polymers which has been used by other researchers (Hutchinson and McCormick 1986; Moradi-Araghi et al. 1988). To prepare a sample for ^{13}C NMR, a predetermined amount of salt (NaCl or NH_4Cl) was added to PAM while stirring. All hydrolysis of PAM in this work was carried out under alkaline conditions. This is due to the fact that PAM/PEI crosslinking reactions take place under alkaline conditions (pH of 9.9 to 10.5) because of the high pH of the PEI (11.7). Use has been made of NaOH (1M) to adjust the pH of the solution to 10. After that, the polymer solutions were transferred to the Screw-Thread GL 18 Schott-type high thermal resistance glass tubes. The tubes were sealed while heating. All samples were placed in a Haake N3 oil bath maintained at 120°C (248°F). This oil bath is equipped with a digital temperature display having an accuracy of $\pm 0.1^\circ\text{C}$. The samples were maintained at these conditions for one week and each day a sample was taken for NMR testing. A Jeol 500 MHR NMR spectrophotometer equipped with multinuclear probes was used for the ^{13}C NMR characterization. The NMR spectroscopy was run at 125.65 MHz, and the spectra were collected at room temperature (25°C) (77°F). P-dioxane was used as a reference at 67.4 ppm. Few drops of D_2O were added to the polymer solution to lock the signal. Other experimental parameters comprised the use of 6 seconds delay time, a pulse width of 4.3 μsec , 8,246 scans and acquisition time of 0.96 second. Inverse-gated decoupling was used to overcome Nuclear Overhauser Enhancement (NOE). It should be mentioned that all spectra were collected for at least 10 hours to improve noise to signal ratio. The resultant spectra were integrated and their degree of hydrolysis was calculated.

In the compatibility tests, samples of PAM / PEI (7/1) wt% were prepared in a pre-flush (field water in 2 wt% KCl) with a total of 250 lb/ 1000 gal (30,000 ppm) of three retarders; sodium chloride, sodium carbonate, and ammonium chloride. Other samples of 1 wt% PEI were prepared in field water without PAM with the three retarders using the same previously

mentioned concentration of salts. 10 ml of the solution was mixed with 10 ml of pre-flush. Then the samples were heated in the oven which was maintained at 150°C (302°F). The samples were aged for one day.

All rheology measurements were conducted in a Discovery Hybrid Rheometer (DHR) from TA Instruments. The rheometer is equipped with a high-pressure cell. For steady shear measurements, concentric cylinder geometry with bob and cup diameters of 28 and 30.43 mm respectively was used. The gelation tests were performed in the high-pressure cell setup with bob and cup diameters of 26 and 28 mm. The setup has a torque limit of 100 $\mu\text{N}\cdot\text{m}$ to 0.2 Nm, pressure of 500 psi, and a maximum temperature of 150°C (302°F).

Differential Scanning Calorimetry (DSC) measurements were using a Q1000 DSC instrument provided by TA Instruments. This machine is equipped with a refrigerating cooling system (RCS) which uses nitrogen and an auto-sampler. The instrument was purged by nitrogen at a flow rate of 50 mL/min. The samples were put in Aluminum hermetic pans and were then sealed with a pressing tool. The empty Aluminum hermetic pan was used as a reference. All samples were calibrated at 30°C (86°F) for 5 minutes, then ramped at 1.5°C/min to 120°C (248°F), and then kept at this temperature until no change in heat flow observed.

An additional technique to characterize the hydrolyzed polymers was used. That was Fourier Transform Infrared (FTIR) Spectroscopy. A Nicolet 6700 spectrometer provided by Thermo Electron was used for the FTIR characterization. The FTIR data were taken at room temperature in a wave length ranging from 600 to 4000 cm^{-1} .

3.3 Results and Discussion

3.3.1 Analysis of the NMR Spectra

Samples of PAM were aged at 120°C (248°F) for different times after adjusting their pH to 10. Then the degree of hydrolysis was determined through ^{13}C NMR by using the following equation:

$$\tau = \frac{(I_{\text{C=O}})_{\text{OH}}}{(I_{\text{C=O}})_{\text{OH}} + (I_{\text{C=O}})_{\text{NH}_2}} \times 100 \quad (1)$$

where, $(I_{\text{C=O}})_{\text{OH}}$, and $(I_{\text{C=O}})_{\text{NH}_2}$ represent the areas under resonance peaks of the carbonyl carbons attached to the carboxylate and amide groups, respectively. These were located at (181-184) and (177-180) ppm, respectively. Note that the degree of hydrolysis of neat PAM was found to be zero percent as disclosed by the supplier. This is confirmed through ^{13}C NMR test for neat PAM and the spectrum did not show any peak for the carboxylate group in the chemical shift range 180-184 ppm (Fig. 3.3).

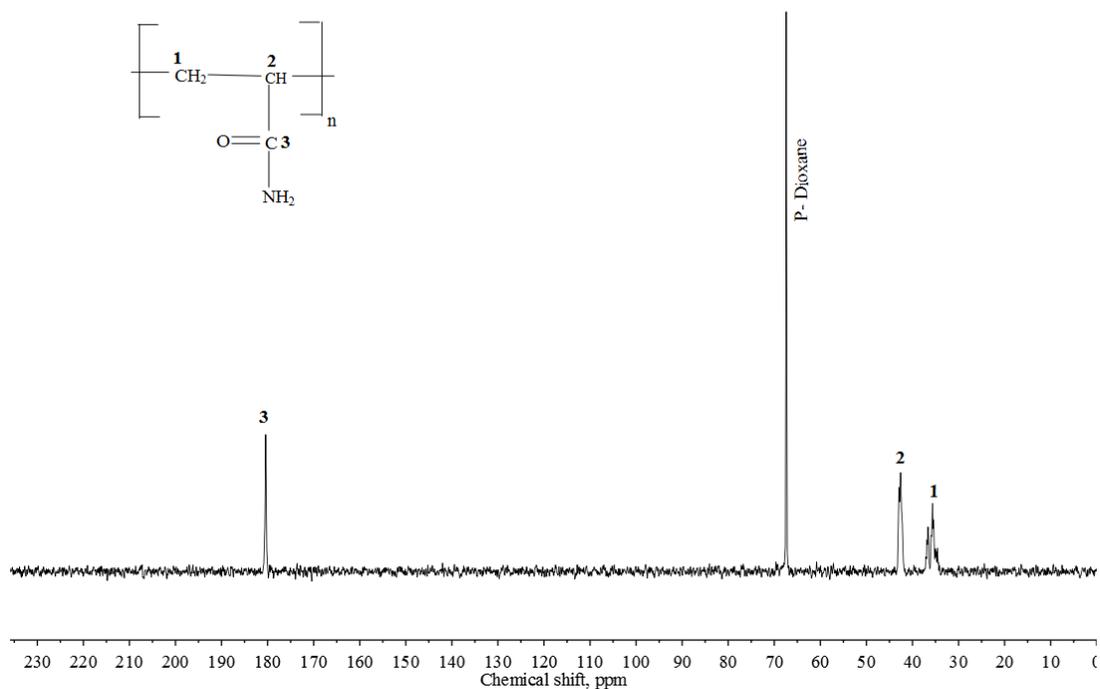


Figure 3. 3: ¹³C NMR spectrum of neat sample of PAM

3.3.2 Hydrolysis of Polyacrylamide

The degree of hydrolysis plays a major role in the thermal instability of polymeric gels. At the same time, adding retarders (salts) is very important to extend the gelation time to allow for successful and safe gel placement in the target zones. Hence, it is important to investigate the effect of these salts on the degree of hydrolysis and its extent at high temperatures.

The degree of hydrolysis was plotted vs. time as illustrated in **Fig. 3.4** which shows the hydrolysis of neat PAM at 120°C (248°F). These results are characterized by two different steps. In the first step, the degree of hydrolysis has increased at a high rate until about 42 mol%. Then, the rate of increase of the degree of hydrolysis decreased. The initial high rate can be explained

by the catalytic effect of the neighboring amides and the high concentration of the OH^- (Kurnekov et al., 2001). The high increase can be explained by the effect of the carboxylate groups formed during the hydrolysis. It was reported that the carboxylate groups increase the hydrolysis of the amide groups attached nearby (Kurenkov et al., 2001). Note that at high degree of hydrolysis, more than 45%, another mechanism takes place. The repulsion between the negative carboxylate and hydroxide ions causes a reduction in the hydrolysis rate.

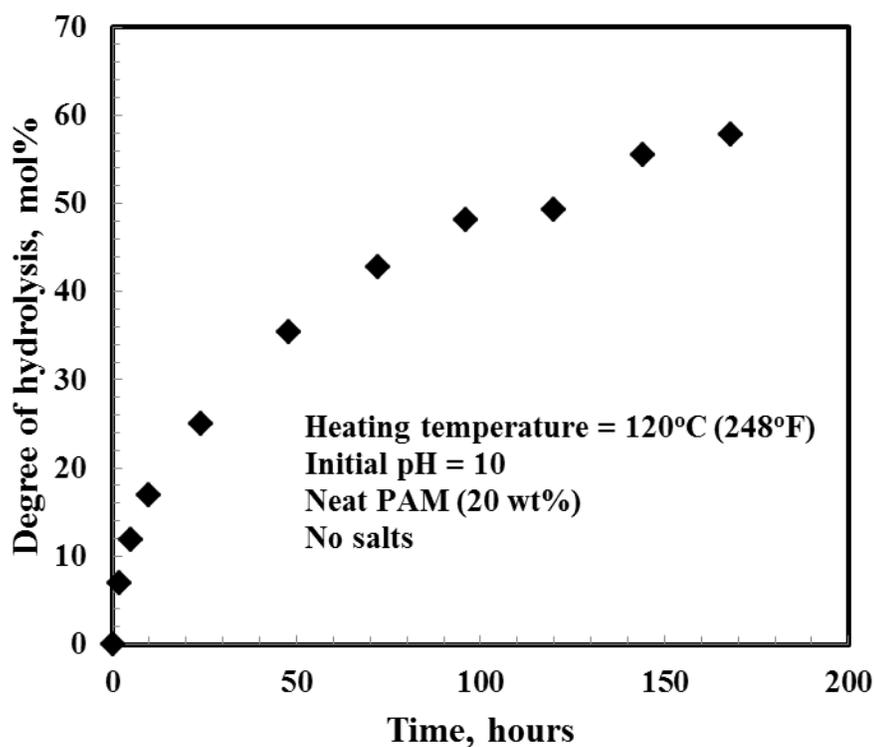


Figure 3. 4: Hydrolysis of neat PAM at 120°C (248°F) & pH 10

The experimental data in **Fig. 3.4** shows a strong dependency of degree of hydrolysis on time. The hydrolysis of PAM has been reported as first order reaction with respect to amide concentration (Higuchi and Senju 1972; Halverson et al. 1985; Kudryavtsev et al. 1998; Levitt et

al. 2011, Ilavsky et al. 1984; Parker and Lezzi. 1993; Caulfield et al. 2002) which can be represented as follows:

$$-\frac{dA}{dt} = k_A A \quad (2)$$

where k_A is the first order hydrolysis reaction rate constant. Equation 2 can be integrated and rewritten to give the below equation:

$$\tau = (1 - \exp(-k_A t)) \times 100 \quad (3)$$

where t is time in seconds.

In order to investigate the effects of salts on the hydrolysis behavior of the polymer, additional tests were conducted using inorganic salts that are used as retarders in water control treatments. The salts were introduced to PAM and the pH of the solution was adjusted to 10, then the samples were heated and the degree of hydrolysis was obtained from ^{13}C NMR as discussed earlier. The results of the degree of hydrolysis are shown in **Fig. 3.5** for 30,000 ppm salt. The data shows that there is a difference between the various salts and the base case with no salts. For example, after one day, the degree of hydrolysis was found to be 53%, 30% and 25% for PAM solution with NH_4Cl , NaCl , PAM, respectively. It is evident that the influence of NH_4Cl on the extent of PAM hydrolysis is very strong while that of NaCl was less.

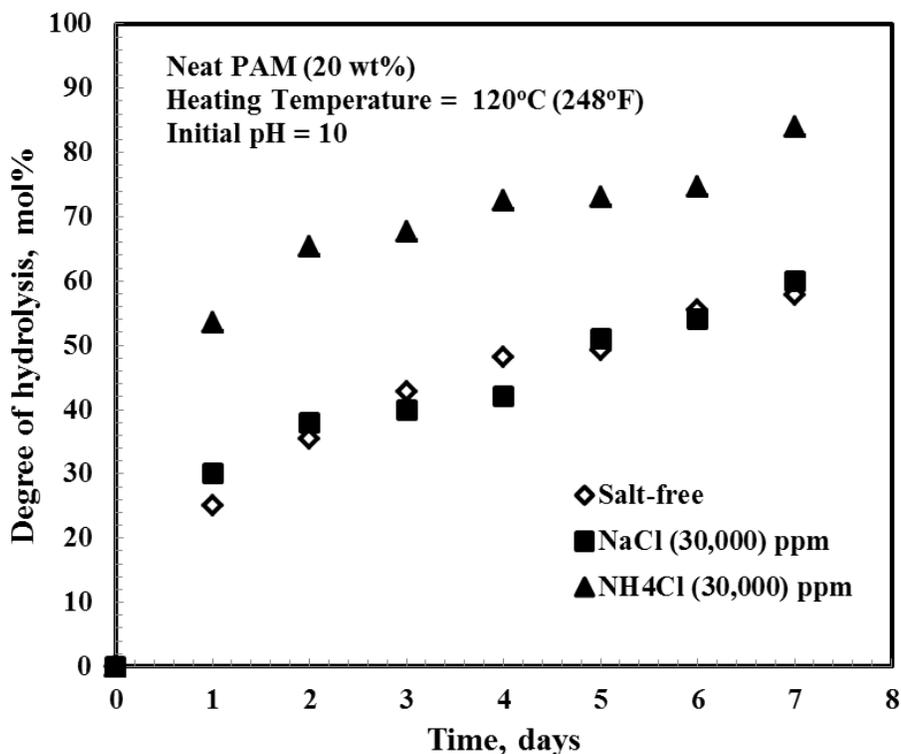


Figure 3. 5: Effect of high salts concentration (30,000 ppm) on DH of PAM at 120°C (248°F)

Since the effect of salt was significant, further tests were conducted to examine the effect of salt concentration on the hydrolysis extent of PAM. PAM solutions containing NaCl and NH₄Cl by maintaining the same number of moles (0.0114 moles). The results are shown in **Fig. 3.6**. The same trend of increasing degree of hydrolysis was observed. High degree of hydrolysis was obtained in the case of NH₄Cl in comparison with NaCl and neat PAM. The results for NaCl and neat PAM are almost identical suggesting the weak influence of NaCl on PAM hydrolysis. Although, NaCl was doubled in an additional run (**Fig. 3.7**), it was found that this increase in the number of moles did not increase the degree of hydrolysis of PAM. The hydrolysis data was fitted by an exponential relationship and values of k_A were reported in **Table 3.2**. The value of k_A reported was found by fitting the experimental data using equation 3. It should be mentioned that

the data was fitted by an exponential form ($y = a \exp(-b t)$), where a & b are a factor and reaction rate constant (k_A), respectively

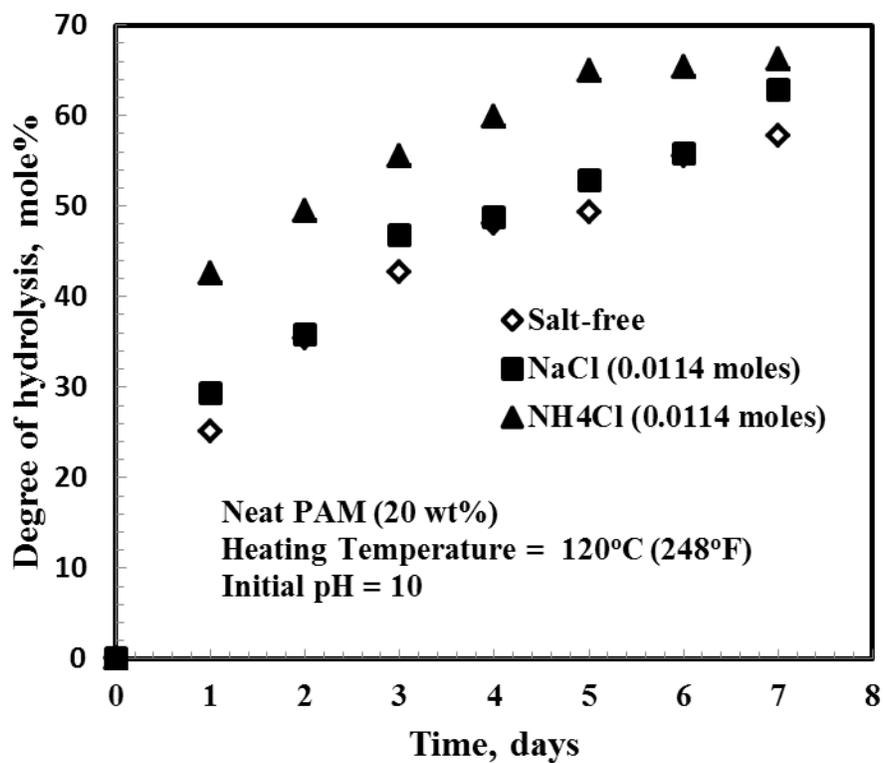


Figure 3. 6: Effect of salts concentration (0.0114 moles) on D_H of PAM at 120°C (248°F)

Table 3. 2: PAM Hydrolysis rate constant at 120°C (248°F) at different salt concentrations

Salt Type	$k_A * 10^{-3}, \text{hr}^{-1}$	a
No salt	5	86.3
NaCl (0.0114 moles)	4	76.8
NaCl (0.0228 moles)	5	79.2
NaCl (30,000 ppm)	5	85.9
NH ₄ Cl (0.0114 moles)	6	74.3
NH ₄ Cl (30,000 ppm)	8	67.4

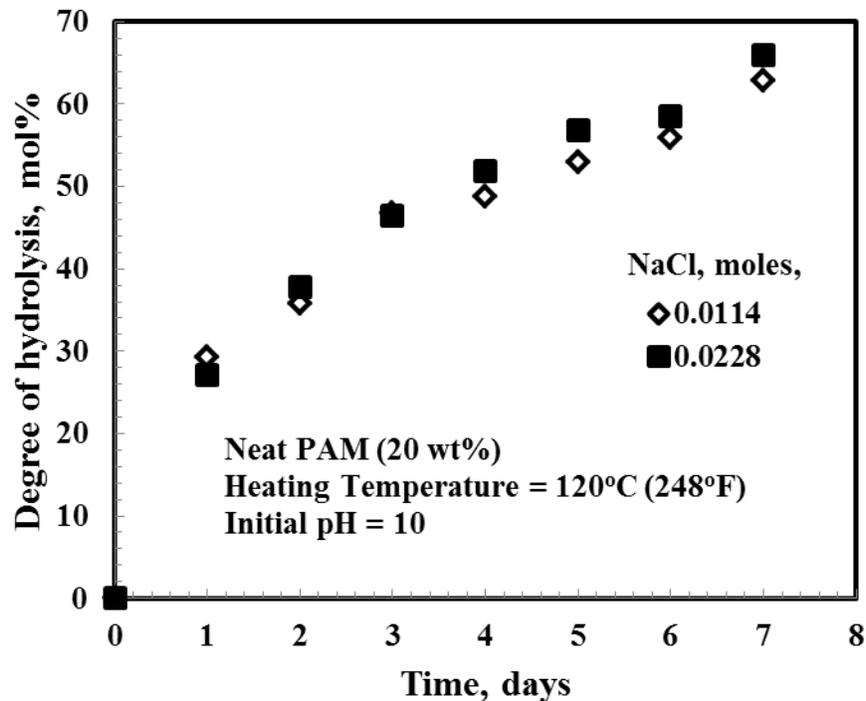


Figure 3. 7: Effect of number of moles of NaCl on DH of PAM at 120°C (248°F), 20 wt% PAM

3.3.3 Effect of Salts on Cross-linking of PHPA with PEI

The cross-linking of PAM with PEI needs to be delayed at high temperature applications to give oilfield operators adequate time to place the gelling solution safely. Different salts were tested and applied such as NaCl and NH₄Cl. These salts increase the gelation time when neat polymers were used with a cross-linker. Hence, the effect of salts on PHPA with different degrees of hydrolysis will be introduced in the following section. Also, the strength of the polymer system which is an important factor for the life time in field application will be investigated.

In order to investigate the effect of salts on PHPA/PEI cross-linked gel, samples of PAM were hydrolyzed at different times. The pH was adjusted to 10, and then the samples were heated to 2, 5, 10, and 168 hours at 120°C in an oil bath. The degrees of hydrolysis of these samples were measured by ¹³C NMR and found to be 7, 11.83, 16.92, and 57.8` mole%, respectively.

These polymer samples were cross-linked with PEI in the presence and absence of salt. The concentration of each salt (NaCl & NH₄Cl) used in these experiments was 100 lb/1000 gal (12,000 ppm).

Salts were reported to increase the gelation time of PAM/PEI gel system as well as other systems like polyacrylamide t-Butyl acrylate (PA_tBA) cross-linked with PEI. The data from **Fig. 3.8** through **Fig. 3.9** show that the addition of salts increases the gelation time even if partially hydrolyzed polymer is used instead of neat polymer. However, the addition of salts is found to have a negative impact on the final gel strength. NH₄Cl increases the gelation time more compared to NaCl. However, NH₄Cl weakens the produced gel more compared to NaCl. The higher effect on gelation time caused by NH₄Cl can be explained through the progress of hydrolysis.

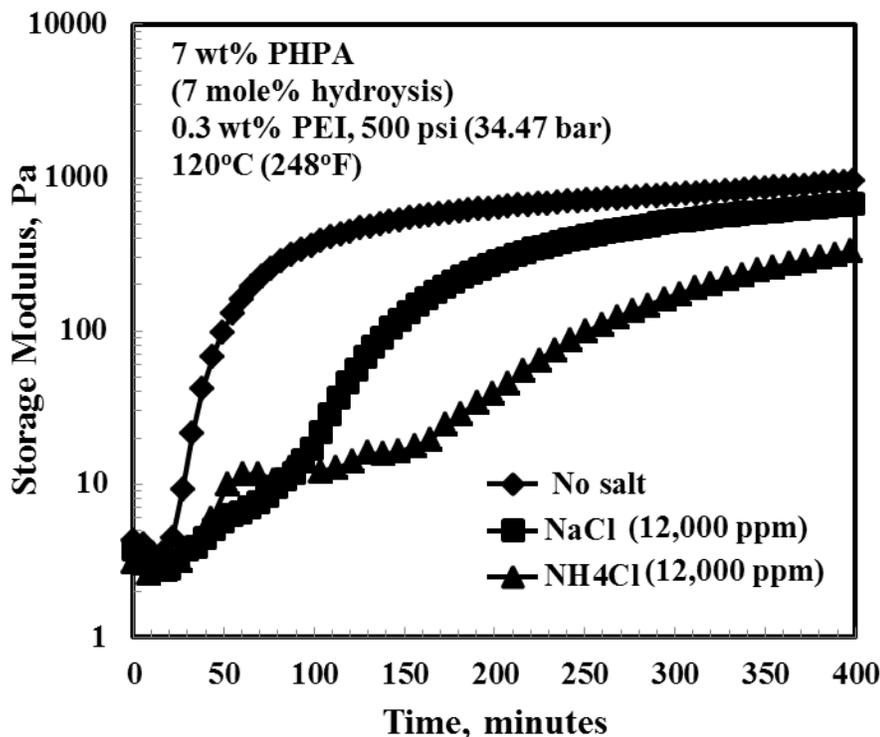


Figure 3. 8: Effect of salts on cross-linking of PHPA (7 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)

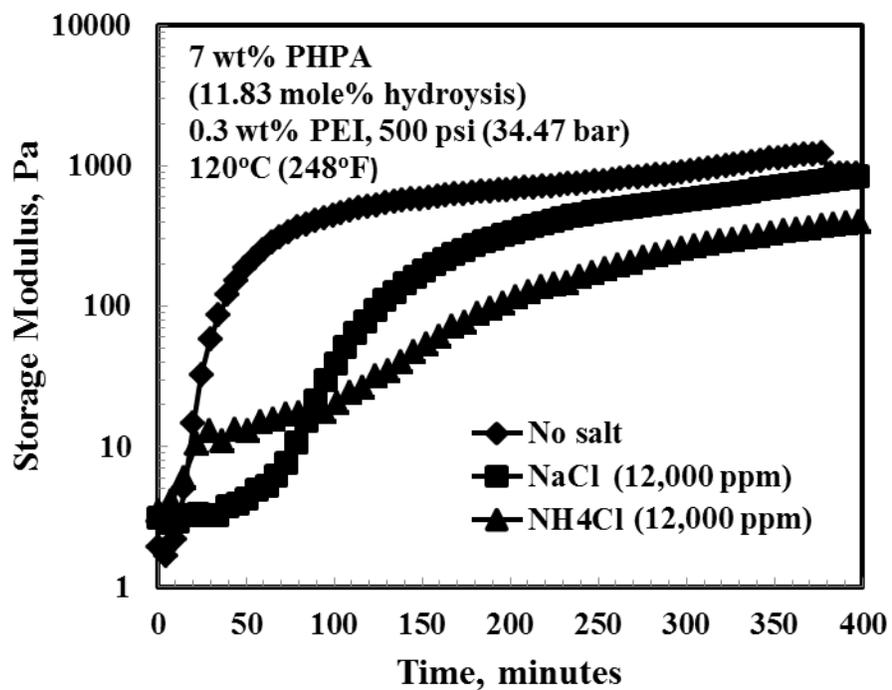


Figure 3. 9: Effect of salts on cross-linking of PHPA (11.83 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)

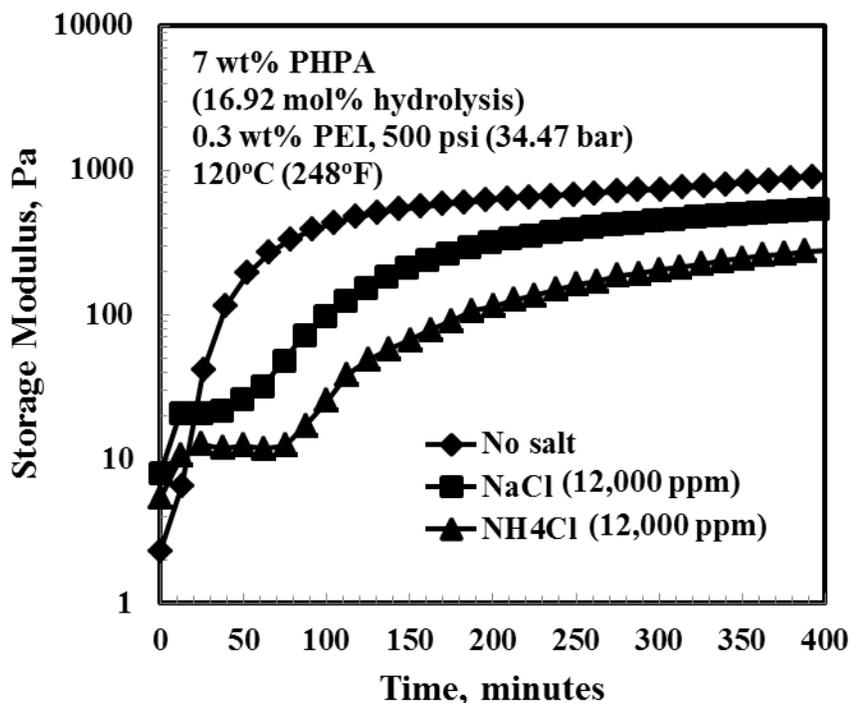


Figure 3. 10: Effect of salts on cross-linking of PHPA (16.92 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)

The data in **Table 2** is extracted from the cross-linking tests done via dynamic oscillatory measurements. Here, gelation time and gel strength (storage modulus vs. time) were measured. The measurement of storage modulus represents a quantitative approach in comparison with the qualitative Sydansk's codes. Our results for the different retarders show that the gelation time has decreased with increased degree of hydrolysis which is in agreement with previous reports on salt-free PHPA (Al-Muntasheri et al., 2008).

Table 3. 3: Effect of salts (12,000 ppm) on PHPA/PEI system at 120°C (248°F)

Heating Time (minutes)	Initial Degree of Hydrolysis (mol %)	Gelation Time (minutes)			Equilibrium Storage Modulus (Pa)		
		Salt-free	NaCl	NH ₄ Cl	Salt-free	NaCl	NH ₄ Cl
120	7	47	123	194	900	636	286
300	11.83	41	104	154	1139	773	360
600	16.92	46	52	145	1042	630	368
10,080	57.8	27	34	31	1183	598	962

It was observed that when the degree of hydrolysis was increased to about 57.8 mol% (obtained by aging the PAM for 7 days), there is no effect on gelation time (the same gelation time in all cases) and there is no trend in the storage modulus as well (NH₄Cl gives higher G' compared to NaCl) (**Fig. 3.10**). This may be due to the high degree of hydrolysis of the polymer where the charges cannot be shielded efficiently by the cations. It could also indicate a different gelation mechanism which will be discussed in the next section.

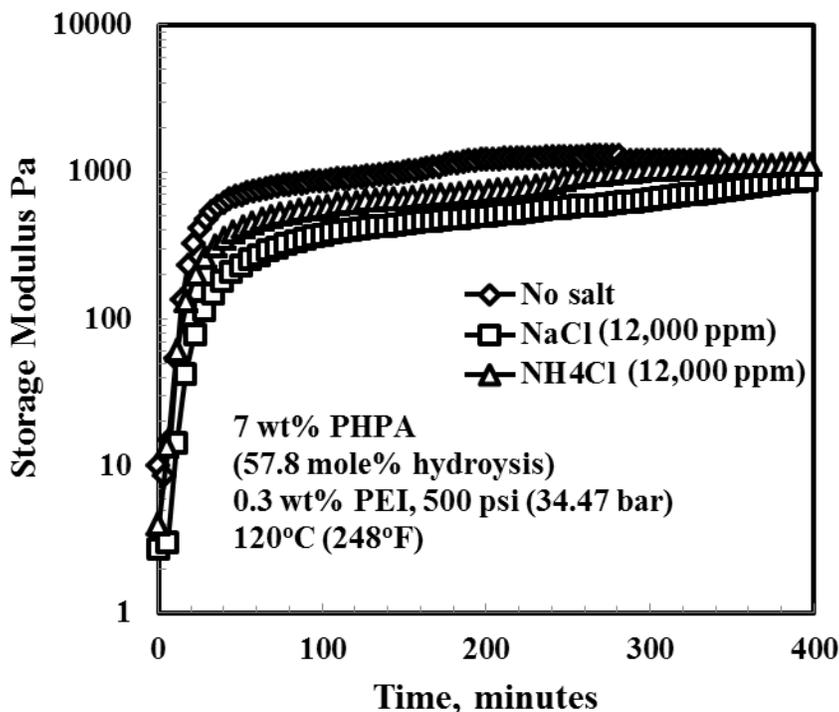


Figure 3. 11: Effect of salts on cross-linking of PHPA (57.8 mol% hydrolysis) with PEI at 120°C (248°F) and 500 psi (34.47 bar)

In **Fig. 3.11**, a plot of the storage modulus vs. time is illustrated at different degrees of hydrolysis to examine if PHPA can be used instead of PAM to produce a gel with high strength. The plateau values of G' at 0, 7.02, and 57.8 mol% degrees of hydrolysis were found to be 680, 900, and 1183 Pa, respectively. It is clear that higher degree of hydrolysis produces higher storage modulus, but at the expense of increasing the gelation time.

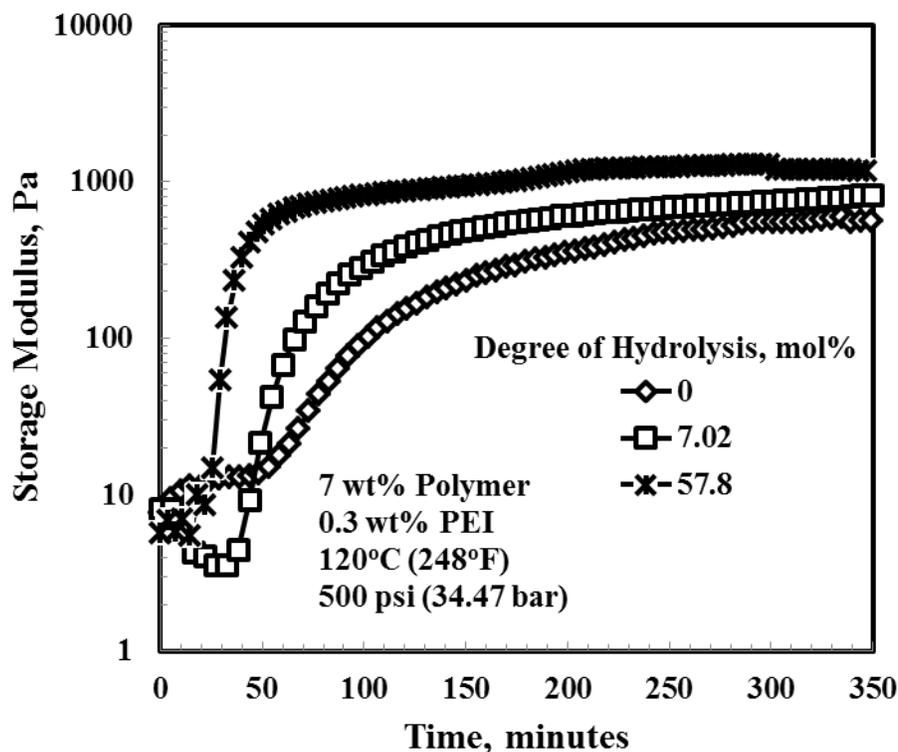


Figure 3. 12: Effect of degree of hydrolysis on gel strength at 120°C (248°F)

Generally, the samples of PHPA/PEI without salts exhibited the highest storage modulus followed by that which contains NaCl. The addition of NH₄Cl resulted in lower values of storage modulus in comparison with NaCl and the salt-free gel systems. The reasons behind these observations will be explained by the following differential scanning calorimetry results.

3.3.4 Insights into Retardation Mechanisms of PAM/PEI Crosslinking Reactions

In this section, light will be shed on the conclusions that can be drawn from the NMR and the dynamic rheological measurements. Retardation of PAM/PEI crosslinking reaction by the addition of simple inorganic salts is evident. Although the NH₄Cl has been more effective retarding the gelation time of PAM/PEI gels, its presence accelerated the hydrolysis of PAM significantly. On the other hand, NaCl which was found less effective retarding gelation had

lesser hydrolysis extent. This indicates that the retarding mechanism by which these salts function is not by retarding the hydrolysis reaction of the polymer. However, the presence of carboxylate groups on the polymer is known to cause a screening effect by which the viscosity drops of these solutions drops. To explore this further and to see how effective these salts are in screening the negative charges on the PHPA, additional tests were conducted using steady shear viscometry.

Samples of PAM solutions were prepared by adding NaCl & NH₄Cl at concentrations of 7,500 and 30,000 ppm (corresponding to 0.0114 and 0.059 mol/L, respectively) which are the same concentrations used in the hydrolysis analysis of **Figs. 3.5 & 3.6**. Then, the pH was adjusted to 10 and all samples were aged for 7 days in the oil bath maintained at 120°C (248°F) following the same procedure used for preparing ¹³C NMR samples. Then, the viscosity of these samples was measured every day for 7 days. The viscosity was found to be Newtonian in the shear rate range of 1 to 200 s⁻¹.

As shown in **Fig. 3.12**, samples containing NH₄Cl had lower viscosities than those with NaCl. This is despite the fact that the number of moles (0.059 moles) was kept the same by adding 3.44 g and 3.14 g of NaCl & NH₄Cl, respectively to the polymer sample (180 ml). Hence, the low viscosity caused by NH₄Cl is due to the polymer structure (shrinkage). Different literature reports discussed the interaction of salts with carboxylate groups. Kherb et al. (2012) showed that ammonium ions have stronger binding to carboxylate groups compared with sodium ions at low salt concentration. Kowblansky and Zema (1981) reported an interaction constant for NH₄⁺ higher than Na⁺ at salts concentration of 1.5 N. From the NMR results, addition of NH₄Cl showed higher degree of hydrolysis which supposed to give lower gelation time in cross-linking with PEI, but the gelation time was observed to be elongated in this case. Also, in case of

increasing the PEI concentration in the presence of the same NH_4Cl concentration, the gelation time was also increased (**Fig. 3.13**). This confirms that PEI is not a limiting reactant in this case. As a tentative explanation, although there are more carboxylate groups in the solution as a result of the addition of NH_4Cl , but these groups are not accessible to PEI due to the shrinkage of the polymer chain. This finding is further confirmed by using mixing waters from the field and from the sea. The hydrolysis of the polymer using these waters is reported in **Fig. 3.14**. As can be seen from this figure, there is no appreciable difference in the degree of hydrolysis using these waters. In view of the effect of these salts on gelation time, it is clear that salts do not elongate gelation by retarding hydrolysis. This could also indicate that the gel is partly based on the ionic interaction between the PEI and the negatively charged carboxylate as an additional crosslinking mechanism.

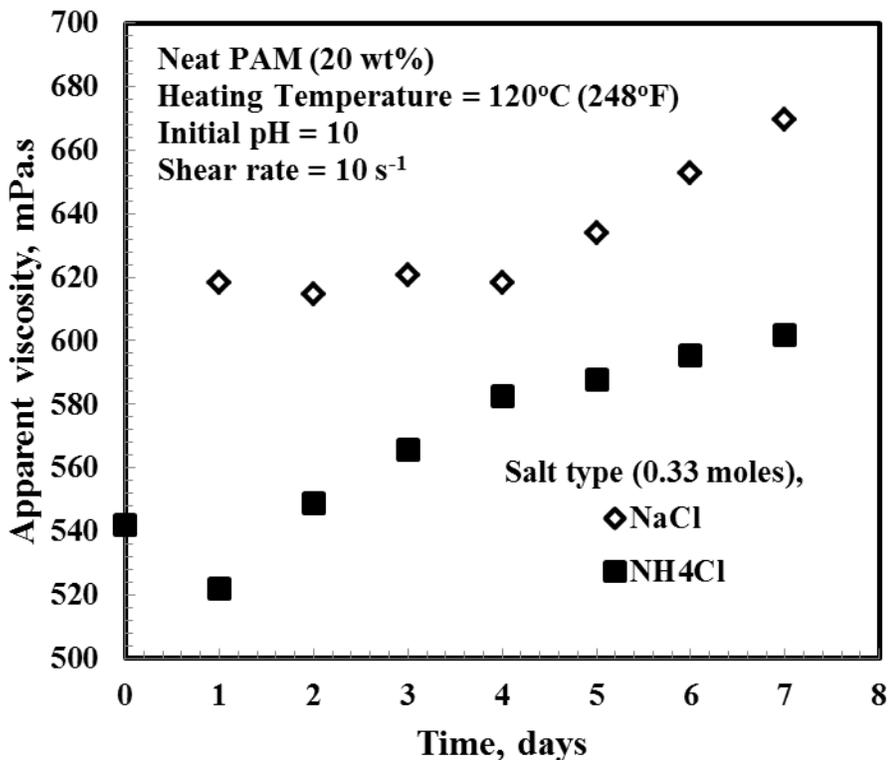


Figure 3. 13: Effect of salt type on PAM viscosity at 10 s^{-1} after ageing at 120°C (248°F) for 7 days for a salt concentration of 7,500 ppm

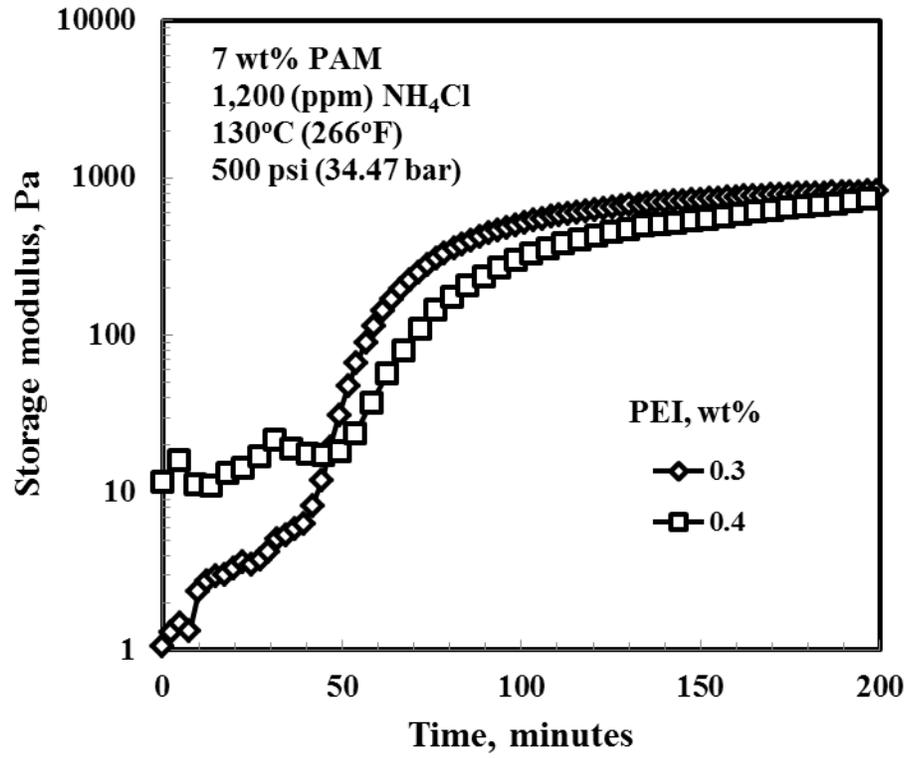


Figure 3. 14: PAM cross-linked with different PEI concentrations & 1,200 ppm NH_4Cl

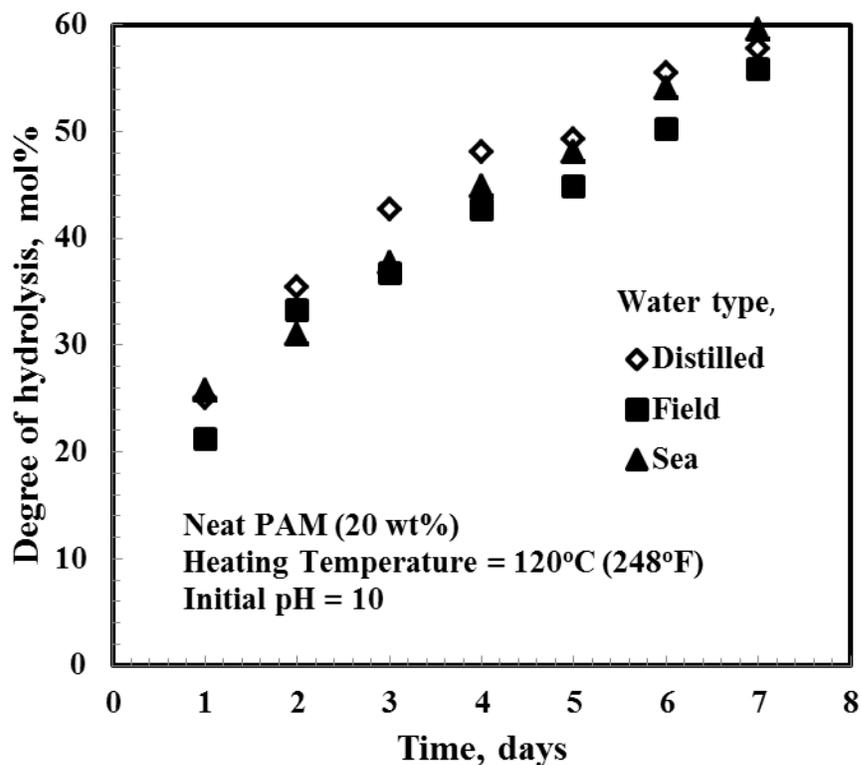


Figure 3. 15: Effect of distilled, field, and sea water on D_H of PAM at 120°C (248°F), 20 wt%

PAM

DSC was used as an additional method to further explain these trends. Two samples of gelling solutions (PAM/PEI containing 9/1 wt%) with NaCl and NH_4Cl (1,200 ppm) were heated to 120°C (248°F) at a rate of 1.5°C/min. The DSC dynamic scans showed that more heat was absorbed with the sample having NH_4Cl . The heat absorbed is found to be ~ 375 J/g for PAM. This amount of heat has increased to 2,139 J/g when NH_4Cl was added to PAM. As shown in **Figs. 3.15**, the heat absorbed (endothermic) by the addition of NH_4Cl is higher than that of NaCl. It should be mentioned that the alkaline hydrolysis of PAM is endothermic in nature. The onset of cross-linking temperature has shifted to ~ 80°C by adding NH_4Cl , whereas it was 68.18°C in the case of NaCl (**Fig. 3.16**). The heat released (exothermic) is higher in the case of NaCl (27.7

J/g) compared to that of NH_4Cl (12.18 J/g) (Fig. 3.17). This suggests that more cross-linking reactions are taking place in the case of NaCl which results in higher gel strength which explains the earlier measurements. For NH_4Cl , the observed low strength can be explained by this DSC results. Therefore, addition of NH_4Cl to PAM solution leads to more hydrolysis but shifts the onset of gelation to higher temperatures. This shift explains the observed weakness in gel strength.

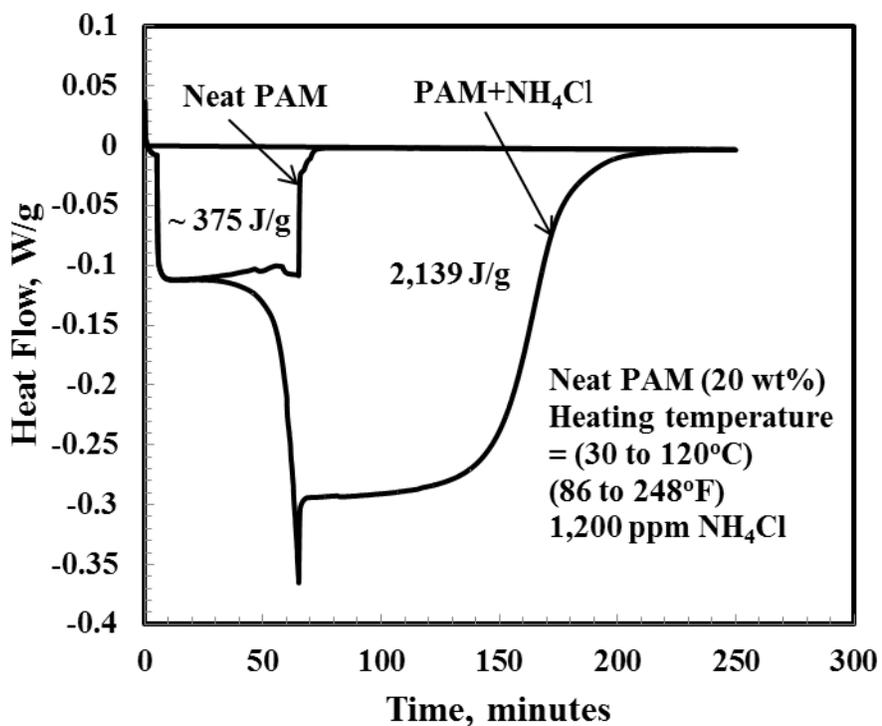


Figure 3. 16: Effect of NH_4Cl on PAM hydrolysis (DSC scan)

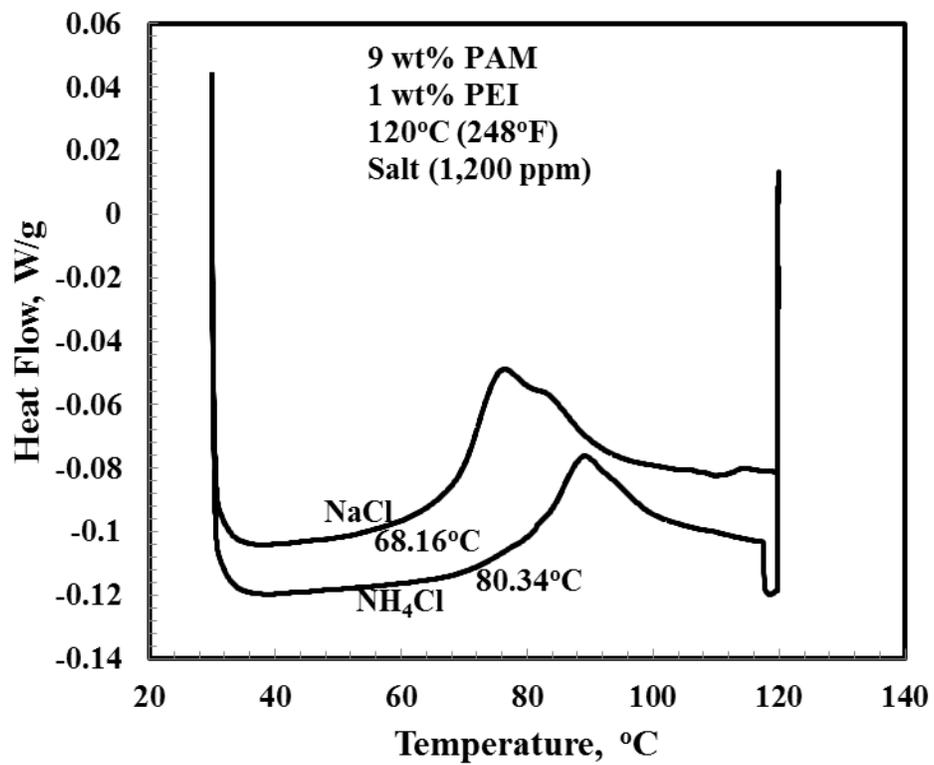


Figure 3. 17: Effect of salts on onset gelation temperature for PAM/PEI (9/1) wt%

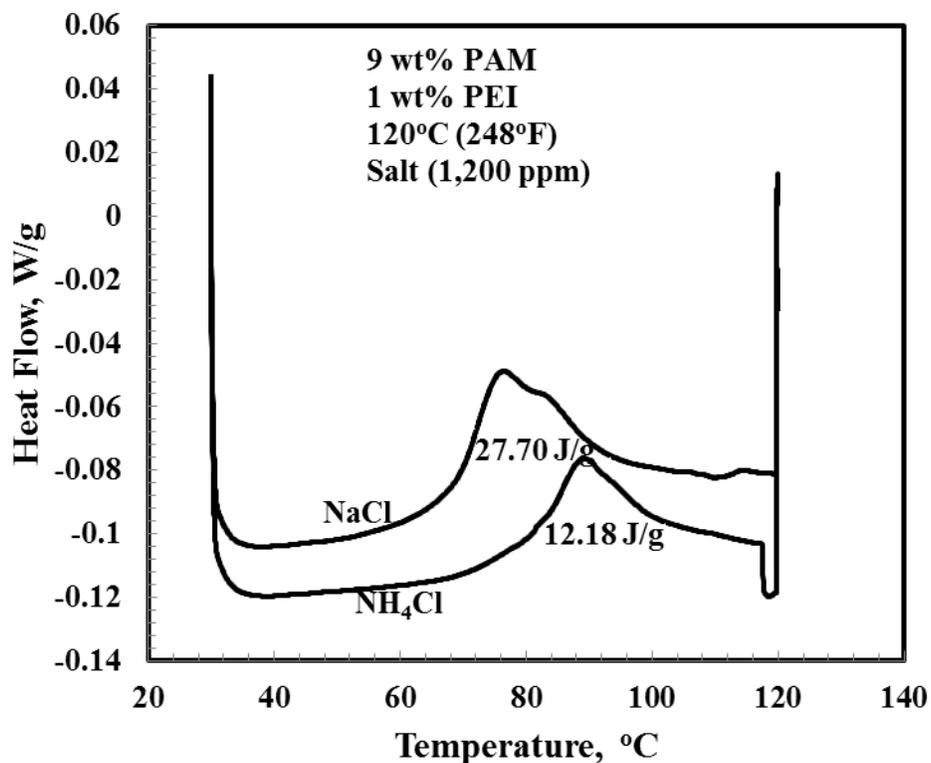


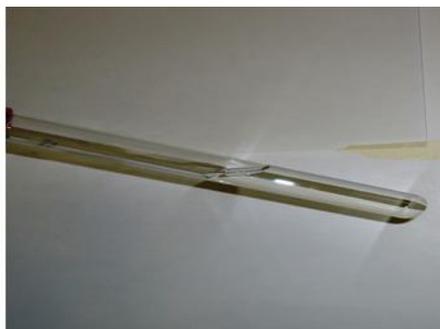
Figure 3. 18: Effect of salts on heat of gelation for PAM/PEI (9/1) wt%

3.3.5 Thermal stability of PAM/PEI gel

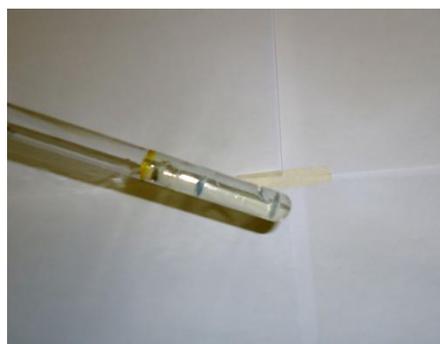
The first study of PAM/PEI gel system was reported by Allison and Purkaple (1988) at room temperature. Al-Muntasheri et al. (2008) studied PAM/PEI gel system at 130°C (266°F). The authors observed a rigid ringing gel system at PAM concentrations of 7 and 9 wt%, and PEI concentrations in the range 0.3 to 3 wt%. The stability of the system was investigated in distilled water during a period of 2 months.

In this study, the thermal stability of PAM/PEI system is studied in bulk at 150°C (302°F) using different salinities. This includes distilled, field, and sea water. The concentration of PAM ranged from 9 to 3 wt%. PEI concentration was 1, 0.6, and 0.3 wt%. Gel formation was observed within 24 hours. **Fig. 3.18** shows a sample of PAM/PEI before and after one day. The flowable

low viscosity gelling solution in **Fig. 3.18a** turned into a rigid nonflowing gel in **Fig. 3.18b** by forming a 3-Dimensional (3-D) structure.



(a)



(b)

Figure 3. 19: A sample of PAM/PEI, (9/1) wt% in distilled water, (a) 0 day, (b) 1 day

For the samples prepared in distilled water, de-gelation occurred after 13 to 35 days for the gelling solution containing 0.3 wt% PEI. For the 0.6 wt% PEI, the de-gelation time ranged from 10 to 44 days. **Fig. 3.19** shows a sample of PAM/PEI solution of (9/0.3) wt% after ageing to 49 days. At PAM/PEI of (9/1) and (7/1) wt%, a thermally stable rigid ringing gel was

observed for 2 months. The physical strength of PAM/PEI at (7/1) wt% decreased after 2 months and a surface deformed gel was observed with syneresis (expulsion of water out of the gel structure). Sydansk's codes (**Table 3.3**) were used to describe the physical strength of the gel systems. **Table 3.4** shows the observations for polymer gel samples prepared in distilled, field, and sea water.



Figure 3. 20: Sample of PAM/PEI, (9/0.3) wt% aged for 49 days at 150°C (302°F)

Table 3. 4: Sydansk strength codes (Sydansk, 1990)

Code	Physical description
A	No detectable gel
B	Highly flowing gel
C	Flowing gel
D	Moderately flowing gel
E	Barely flowing gel
F	Highly deformable non-flowing gel
G	Moderately deformable non-flowing gel
H	Slightly deformable non-flowing gel
I	Rigid gel
J	Ringing rigid gel

Table 3. 5: Bottle testing of PAM/PEI gels after 16 weeks of thermal treatment at 150°C (302°F) in different types of mixing waters

PAM/PEI Content (%wt)	Observation			Sydansk code		
	Water type			Water type		
	Distilled	Field	Sea	Distilled	Field	Sea
9/1	Brown	Brown 50% flow	Brown	G-S	F	J
7/1	Brown De-gelation	Brown 30% flow	Brown	NA	F	G
5/1	Brown De-gelation	Brown De-gelation	Light brown	NA	NA	G-S
3/1	Brown De-gelation	Brown De-gelation	Transparent gel	NA	NA	A
9/0.6	Brown De-gelation	Brown De-gelation	Light brown	NA	NA	G-S
7/0.6	Brown De-gelation	Brown De-gelation	Brown	NA	NA	J-S
5/0.6	Brown De-gelation	Brown De-gelation	Light brown	NA	NA	G-S
3/0.6	Brown De-gelation	Brown De-gelation	Transparent gel	NA	NA	A
9/0.3	Brown De-gelation	Brown De-gelation	Brown De-gelation	NA	NA	NA
7/0.3	Brown De-gelation	Brown De-gelation	Brown De-gelation	NA	NA	NA
5/0.3	Brown De-gelation	Brown De-gelation	Light brown De-gelation	NA	NA	NA
3/0.3	Brown De-gelation	Brown De-gelation	Transparent gel	NA	NA	A

NA: Not Assigned

S: Syneresis

Sea water samples were found to be more stable than distilled and field water samples. This may be due to the presence of salts in high concentration. It can be seen from **Table 4** that the de-gelation occurred only at PEI concentration of 0.3 wt%. The de-gelation period ranged from about 20 to 60 days. At a polymer concentration of 3 wt%, no gel was formed. Syneresis was observed at PEI concentration of 0.6 wt%. On the other hand, samples prepared in field water showed poor stability. Samples containing 9 and 7 wt% PAM and 1 wt% PEI showed surface deformed gel with some flowing gel. De-gelation took place in all other formulations.

Generally, the best formulation of PAM/PEI system that is more thermally stable in sea water at 150°C (302°F) is the (9/1) wt%. This system was observed to have a good thermal stability in deionized water at 130°C (266°F) (Al-Muntasheri et al. 2008) by using bottle testing method. At PAM concentration of 9 and 7 wt% and PEI concentration in the range 0.3 to 3 wt%, the system showed a rigid or rigid ringing gel for two months.

3.3.6 Compatibility of Salts with PAM/PEI Gel System

Pre-flush fluids (2 wt% KCl in field water) are usually injected into the wellbore to displace divalent cations such as Ca^{2+} and Mg^{2+} as well as to cool down the near wellbore area (Fulleylove et al. 1996; van Eijden et al. 2004; Stavland et al. 2006). The pre flush must be compatible with the gelant and the formation brine. This is to avoid any precipitation in the formation face which may result in difficulties for gelant placement and high injection pressures. Thus, it is highly important to examine the compatibility of the gelant with the pre-flush fluids. Samples of PAM/PEI (7/1) wt% were prepared in a pre-flush with different kinds of salts such that the concentration of these salts is 250 lb / 1000 gal (30,000 ppm). This level of concentration was selected due to the high gelation time (about 4.4 hours) obtained in a previous study by using NaCl. All salts were added at the same concentration. Upon the addition of NaCl and

NH_4Cl , the solutions were transparent and no precipitation was observed. So, Sodium chloride and ammonium chloride were found to be compatible with the polymeric gel system PAM /PEI (7/1) wt%. In the case of Na_2CO_3 , the gel solution was observed to be milky and white precipitate was observed after heating to 150°C (302°F). **Fig. 3.20** shows samples of PAM and PEI (7/1) wt% with the three retarders. Other samples were prepared in field water without PAM to examine the compatibility of salts with PEI. NaCl and NH_4Cl samples mixed with a pre-flush (50/50 vol%) and then heated at 150°C (302°F) showed transparent solutions. However, white solids precipitate was observed in the case of Na_2CO_3 . These solids precipitate were filtered from the solution and X-ray diffraction (XRD) was used to analyze the nature of these solids. XRD revealed that the solids precipitate were calcium carbonate (Ca_2CO_3) (31%) and calcium silicate chloride ($\text{Ca}_2\text{SiO}_3\text{Cl}_2$) (69%). The formation of this precipitate is due to the presence of Ca^{+2} in field water.

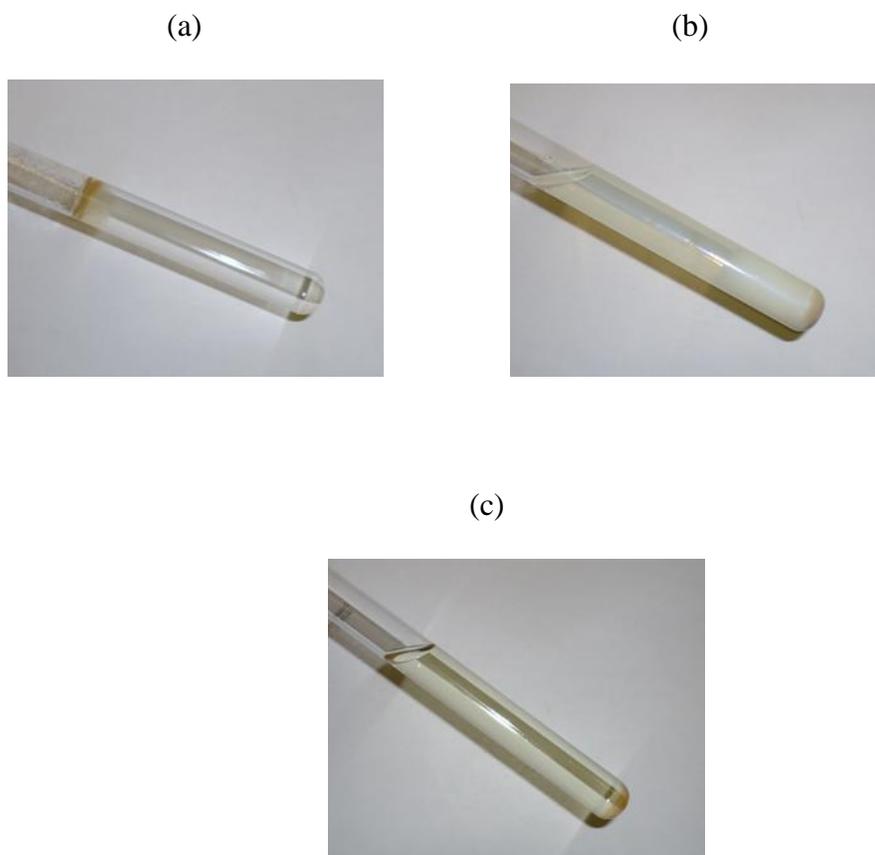


Figure 3. 21: Sample of PAM/ PEI, (7/1) wt% with 30,000 ppm retarders: (a) NaCl,
(b) Na₂CO₃, (c) NH₄Cl

3.3.7 Characterization of PHPA by Fourier Transform Infra-Red (FTIR)

The functional groups of the PHPA were characterized by FTIR. A couple of different concentration (i.e. 7,500 ppm and 30,000 ppm) of alkaline solutions (NH₄Cl and NaCl) were used for hydrolysis reaction and shown in **Figs. 3.21** and **3.22**, respectively. The spectrum of the polymers in both cases confirms the existence of the carboxylate and amide functionalities evidenced by the absorption peaks at 1550 - 1650 cm⁻¹. The disappearance of peak at 1615 cm⁻¹ (amide group) located in neat PAM (spectrum a) and the appearance of new peak at 1550 cm⁻¹

(stretching frequency of O-C-O) in the case of PHPA (spectrum b and c) confirms that the hydrolysis of PAM takes place in both the alkaline solution mediums. In **Fig. 3.22** and **3.23**, the intensity of the peak in PHPA indicates that the disappearance of the amide group is more in NH_4Cl medium than NaCl medium in both concentrations. That was calculated qualitatively from intensity of peaks by considering the intensity of amide peak in neat PAM as a base. From calculation, NH_4Cl increases the hydrolysis by 3.28% and 8.19% higher than NaCl in both low (7,500 ppm) and high (30,000 ppm) salt concentration. These results support the previous findings of NMR and DSC.

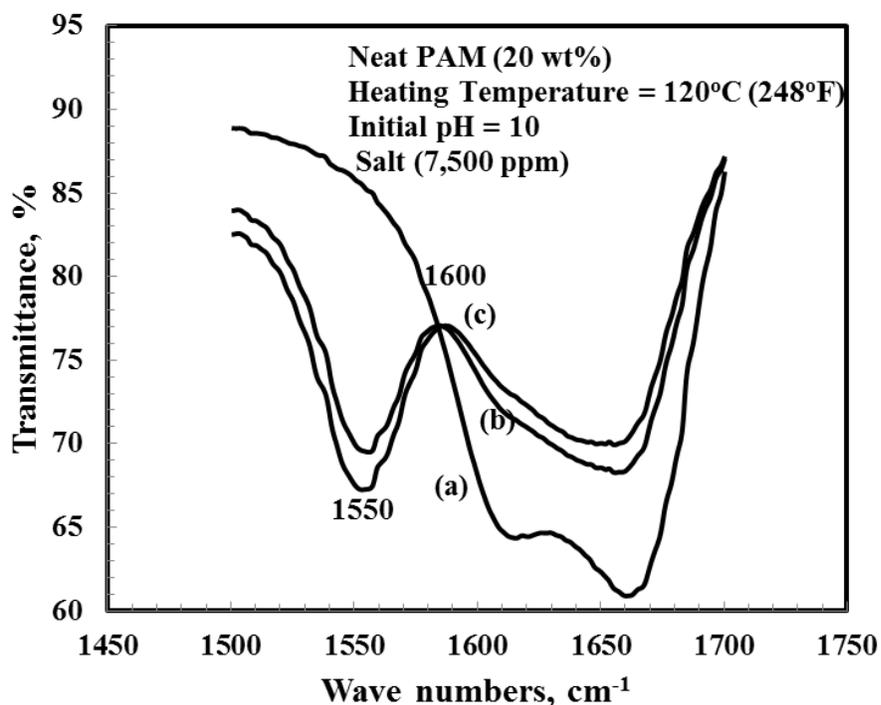


Figure 3. 22: FTIR spectrum of PAM with, 7,500 mg/l aged at 120°C (248°F) for 3 days

(a) Neat PAM (b) NaCl (c) NH_4Cl

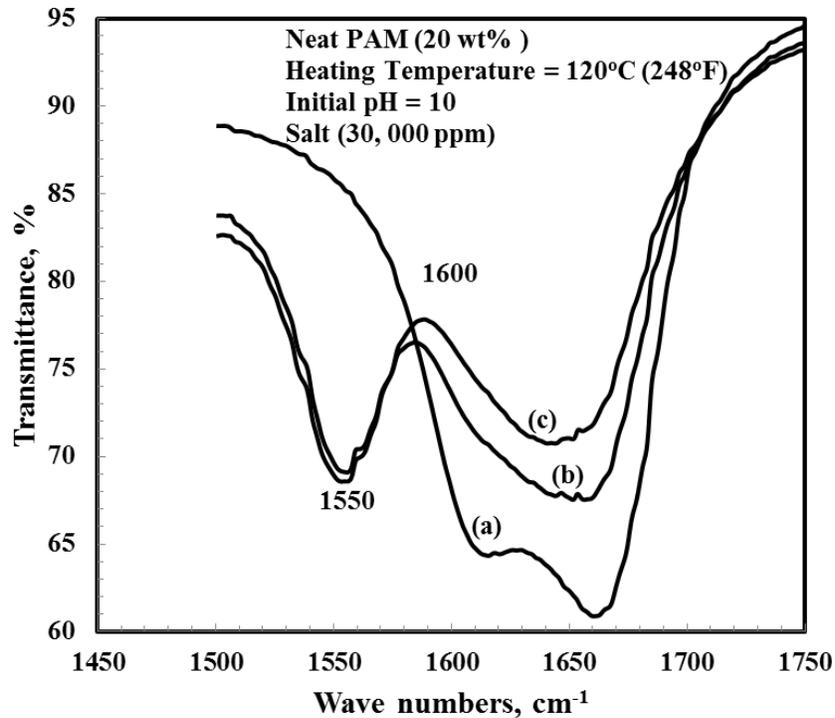


Figure 3. 23: FTIR spectrum of PAM with 30,000 mg/l aged at 120°C (248°F) for 3 days (a) neat PAM (b) NaCl (c) NH₄Cl

3.4 Conclusions

In this work, the thermal stability of PAM/PEI was examined for a wide range of PAM and PEI concentrations for more than 16 weeks in different types of water at 150°C (302°F). The compatibility of salts with PAM/PEI gel system was also checked. ¹³CNMR was used to study the effect of salts on PAM hydrolysis. The hydrolyzed samples of PAM were characterized by FTIR to confirm the ¹³CNMR data. Moreover, steady shear measurements were conducted to correlate the viscosity to the degree of hydrolysis. The cross-linking of PHPA with PEI along with salt addition was performed through dynamic oscillatory test.

The conclusions from this study are summarized in the following points:

- (1) PAM/PEI gel system is more stable in sea water at 150°C (302°F) compared to distilled and field water.
- (2) The hydrolysis of 20 wt% PAM at 120°C (248°F) was correlated to a first order reaction kinetics with a rate constant of $\sim 4.6 * 10^{-3} \text{ hr}^{-1}$. This value increased to $8.1 * 10^{-3} \text{ hr}^{-1}$ when NH_4Cl was added by a concentration of 30,000 ppm, while NaCl showed $3.7 * 10^{-3} \text{ hr}^{-1}$ at this concentration.
- (3) Ammonium chloride increases the hydrolysis more compared to sodium chloride.
- (4) The viscosity of the hydrolyzed polymer upon the addition of salts dropped in the first day of aging, followed by an increase in the subsequent six days. The increase of viscosity can be well correlated to the degree of hydrolysis.
- (5) Sodium chloride and ammonium chloride were found to be compatible with PAM/PEI gel system, whereas, sodium carbonate was observed to produce a white precipitate with the gelling solution.
- (6) Increasing the degree of hydrolysis was found to increase the strength of the produced gel, but the gelation time has decreased at the same time.
- (7) The addition of salts to PHPA/PEI leads to two counter effects. The gelation time has increased but the strength has decreased.
- (8) Ammonium chloride increases the gelation time of PHPA/PEI more compared to sodium chloride. However, NH_4Cl leads to weaker gels due to shifting of the gelation onset temperature. The point at which the heat starts to release is assumed to be the onset of cross-linking.

3.5 References

Al-Assi, A.A., Willhite, G.P., Green, D.W. and McCool, C.S. 2006. Formation and Propagation of Gel Aggregates Using Partially Hydrolyzed Polyacrylamide and Aluminum Citrate. Paper SPE 100049 presented at the 2006 SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 22-26 April.

Albonico, P. and Lockart, T.P. 1993. Divalent ion-resistant polymer gels for high temperature applications: syneresis inhibiting additives. Paper SPE 25220 presented at the 1993 SPE International Symposium on Oilfield Chemistry, New Orleans, LA, March 2-5.

Allison, J.D. and Purkapple, J.D. 1988. Reducing Permeability of Highly Permeable Zones in Underground Formations. US Patent No. 4,773,481.

Al-Muntasheri, G.A. 2008a. Polymer Gels for Water Control: NMR and CT Scan Studies. PhD thesis, Delft University of Technology, Delft, The Netherlands (September 2008).

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha., P.L.J. 2008. Gelation Kinetics and Performance Evaluation of an Organically Crosslinked Gel at High Temperature and Pressure. *SPEJ* **13** (3): 337-345. *SPE-104071-PA*.

Al-Muntasheri, G.A., Sierra, L., and Bakhtiyarov, A. 2011. Ammonium Halide as Gelation Retarder for Cross-linkable Polymer Compositions. U.S. Patent Application WO 2011/ 107744.

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. 2010. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Caulfield, M.J., Qiao, G.G., and Solomon, D.H. 2002. Some Aspects of the Properties and Degradation of polyacrylamides. *Chem. Rev*, **102**(9): 3067-3083.

Eoff, L., Dalrymple, D., and Everett, D. 2006. Global Field Results of a Polymeric Gel System in Conformance Applications. Paper SPE 101822 presented at the SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, 3-6 October.

Fulleylve, R.J., Morgan, J.C., Stevens, D.G., and Trasher, D.R. 1996. Water Shut-Off in Oil Production Wells-Lessons from 12 Treatments. Paper SPE 36211 presented at the International Petroleum Exhibition and Conference. Abu Dhabi, October 13-16. DOI: <http://dx.doi.org/10.2118/36211-MS>.

Gaillard, N., Thomas, A., and Favero, C. 2013. Novel Associative Acrylamide-based Polymers for Proppant Transport in Hydraulic Fracturing Fluids. Paper SPE 164072 presented at the SPE International Symposium on Oilfield Chemistry, Woodlands, April 8-10.

Halverson, F., Lancaster, J.E., and O'Connor, M.N. 1985. Sequence Distribution of Carboxyl Groups in Hydrolyzed Polyacrylamide. *Macromolecules*, **18** (6): 1139-1144.

Hardy, M.B. 2001. Methods and Compositions for Reducing the Permeabilities of Subterranean Zones. US Patent No. 6,196,317.

Hardy, M.B., Botermans, C.W., and Smith, P. 1998. New Organically Cross-linked Polymer System Provides Competent Propagation at High Temperatures in Conformance Treatments. Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19-22 April.

Higuchi, M., and Senju, R. 1972. Kinetic Aspects of the Alkaline Hydrolysis of Poly(acrylamide). *Polym J* **3**(3): 370-377.

Holtsclaw, J. and Funkhouser, P. 2010. A Crosslinkable Synthetic-Polymer System for High-Temperature Hydraulic-Fracturing Applications. *SPEJ* 25(4): 555-563. SPE-125250-PA.

Hutchinson, B.H., and McCormick, C.L. 1986. Water-Soluble copolymers: 15 studies of random copolymers of acrylamide with N-substituted acrylamides by ¹³C NMR. *Polymer Journal*, **27**(4): 623-626.

Ilavsky, M., Hrouz, J., Stejskal, J., and Bouchal, K. 1984. Phase Transition in Swollen Gels. 6. Effect of Aging on the Extent of Hydrolysis of Aqueous Polyacrylamide Solutions and on the Collapse of Gels. *Macromolecules*, (**17**): 2868-2874.

Kheradmand, H., Francois, J., and Plazanet, V. 1988. Hydrolysis of polyacrylamide and acrylic acid-acrylamide copolymers at neutral pH and High temperature. *Polym J*, **29**(5): 860-870.

Kherb, J., Flores, S.C., and Cremer, P.S. 2012. Role of Carboxylate Side Chains in the Cation Hofmeister Series. *J. of Phys. Chem. B*, (**116**): 7389-7397.

Kowblansky, M., and Zema, P. 1981. Effect of Charge Density and Ion Binding on Intrinsic Viscosity of Polyelectrolyte Solutions. *Macromolecules*, (**14**): 1451-1456.

Kudryavtsev, Y.V., Litmanovich, A.D., and Plate, N.A. 1998. On the Kinetics of Polyacrylamide Alkaline Hydrolysis. *Macromolecules* 31: 4642-4644.

Kurenkov, V.F., Hartan, H.G., and Lobanov, F.I. 2001. Alkaline Hydrolysis of Polyacrylamide. *Russian Journal of Applied Chemistry* 74 (4): 543-554.

Levitt, D.B., Pope, G.A., and Jouenne, S. 2011. Chemical Degradation of Polyacrylamide Polymers Under Alkaline Conditions. *SPE Res Eva & Eng* **12** (3): 281-286. SPE- 129879-PA.

Lockhart, T.P.1994. Chemical and Structural Studies on Cr⁺³/ Polyacrylamide Gels. SPE Advanced Technical Series, **2**(2): 199-205.

Lockhart, T.P. 1991. Chemical and Structural Studies on Cr⁺³/ Polyacrylamide Gels. Paper SPE 20998 presented at the 1991 SPE International Symposium on Oilfield Chemistry, Anaheim, February 20-22.

Mandel, M. 1970. The Potentiometric Titration OF Weak Polyacids. *Euro Polym J* **6**(6): 807-822.

Moradi-Araghi, A. 2000. A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production. *Journal of Petroleum Science and Engineering* **26** (1-4): 1-10.

Moradi-Araghi, A., Hsieh, E.T., and Westerman, I.J. 1988. Role of Imidization in Thermal Hydrolysis of Polyacrylamides in G.A. Stahl and D.N. Schulz (eds.), *Water Soluble Polymers for Petroleum Recovery*. New York City: Plenum, pp. 271-278.

Moradi-Araghi, A. and Doe, P. 1987. Hydrolysis and Precipitation of Polyacrylamide in Hard Brines at Elevated Temperatures. *SPE Res Eng* **2** (2): 189-198. SPE-13033-PA.

Morgan, J.C., Smith, P.L., and Stevens, D.G. 1997. Chemical Adaptation and Deployment Strategies for Water and Gas Shut-off Gel Systems. Paper presented at the 1997 Royal Chemistry Society's Chemistry in the Oil Industry International Symposium, Ambleside, April 14-17.

Parker Jr, W.O., and Lezzi, A. 1993. Hydrolysis of sodium-2-acrylamido-2-methylpropanesulfonate copolymers at elevated temperatures in aqueous solution via ^{13}C NMR spectroscopy. *Polymer J*, **34**(23): 4913-4918.

Prud'homme, R.K., Jonathan, T.U., Poinatte, J.P. and Halverson, F. 1983. Rheological Monitoring of the Formation of Polyacrylamide/ Cr^{+3} Gels. *SPEJ* **32**(5): 804-808.

Reddy, B.R., Eoff, L., Dalrymple, E.D., Black, K., Brown, D., and Rietjens, M. 2003. A Natural Polymer-Based Cross-linker System for Conformance Gel Systems. *SPEJ* **8** (2): 99-106. SPE-84937-PA. DOI: <http://dx.doi.org/10.2118/84937-PA>.

Ryles, R.G. 1983. Elevated Temperature Testing of Mobility Control Reagents. Paper SPE 12008 presented at the 1983 SPE Annual Technical Conference and Exhibition, San Francisco, October 5-8.

Sawant, S. and Morawetz, H. 1984. Microstructure, neighboring group inhibition, and electrostatic effects in the base-catalyzed degradation of polyacrylamides. *Macromolecules*, **17**(11): 2427-2431.

Seright, R.S., Lane, R.H., and Sydansk, R.D. 2003. A Strategy for Attacking Excess Water Production. *SPE Prod & Fac* **18** (3): 158-169. SPE-84966-PA.

Shupe, R.D. 1981. Chemical Stability of Polyacrylamide Polymers. *JPT* **33**(8): 1513-1529.

Stavland, A., Andersen, K.I., SandØy, B., Tjomsland, T., and Mebratu, A.A. 2006. How To Apply a Blocking Gel System for Bullhead Selective Water Shutoff: From laboratory to Field. Paper SPE 99729 presented at the SPE/DOE Symposium on Improved Oil Recovery Tulsa, April 22-26 April. DOI: <http://dx.doi.org/10.2118/99729-MS>.

Sydansk, R.D. and Southwell, G.P. 2000. More than 12 Years' Experience with a Successful Conformance-Control Polymer-Gel Technology. *SPEPFJ* **15**(4): 270-278.

Sydansk, R.D. 1990. A Newly Developed Chromium (III) Gel Technology. *SPE Res Eng* **5** (3): 346-352. SPE-19308-PA.

Sydansk, R.D. 1988. New Conformance-Improvement-Treatment Chromium(III) Gel Technology. Paper SPE 17329 presented at the SPE Enhanced Oil Recovery Symposium, Tulsa,, 16-21 April.

Taylor, K.C., and Nasr-El-Din, H.A. 1994. Acrylamide copolymers: a review of methods for the determination of concentration and degree of hydrolysis. *J Pet Sci Eng*, **12**(1): 9-23.

te Nijenhuis, K., Mensert, A., and Zitha, P.L.J. 2003. Viscoelastic Behavior of Partly Hydrolyzed Polyacrylamide/Chromium(III) Gels. *Rheologica Acta* **42**(1-2): 132-141.

Urlwin-Smith, P.L. 1998. Oil and Gas Field Chemicals. US Patent No. 5, 836, 392.

Urlwin-Smith, P.L. 2001. Blocking Composition for Use in Subterranean Formation. US Patent No. 6, 192, 986.

Van Eijden, J., Arkesteijn, F., Akil, I., Vliet, J., van, Batenburg, D., and McGinn, P. 2004 Gel-Cement, a Water Shut-Off System: Qualification in a Syrian Field. Paper SPE 88765 presented at the International Petroleum Exhibition and Conference, Abu Dhabi, 10-13 October.

Vasquez, J., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Civan, F. 2005. Development and Evaluation of High Temperature Conformance Polymer Systems. Paper SPE 93156 presented at

the SPE International Symposium on Oilfield Chemistry, The Woodlands, 2-4 February. DOI:

<http://dx.doi.org/10.2118/93156-MS>

CHAPTER FOUR

Gelation of a Water Shut-off Gel at High Pressure and High Temperature: Rheological Investigation

Khalid S.M. El-Karsani¹, Ghaithan A. Al-Muntasheri^{2}, Abdullah S. Sultan³ & Ibbelwaleed A. Hussein⁴*

^{1&4}Chemical Engineering Department, King Fahd University of Petroleum & Minerals; Dhahran 31261, PO BOX 5050, Saudi Arabia

²Production Technology Team, EXPEC Advanced Research Center, Dhahran 31311, Saudi Aramco, Saudi Arabia

³Petroleum Engineering Department, and Center for Petroleum & Minerals (CPM), King Fahd University of Petroleum & Minerals; Dhahran 31261, Saudi Arabia

Abstract

One of the most important applications of polymeric gels is to reduce or shut-off the excess water in petroleum reservoirs. The strength of polymeric gels needs to be high enough to withstand the water flow. This study investigates the strength of an organically cross-linked polymeric gel through dynamic testing measurements at high temperatures up to 130°C (266°F) and high pressure (500 psi) taking different parameters into account. The elastic modulus was found to increase with temperature from 120 to 130°C (248 to 266°F), but no more appreciable increase was observed above 130°C. Also, the elastic modulus increased with the increase in polymer and cross-linker concentrations. Increasing the polymer concentration by a factor of 3 resulted in an increase in storage modulus by a factor of about 4. However, this factor was decreased to about 1.1 when the cross-linker was increased by the same factor. The increases in elastic modulus with polymer and cross-linker concentrations follow an exponential relationship. Salinity of mixing water has a negative impact on elastic modulus. High elastic modulus was

observed in distilled water (1044 Pa) in comparison with field water (725 Pa) at 130°C (266°F). Moreover, the alkaline and acidic media produced stronger gel compared to neutral media. However, the gelation time is higher in neutral media. The effect of retarders (NaCl & NH₄Cl) which are used for gelation time delay was also examined. These retarders were observed to decrease the elastic modulus of the polymer gel. NH₄Cl was found to decrease the elastic modulus by about 35%. Negligible effect was noticed from NaCl for the same concentration (12,000 mg/L). However, from the aspect of gelation time, NH₄Cl is very effective in increasing the gelation time even at high polymer concentrations. The yield stress of the gel was correlated to the pressure gradient for the gel extrusion through fractures. It was found that gels with 7/0.3 and 5/0.3 wt.% gave pressure gradients of 155.5 kPa/m (55.2 psi/m) and 3,572 kPa/m (518 psi/m), respectively.

4.1 Introduction

Large amounts of water are produced as oil or gas fields mature. This results in operational problems, economic impacts as well as environmental concerns. The problems associated with the production of oil or gas includes corrosion or scale in pipelines and a decrease or loss in productivity of oil and gas (Bailey et al. 2000). Hence, additional costs are imposed with the excessive water production. It was reported that \$40 billion is spent annually by the petroleum industry to deal with the production of water (Bailey et al. 2000). This amount increased to \$45 billion in 2002 (Mercado et al. 2009; Boye et al. 2011). The water produced from mature oil or gas fields may contain mercury, arsenic, and other salts (Hibbeler and Rae 2005) which will affect the environment seriously if not disposed properly. Therefore, the excessive water production needs a remediate technique to reduce or totally block the water source. Polymer gels are one of the most common methods used in oilfields to overcome water production.

The polymer gel is based on a low viscous mixture of water, a polymer, and a cross-linker. This mixture is referred to as gelant. The gelant is injected to the target zone through techniques like bullheading or coiled tubing (Romero-Zerón et al. 2008). During the gelant flow to the target zone, a cross-linking reaction occurs between the polymer and the cross-linker. This chemical reaction is referred to as gelation which results in formation of a 3-dimensional (3D) structure network called gel. It should be noted that the 3-D structure should only form when the gel is placed in the target zone. The resultant gel exhibits viscoelastic properties. In treatments of polymeric gels, the gel forms a physical hindrance (total blocking) to water flow in the formation. These treatments (polymeric gels) are referred to as conformance improvements treatments (CITs) (Sydansk 1990). In another application, polymer gels were also used to decrease the permeability to water (partial blocking) without affecting oil permeability (Zaitoun and Kohler 1988; Sydansk and Seright 2007). This application is referred to as disproportionate permeability reduction (DPR) (Liang et al. 1995; Stavland et al. 2006). The application of polymer gels is not limited to production wells only. In water injection wells, gels were used to improve reservoir sweep efficiency when oil is bypassed by water in high permeability streaks. This is done by diverting injected water into less swept (less permeable) zones. Therefore, more oil will be recovered.

Polymer gels are formed by cross-linking polyacrylamide based-polymers with either organic or inorganic cross-linkers. Literature reports revealed that organically cross-linked gels were more thermally stable in comparison with inorganic gels (Moradi-Araghi 1991; Albonico et al. 1994; Hutchins et al. 1996; Hardy et al. 1999). This is due to the covalent bonding in the case of organic gels whereas, it is coordination covalent bonding in inorganically polymer gels (Sydansk 1990). The rheological measurements of polymer gels were reported from two

approaches. The first approach is to find the gelation time at which the 3-D structure is formed. The accurate determination of gelation time is a very important factor in gelant placement. The second approach is to measure the gel strength which determines the life time of the gel to withstand the water flow. The gel strength depends mainly on the elasticity which can be evaluated by measuring the elastic properties (storage modulus) through dynamic shear testing. **Table 4.1** gives a summary of the storage modulus for different types of polymer gels used for water shut-off.

Table 4. 1: Summary of storage modulus data reported in literature for polymer gels

Polymer Type	Cross-linker Type	Curing Temp. (°C)	Curing Pressure, Pa	Measurement Temperature (°C)	G_e' , Pa	Reference
PHPA (1 - 3 wt%)	Chromic-tri-acetate (0.017 - 0.034 wt%)	60	2.07 - 3.45	60	3.98 - 8.92 *	Sydansk (1990)
PAM (High-Mwt) (12,000 ppm)	Cr ⁺³ -acetate (960 ppm)	30	-	30	34	Broseta et al. (2000)
PAM (Low-Mwt) (40,000 ppm)	Cr ⁺³ -acetate (3,500 ppm)	40	-	40	70	Broseta et al. (2000)
PHPA (1.7 wt%)	Cr ⁺³ -acetate (0.142 wt%)	41	-	20	100	Liu and Seright (2001)
PAM (3 wt%)	Cr ⁺³ -acetate (200 ppm)	70	-	70	91.2	Grattoni et al (2001)
Acrylamide-AMPS (9,500 ppm)	Cr ⁺³ -acetate (1900 ppm)	90	-	90	9,000	Koohi et al. (2010)
PAtBA (7 wt%)	PEI (0.3 wt%)	150	3.45*10 ⁶	23.5	700	Al-Muntasheri et al. (2007)
PAM (7 wt%)	PEI (0.3 wt%)	150	3.45*10 ⁶	150	1087	Present study

The dynamic shear measurements are based on applying dynamic (oscillatory) shear on the sample. The elastic and viscous responses are characterized by the storage and loss modulus, respectively. The storage modulus measures the stored recoverable energy of the material, whereas, the loss modulus counts the mechanical energy dissipated into heat due to viscous forces. The ratio of the loss to storage modulus (G''/G') determines the shift angle ($\tan \delta$) between the stress and strain. Gelation kinetics can be determined by monitoring the evolution of the storage and loss moduli with time (Grattoni et al. 2001). More fundamental details of dynamic oscillatory testing can be found elsewhere (Kakadjian et al. 1999; Liu and Seright 2001; Calvet et al. 2004; Al-Muntasheri et al. 2007; Koohi et al. 2010).

Most of the previous dynamic rheological measurements had focused on inorganically cross-linked gels (Kakadjian et al. 1999; Liu and Seright 2001; te Nijenhuis et al. 2003). A study on dynamic testing of an organically cross-linked gel was reported by Al-Muntasheri et al. 2007. Polycrylamide tert-butyl acrylate (PAtBA) was cross-linked with polyethylenimine (PEI) at temperatures ranging from 100 to 150°C (212 to 302°F) and different parameters were studied. Samples of PAtBA / PEI were cured first at high temperatures and then the dynamic measurements were done at room temperature. The authors observed higher elastic modulus compared with those for inorganically cross-linked gels. Higher temperature ($> 100^\circ\text{C}$), higher polymer and cross-linker concentrations lead to higher elastic modulus. However, increasing the cross-linker concentration to 1.2 wt% resulted in gel syneresis (expulsion of water out of the gel structure and the equilibrium elastic modulus decreased at 150°C (302°F). Note that these dynamic tests were conducted at room temperature using ready-formed gels. These gels were cured under high temperature and pressure conditions. Increasing the salinity of the mixing water caused a negative impact on elastic moduli. PAtBA / PEI system showed a higher thermal

stability (Hardy et al. 1998). Moreover, it was successfully applied at high temperatures and low temperatures in different reservoir lithologies; carbonate and sandstone reservoirs (Polo et al. 2004).

However, this system showed incompatibility with high salinity mixing water when a retarder was used to delay the gelation time (Al-Muntasheri et al. 2010a). The gelation mechanism of this system was reported as a nucleophilic substitution between the imine nitrogen from PEI with the carbonyl carbon at the ester group. In this reaction, the imine nitrogen will replace the tertiary butyl ester in PAtBA co-polymer (Hardy et al. 1999; Al-Muntasheri et al. 2007). At the same time, recent literature reports revealed that polyacrylamide (PAM) homopolymer could replace PAtBA in an attempt to replace PAtBA with more cost-effective alternatives. The cross-linking between PAM and PEI was also believed to be through a nucleophilic substitution in which the imine nitrogen in PEI will replace the amide group at the carbonyl carbon of PAM (Al-Muntasheri et al. 2007). In the past, one of the authors (Al-Muntasheri et al. 2010) performed a detailed lab scale optimization of the composition of PAtBA/PEI which was followed by a field application. The results were excellent in total water blocking in a gas well. The results showed that the water cut reduced to about 60% and the gas rate increased by a factor of 17 for one year.

Therefore, the objective of this study is to investigate the effect of different parameters on the strength of the PAM / PEI system through dynamic shear testing at high temperatures. These parameters include: effect of temperature, polymer and cross-linker concentration, salinity of mixing water, pH, and retarders (salts) on gel strength. Most of the previous dynamic rheological investigations on either organically or inorganically cross-linked gels were performed on matured gels. In this work, the evolution of the gel and gel strength were monitored through high

pressure rheometry during the gelation process up to the equilibrium state. In this study we varied different parameters to come up with a composition that provides the highest gel strength at the lab level. The optimized gel composition(s) will then be used in core-flooding experiments before application in the field. Here we studied the gel strength in the temperature range 120 to 150°C which represents the temperature range of the target reservoirs.

4.2 Experimental studies

4.2.1 Materials

The polyacrylamide (PAM) used in this study was provided as an aqueous solution with 20% activity and it was used without further treatment. The molecular weight of PAM as disclosed by the supplier ranges from 250 to 500 kg/gmol with a pH of ~ 4.0. The degree of hydrolysis of the polymer was measured by ¹³C Nuclear Magnetic Spectroscopy and was found to be less than 0.1 mol%. The cross-linker was polyethylenimine (PEI) with a pH of about 11.7. The molecular weight and the activity of PEI are 70 kg/gmol and 30%, respectively (as disclosed by the supplier). Sodium chloride (NaCl) and ammonium chloride (NH₄Cl) were used. All these chemicals are ACS grade. The pH of the solutions was measured by a HQ40D pH meter. Hydrochloric acid (HCl) was used to adjust the pH of the gelling solutions to 7 and 3 to make the sample neutral and acidic, respectively. Two different types of waters were used and their chemical analysis is given in **Table 4.2**.

Table 4. 2: Chemical analysis of mixing waters

Variable, ppm	Water type	
	Field	Sea
Na	175	17,085
Mg	46.2	2,200
Ca	112	1,040
Cl	377	31,267
SO ₄	266	4,308
HCO ₃	146	140
TDS	1,122	56,040
pH	8.02	7.75

4.2.2 Procedure

The gelling solutions were prepared at room temperature by adding the specific amount of polymer (PAM) to water while stirring, and then the cross-linker (PEI) was added with extra 10 minutes of stirring. To examine the effect of retarders on the gelation time as well as the gel strength, NaCl and/ or NH₄Cl were added to distilled or field water before the addition of the polymer and the cross-linker. Then, the sample was loaded to the high pressure cell mounted on the rheometer.

4.2.3 Instrument

All rheological measurements were conducted in a Discovery Hybrid Rheometer (DHR). The gelation tests were performed in the high-pressure cell geometry with bob and cup diameters of 26 and 28 mm, respectively. All tests were conducted at a pressure of 500 psi (34.47 bar), and temperature ranges from 120 to 150°C (248 to 302°F). The setup has a torque ranging from 100 μN.m to 0.2 Nm and working temperature in the range -10 to 150°C (14 to 302°F). The maximum applied pressure was 138 bar (2,000 psi). The tests were conducted at 500 psi which was much higher than the vapor pressure of water at 150°C (~ 70 psi). Therefore, water is in the liquid phase. Also, it was found that the pressure did not influence the rheology up to 1,000 psi. Since the role of the pressure is to keep the liquid in solution, we do not expect an effect of pressure on the strength of the gel. A dynamic test was performed at 1,000 psi for a system containing PAM / PEI (7/0.3) wt% at 130°C (266°F) in distilled water. No difference was noted compared with the results obtained at 500 psi for the same formulation as shown in **Fig. 4.1**. The dynamic measurements were conducted on matured gel at constant frequency of 1 Hz and a

strain of 10% which was proven to be in the linear viscoelastic range through a separate strain sweep test (Fig. 4.2)

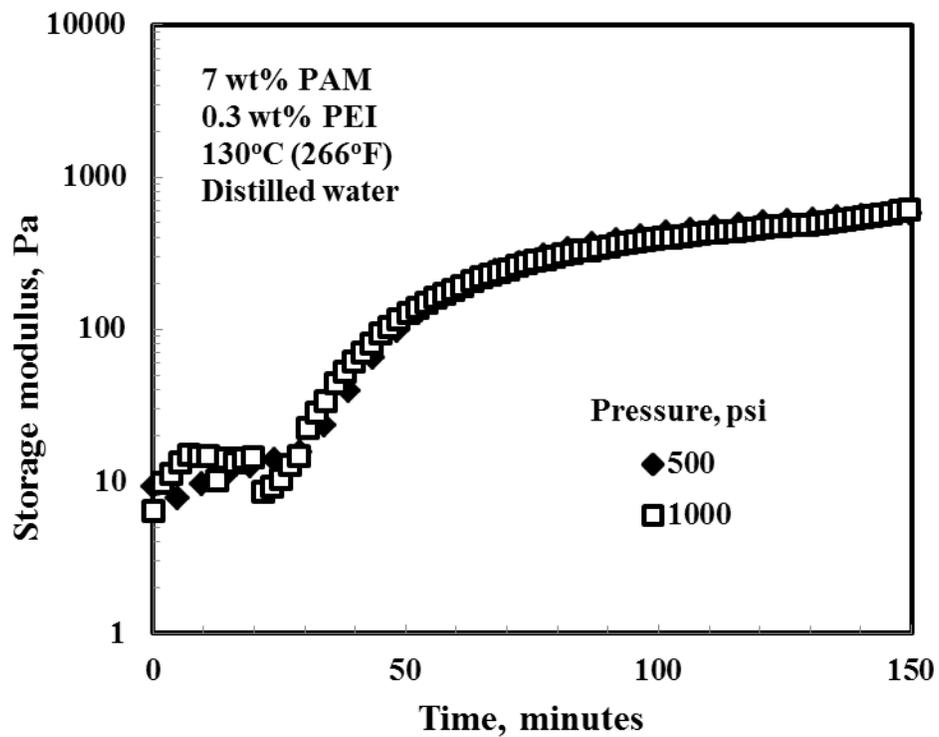


Figure 4. 1: Effect of pressure on dynamic shear measurement

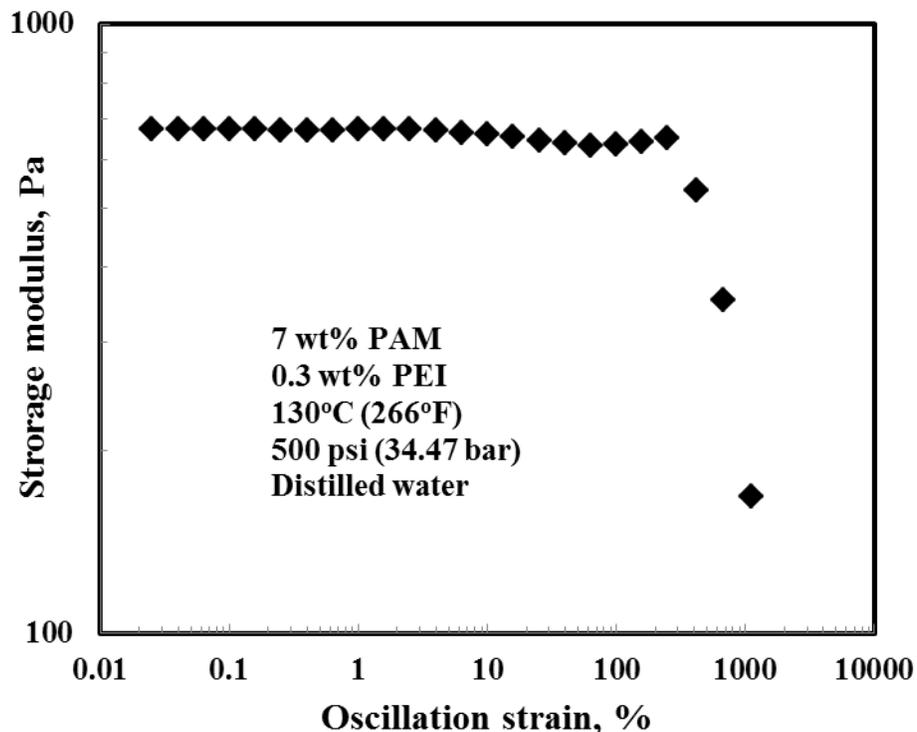


Figure 4. 2: Strain sweep of PAM / PEI (7/0.) wt% at 130°C (266°F) and 1 Hz

4.3 Results and Discussion

In order to perform dynamic oscillatory testing, the strain used should be within the linear viscoelastic range. A gelling solution containing PAM/PEI (7/0.3) wt% was prepared, loaded in the pressure cell and cured for 12 hours then a strain sweep test was performed to identify the linear viscoelastic region. As can be seen from **Fig. 4.2**, the storage modulus was constant (~ 670 Pa) within the range 0.01 to 10% followed by a small drop. So, 10% strain was chosen to study the strength of the PAM/PEI gel systems. Here the identification of the linear viscoelastic range for matured gels will allow for using the same values for gels during gelation. Further, the selection of the highest strain in the linear viscoelastic range helps in amplifying the torque signal and allows for measurements of low values of G'. Different parameters that influence the

strength of the polymer gel system were studied such as: temperature, PAM and PEI concentration, mixing water, pH and retarder type.

4.3.1 Effect of temperature

To examine the effect of temperature on gel strength, four solutions containing PAM/PEI (7/0.3) wt% were prepared at room temperature. Then, the effect of temperature was investigated in the range from 120° to 150°C (248 to 302°F). The gel strength, which is reflected in G' , depends on the cross-links density. The gel strength was predicted to increase with temperature (Kakadjian et al. 1999; Calvet et al. 2004; Al-Muntasheri et al. 2007). This is due to increase in the cross-linking density. Three different regimes can be identified in **Fig. 4.3**. An induction period in which $G'(t)$ oscillate around 10 Pa. During this period, the storage modulus is negligible due to the very low elasticity of the sample which falls below the sensitivity limits of the rheometer. A high strain, within the linear viscoelastic regime, was used. However, it seems that the initial nature of the sample (> 90% water) is not within the torque limit of the machine. It should be mentioned that the zero time is taken as the time at which the sample reached the specified temperature. For example, it took 18 minutes to heat up the sample to 130°C (266°F) from room temperature. There were more fluctuations in the data during the induction period. We do believe that the data loss in the induction period is not so important. The second period showed an inflection in G' after which it increases dramatically. The inflection point can be correlated to the gelation time which was monitored through the increase in elasticity vs. time plots. As can be seen from **Fig. 4.3**, the shape of second period differs with temperature. The shoulder shape weakens with increasing temperature. The same trend was observed with PAM / Cr^{+3} cross-linked gels (Sydansk 1990) in which the gelation was studied in the temperature range 24-60°C (75-10°F). This can be explained through the kinetics of the cross-linking reaction. Higher

temperatures could lead to an increase in molecular mobility; hence, more cross-links could be formed. Consequently, the reaction rate will be enhanced. In another way, higher temperatures could lead to an increase in PAM hydrolysis which accelerates cross-linking. Another possible interpretation is the formation of new cross-links at higher temperatures. It can be concluded that no more difference in cross-links beyond 130°C (266°F) was observed. The last period indicates a slight increase in G' to reach a final equilibrium (plateau) value. It was observed that the equilibrium elastic modulus (G_e') has increased with the increase in temperature. G_e' increased from 680 Pa to 1,044 Pa (i.e. ~ 35% increase) or a factor of 1.5 when the temperature was increased from 120°C (248°F) to 130°C (266°F). Further increase in temperature to 140°C (284°F) lead to less than 5% increase in G_e' . This increase in G_e' with temperature is due to the increase in the rate of cross-linking. However, at 150°C (302°F), G_e' showed a decrease which is likely due to mass transfer limitations of PEI in the presence of highly cross-linked networks. In general, PAM/PEI exhibited higher G' than those observed before for organic systems. For example, a sample of PAtBA/PEI system (7/0.3) wt% heated at 130°C (266°F) for 12 hours showed G_e' of ~ 500 Pa. In this study, G_e' increased to 1,044 Pa when PAM is used instead of PAtBA by using the same formulation and curing temperature. The reader should note that PAtBA / PEI gel system was cured at high temperature, but the storage modulus was measured at room temperature (23.5°C). The decrease in G_e' at higher temperatures was also observed with inorganically cross-linked gels. A decrease in G_e' with temperature was observed when partially hydrolyzed polyacrylamide (PHPA) was cross-linked with titanium (IV) (Cai and Huang 2001). G_e' showed a stable plateau value at 50°C (122°F), whereas, at 75°C (167°F) and 90°C (194°F) it reached a maximum value followed by abrupt decrease. The authors suggested that the hydrolysis of amide group caused gel syneresis. In another publication, in which the dynamic

measurements were conducted on already gelled samples, G_e' showed independency on temperature when PHPA cross-linked with Cr^{+3} -acetate at low temperature range (15-45°C) (Liu and Seright. 2001). The authors reasoned that to the property of rubber-like materials. However, most likely, the low temperature of these measurements did not allow a change in storage modulus that can be observed.

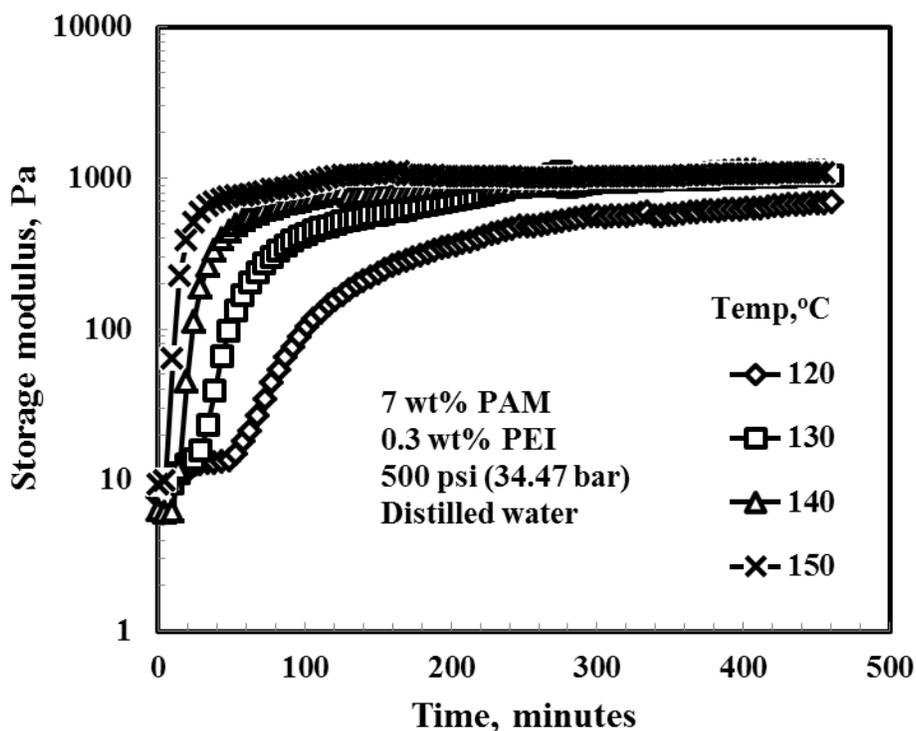


Figure 4. 3: Effect of temperature on elastic modulus

4.3.2 Effect of polymer concentration

To study the influence of polymer concentration, four different gelants were prepared in distilled water with PAM concentration of 3, 5, 7, and 9 wt% with the same concentration of PEI (0.3 wt%). With increasing PAM concentration, one may expect that more cross-linkable sites will be

accessible for PEI and consequently higher G' . As shown in **Fig. 4.4**, G_e' increased with increasing polymer concentration. This observation is in agreement with the data reported for organically cross-linked systems (Al-Muntasheri et al. 2007) where PAtBA was cross-linked with PEI. It also agrees with inorganically cross-linked gels where Cr^{+3} -acetate (Sydansk 1990; Liu and Seright. 2001) or Ti (IV)-sulfate (Cai and Huang. 2001) were used to cross-link either PAM or PHPA. From **Fig. 4.4**, when PAM concentration was increased from 3 to 9 wt% (a factor of 3), G_e' increased from 300 to 1,156 Pa indicating an increase by a factor of ~ 4 . A gel containing 5 & 7 wt% PAM showed G_e' of 550 & 1,044 Pa, respectively. Hence, the production of a gel with higher G_e' requires higher PAM loading. This is likely due to the more cross-linkable sites offered with high PAM concentration. However, higher PAM concentrations resulted in shorter gelation times. So, in treating deeper reservoirs, in which higher gelation time is required, these two effects should be taken into account.

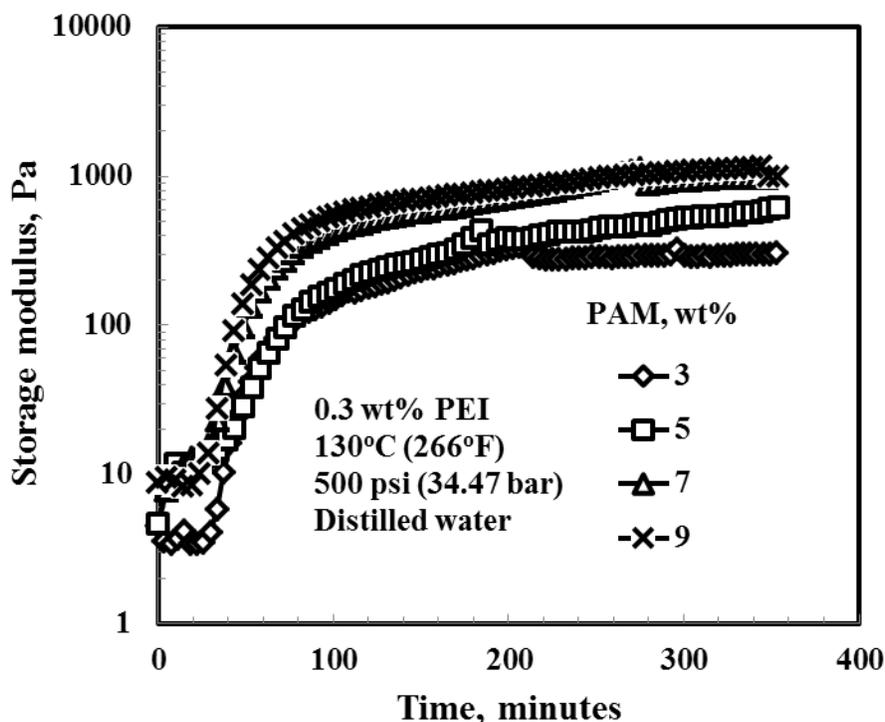


Figure 4. 4: Elastic modulus of PAM/PEI with different polymer concentrations

G_e' depends on polymer and cross-linker concentration in both organically (Al-Muntasheri et al. 2007) and inorganically cross-linked polymer gels (Grattoni et al. 2001; Omari 1995). This dependency was correlated to an equation in the form $[G=a \exp (bC)]$ where C is the polymer concentration in wt%, a and b are constants. G_e' data were extracted from **Fig. 4.4** and correlated to PAM concentration (**Fig. 4.5**) and the following expression was used to fit the data:

$$G_e' = 168 e^{0.22 [\text{PAM}]}$$

where, [PAM] is the polymer concentration in wt%. In order to examine the accuracy of the measurements, two different tests of 7 wt% PAM and 0.3 wt% PEI were performed at 150°C and the values of G_e' were 1,052 and 1,093 Pa indicating a less than 4% experimental error. Note that

the differences (ranges from 14 to 41%) between the data points used to fit the data was above 4% which is the experimental error associated with the measurements.

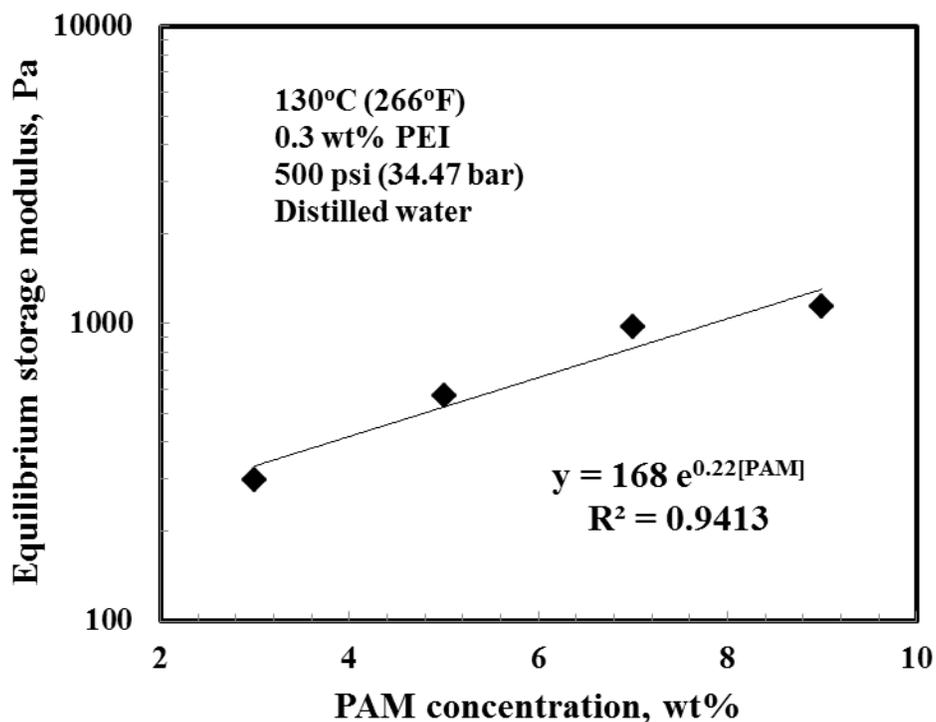


Figure 4. 5: Equilibrium elastic modulus as a function of polymer concentration

4.3.3 Influence of Cross-linker Concentration

The influence of cross-linker (PEI) concentration was examined. Polymer solutions with 0.3, 0.6, 0.9, and 1.2 wt% PEI with a polymer concentration of 7 wt% were used. As shown in **Fig. 4.6**, high cross-linker concentrations resulted in high values of G' . This is expected as higher PEI concentration offer more sites for cross-linking. However, the rate of increase in G_e' is less pronounced compared to the effect of PAM. For instance, G_e' increased from 1,044 to 1,169 Pa when PEI increased from 0.3 to 0.9 wt%. This indicates that G_e' increased by a factor of 1.1

when PEI is increased by a factor of 3. When PAM concentration was increased with the same factor (3), G_e' increased by a factor of 4. As a result, PAM is dominant over PEI in determining the strength of PAM / PEI gel system. There may be an optimum amount of PEI concentration since previous literature reports (Sydansk 1990; Al-Muntasheri et al. 2007) revealed that high cross-linker concentration may lead to over-cross-linking and consequently gel syneresis (expulsion of water out of the gel structure). PAtBA cross-linked with PEI at high temperatures also showed an increase in G_e' with increasing cross-linker concentration. However, the effect of cross-linker on the strength of inorganic gels is different. The strength of the gel was observed to increase to a maximum value then decrease at higher cross-linker concentration. This observation was noticed with other gel systems like PHPA/Cr(III)-acetate (Liu and Seright 2001) , PHPA/Ti(IV) (Cai and Huang 2001), and scleroglucan / zirconium (Omari 1995). This was explained by the formation of higher inorganic polymeric species which competes with the cross-linking reaction.

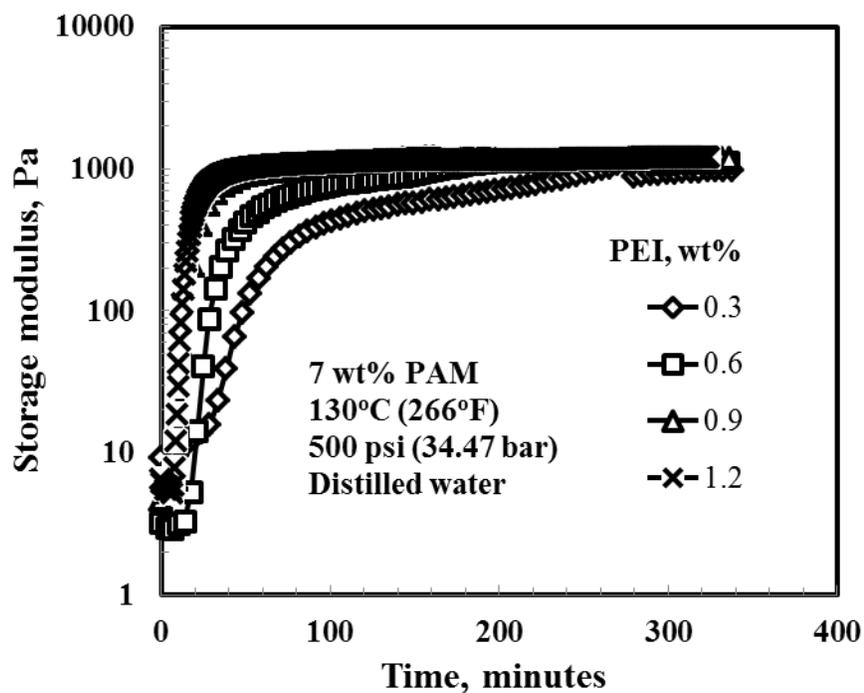


Figure 4. 6: Effect of cross-linker concentration on elastic modulus

G_e' values for the 7 wt% PAM cross-linked with various PEI concentrations were extracted from **Fig. 5** and fitted to PEI concentration as follows (**Fig. 7**):

$$G_e' = 931 e^{0.23 [\text{PEI}]}$$

where [PEI] is the cross-linker concentration in wt%. When the cross-linker concentration was increased from 0.3 to 1.2 wt%, G_e' increased from 1,044 Pa to 1,210 Pa (~20%).

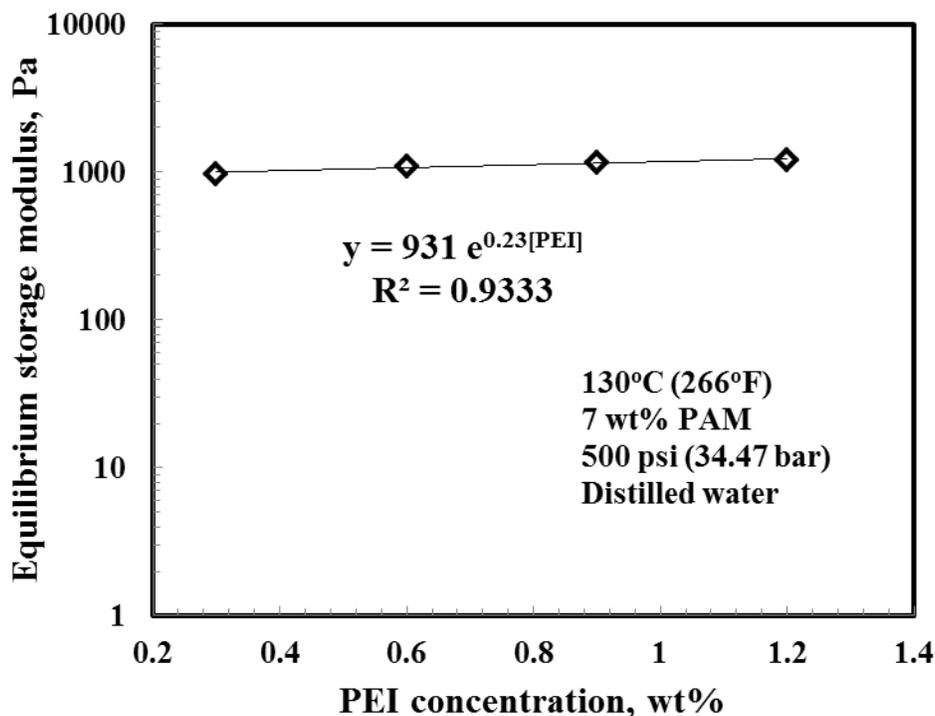


Figure 4. 7: Equilibrium elastic modulus as a function of cross-linker concentration

4.3.4 Effect of Salinity

The influence of distilled, field, and seawater was investigated by preparing representative samples of field and seawater. 7 wt% PAM and 0.3 wt% PEI were used in the formulation at a temperature of 130°C (266°F). The elastic modulus decreased with the increase in water salinity. G_e' values were 1044 Pa and 725 Pa for distilled and field water samples, respectively. This indicates that field water reduces G_e' by a factor of almost 1.5. This factor was also obtained in PAtBA / PEI gelation at high temperature where G_e' (measured at room temperature) decreased from 1,025 Pa in deionized water to 675 Pa in field water. This is likely due to the known shrinkage in polymer chain caused by salts (Nasr-El-Din et al. 1991). Such shrinkage leads to a decrease in the number of cross-linkable sites and consequently low elasticity. Sea water

behaved differently. Initially, G' was lower than that of distilled and field water and surpassed field water at equilibrium state. This observation was confirmed by using the representative seawater as well as synthetic seawater. The gelation time was increased by increasing water salinity. This observation was confirmed in previous literature reports (Kakadjian et al. 1999; Broseta et al. 2000; Romero-Zerón et al. 2008). The reasons for the decrease in G_e' and the increase in the gelation time are related to the impact of salts on the degree of PAM hydrolysis. These salts tend to slow the rate of hydrolysis which will eventually reduce the rate of cross-linking and increase the gelation time. The negative impact of salinity on G' was also noticed in inorganically cross-linked gels. G' decreased in presence of monovalent and divalent cations when a copolymer of 2-acrylamido-2-methyl-propansulphonic-acid (AMPS) and acrylamide was cross-linked with Cr(III)-acetate (Koohi et al. 2010). It was suggested that the cations compete with Cr(III) leading to low cross-links.

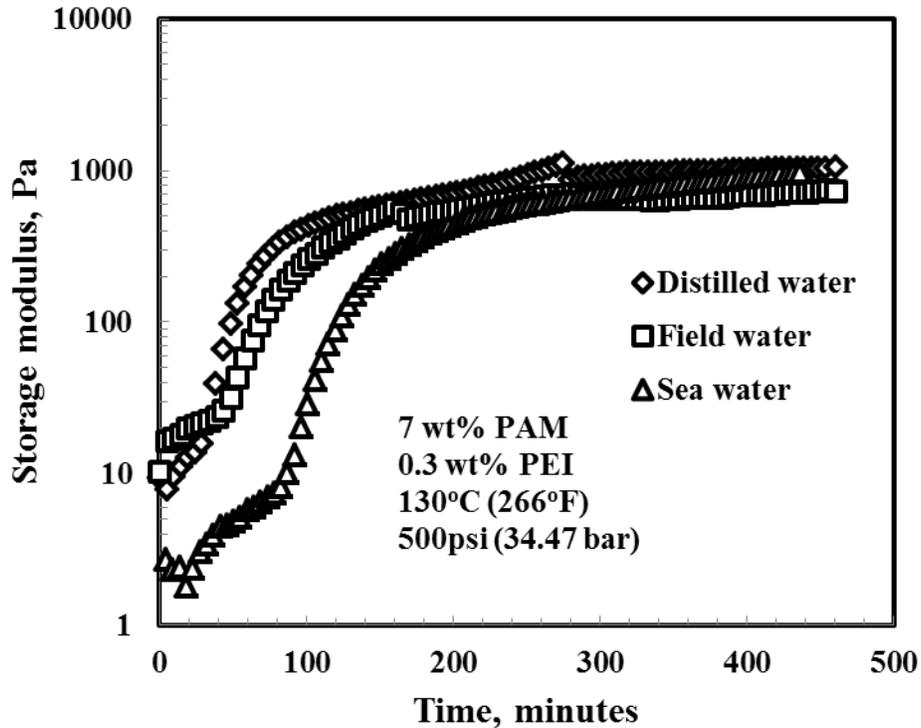


Figure 4. 8: Effect of salinity of mixing water on equilibrium elastic modulus

4.3.5 Effect of Initial pH

In order to examine the effect of pH on the gel strength of PAM/PEI, a sample containing PAM / PEI (7/0.3) wt% was prepared and the pH was found to be about 10.2, this is due to the high pH of the cross-linker (PEI) (~11.7). Hydrochloric acid was used to adjust the pH of another two samples to 7 and 3 to investigate the effect of pH in neutral and acidic media, respectively. Then, all samples were loaded to the pressure cell and a dynamic shear test was performed. As shown in **Fig. 4.9**, the gelation time was observed to be higher in the neutral media, but decreased in the alkaline and acidic media. G_e' data at pH of 10.2, 7, and 3 were found to be 1044, 987, and 1139, respectively. It can be concluded that the gelation at the alkaline and acidic media is associated with higher G' , but lower gelation times if compared with the cross-linking in the neutral media.

The reasons for high G' values in acidic and alkaline environments are related to the kinetics of PAM hydrolysis in both environments where higher or lower degrees of hydrolysis could be achieved away from neutral media (Kurenkov et al., 2001, Al-Muntasheri et al., 2008). The results presented here specify that the degree of hydrolysis of PAM is higher at either lower or higher pH values. The range outside the neutral media showed lower gelation times. Moreover, the cross-linking reaction seems to be fast in acidic media compared to alkaline and neutral media. For Cr^{+3} cross-linked gels, the gel strength increases with increasing polymer pH (Sydansk 1990).

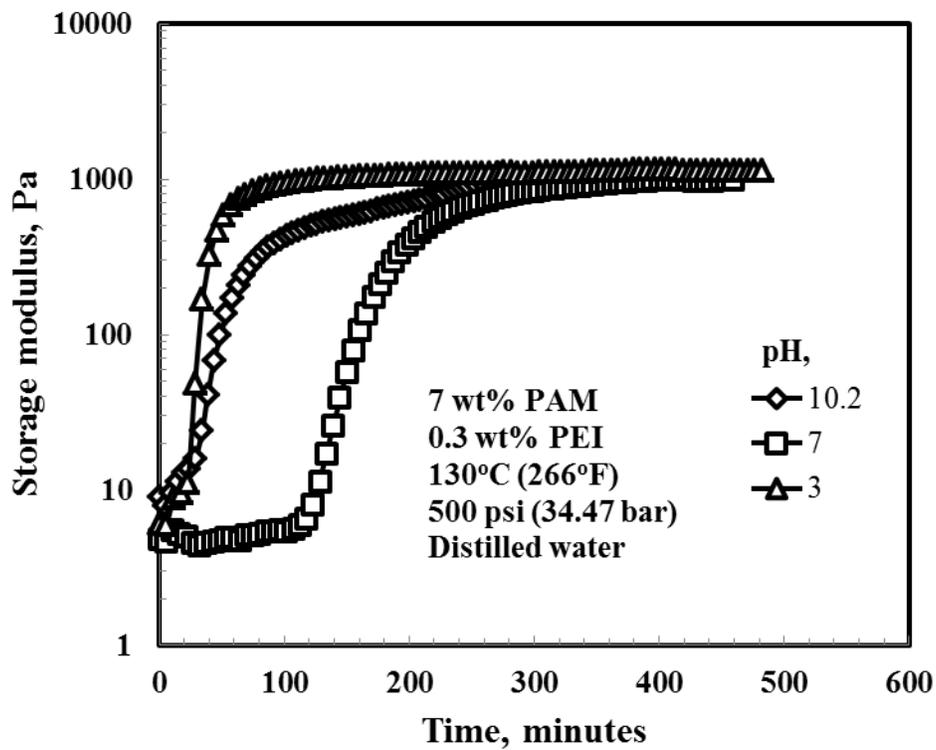


Figure 4. 9: Effect of initial pH value on equilibrium elastic modulus

4.3.6 Influence of Retarders

Sodium chloride

The influence of sodium chloride on gel strength was investigated at 130°C (266°F) by using a formulation of PAM / PEI (7/ 0.3) wt%. A pre-determined amount of NaCl was added such that the concentration is 250, 150, and 100 lb / 1000 gal. These concentrations correspond to 30,000, 18,000, and 12,000 mg/L, respectively. As shown in **Fig. 4.10**, high salt concentration leads to longer gelation time and a weaker gel in comparison with salt-free environment at the given time. This is likely due to charge screening effect by Na⁺ cations on carboxylate groups resulted from PAM hydrolysis (Tam and Tiu 1989; Nasr-El-Din et al. 1991; Ghannam 1999). Low NaCl concentrations caused little effect on gel strength. Upon the addition of 12,000 mg/L NaCl, almost no change in G_e' was observed. However, when NaCl concentration was increased to 18,000 and 30,000 mg/L G_e' was ~820 Pa and 740 Pa, respectively. Note that the G_e' for PAM/PEI in salt-free environment at 130°C (266°F) was ~ 1044 Pa. Therefore, salts delay the gelation and accordingly reduce gel strength and longer heating times may be needed to reach the same ultimate gel strength.

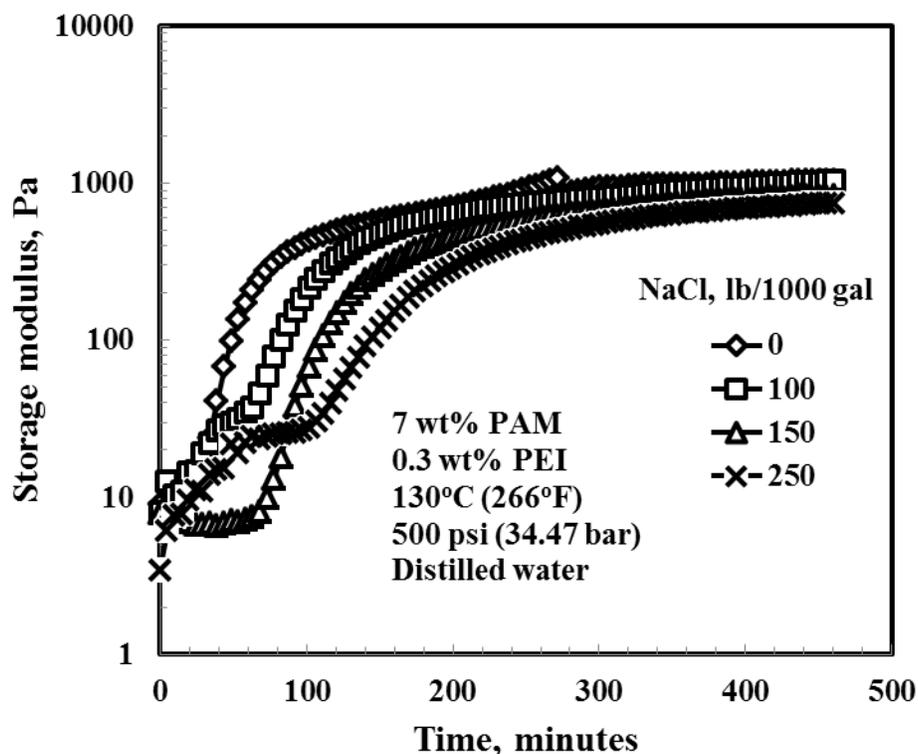


Figure 4. 10: Effect of NaCl concentration on elastic modulus

Ammonium chloride

In order to investigate the effect of NH_4Cl , PAM/PEI (7/0.3) wt% solution was prepared. Then, NH_4Cl was added at a concentration of 250 lb / 1000 gal (30,000 mg / L). It was found that the gelation time was more than 500 minutes and G_e' was obtained after a long time (23 hrs). The polymer concentration was increased to 9 and 15 wt%; however, NH_4Cl was observed to be very effective in elongating the gelation time even at high polymer loading (**Fig. 4.11**). This may be due to the efficiency of NH_4Cl to screen the negative charges on the carboxylate groups. So, it was decided to study the effect of NH_4Cl at lower concentration. The effect of NH_4Cl on PAM / PEI was examined at salt concentrations of 10 to 100 lb / 1000 gal (1,200 to 12,000 mg/L). Again, high ammonium concentrations resulted in weak gels as observed in **Fig. 4.12**.

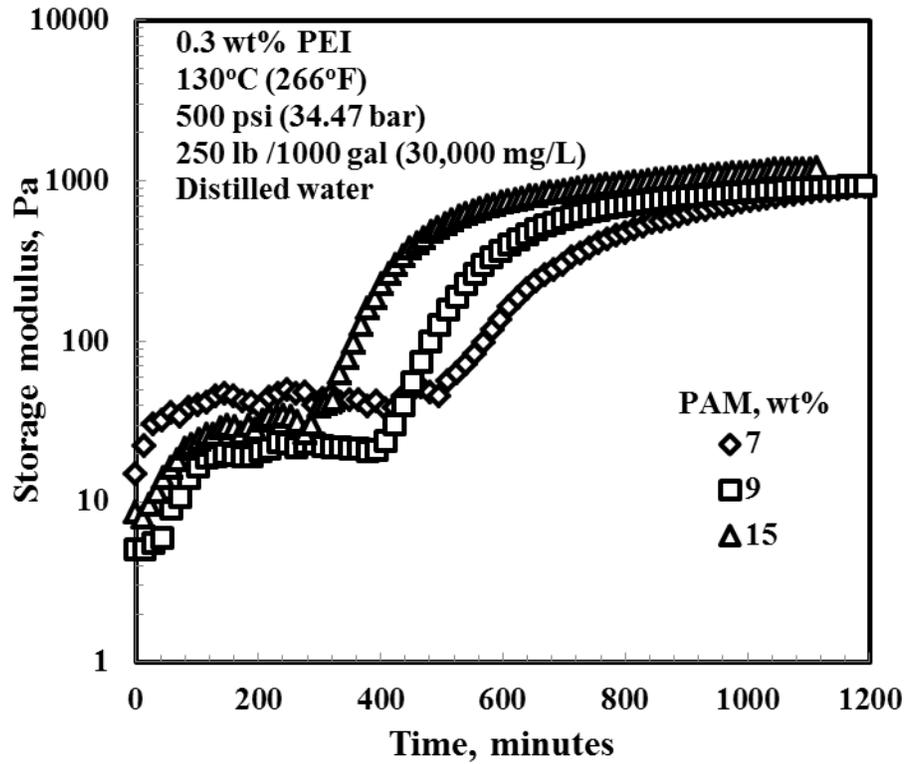


Figure 4. 11: Effect of NH_4Cl on elastic modulus with different polymer concentration

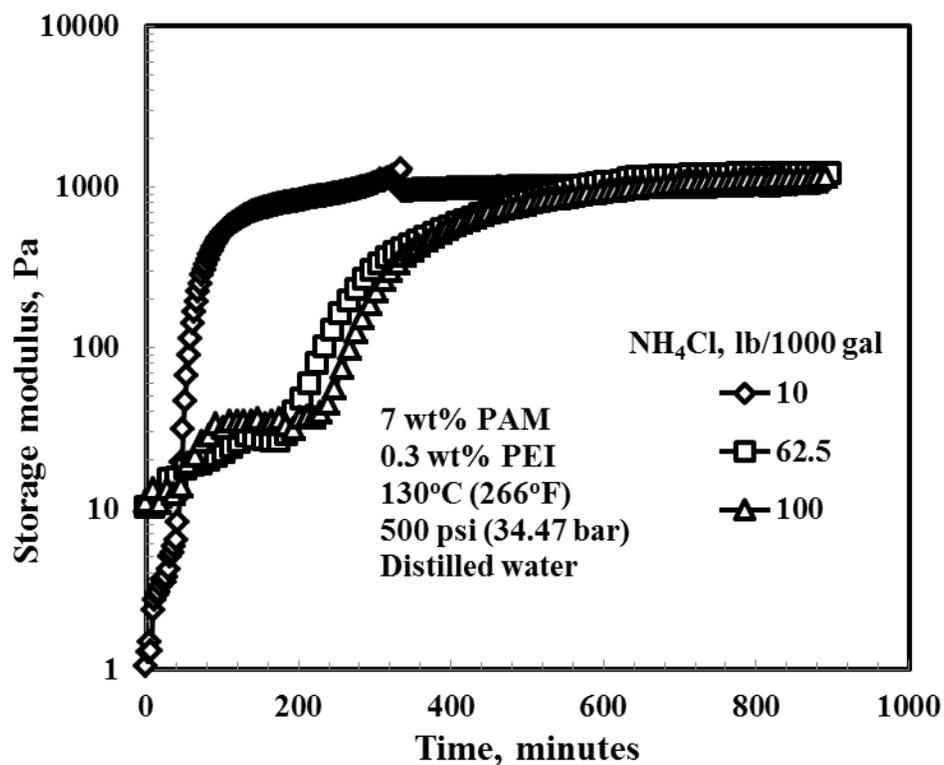


Figure 4. 12: Effect of NH_4Cl concentration on elastic modulus

Effect of salt type

For the influence of salt type, the same concentration of NaCl , and NH_4Cl was added to a polymer solution containing of 7 wt% PAM and 0.3 wt% PEI in distilled water. The results given in **Fig. 4.13** showed that addition of NH_4Cl leads to a weaker gel compared to NaCl . The effect of salts was also examined in field water and the same trend was observed as displayed in **Fig. 4.14**. G_e' decreased by $\sim 35\%$ when 1,200 mg/L of NH_4Cl was added where almost no change was observed when the same amount of NaCl was added. The main reason for this observation could be, tentatively, the strong efficiency of NH_4Cl on screening the negative charges on the carboxylate groups on the PHPA resulted from the hydrolysis of PAM. This is because NH_4^+ was reported to have stronger binding to carboxylate groups compared to Na^+ (Kherb et al. 2012).

The impact of the different retarders on PAM hydrolysis at different temperatures will be the subject of a future publication.

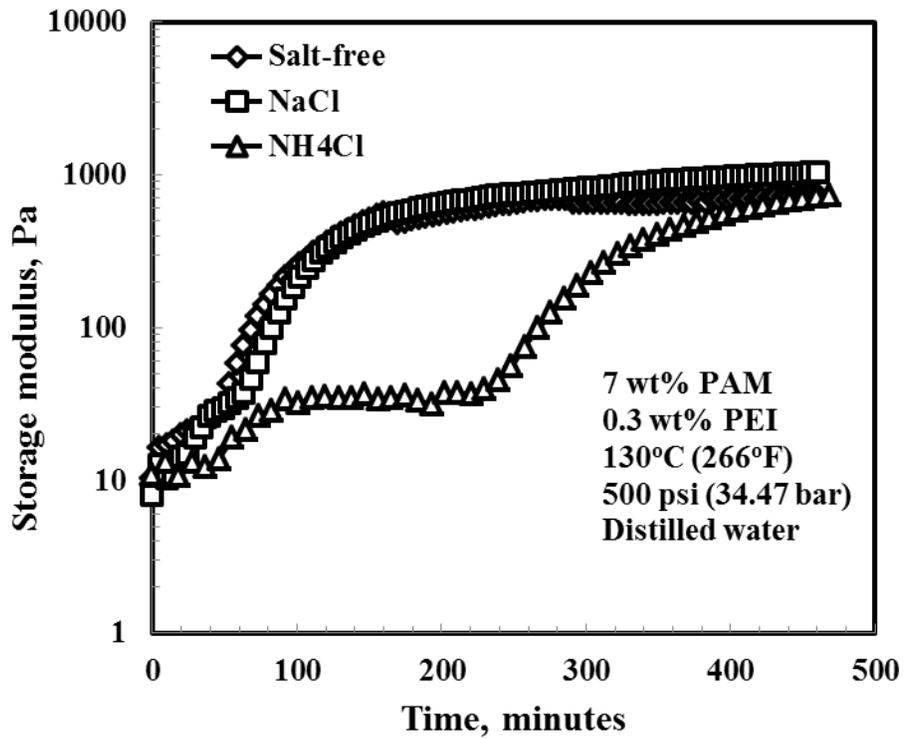


Figure 4. 13: Effect of salts (12,000 mg/l) on elastic modulus in distilled water

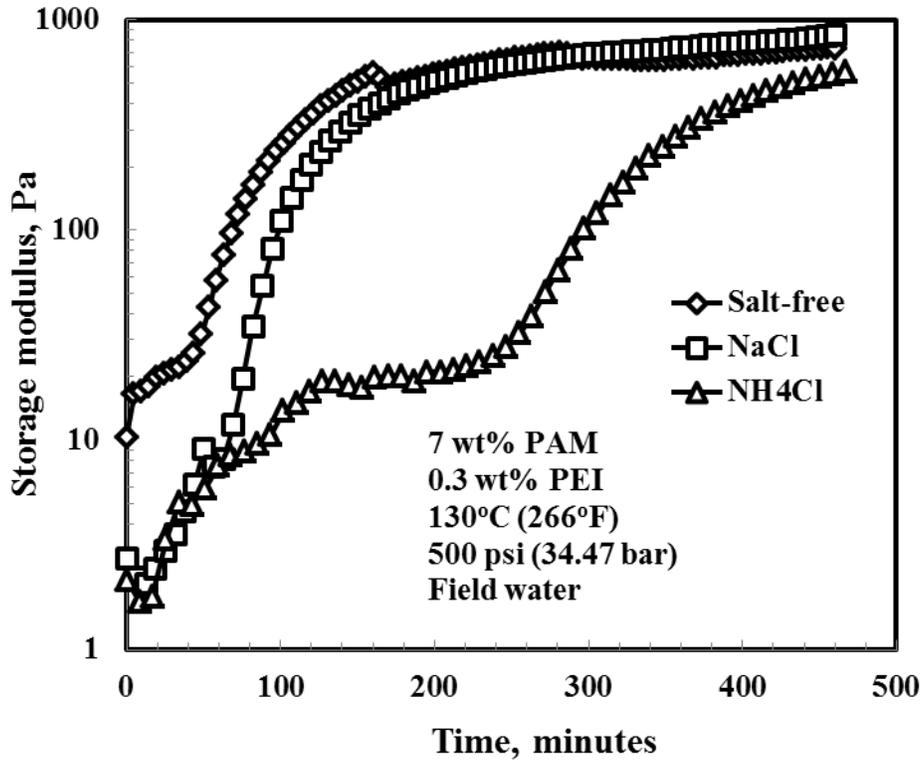


Figure 4. 14: Effect of salts (12,000 mg/l of NaCl and NH₄Cl) on elastic modulus in field water

4.3.7 Gel Yield Stress and Extrusion through Fracture

Elastic modulus data gives information about the gels strength in a rheometer. In a reservoir, the pressure that the gel can handle before it yields is of interest. To determine the yield stress of PAM/PEI gel through rheology, two samples containing 7 and 5 wt% PAM with 0.3 wt% PEI were prepared. Three consecutive tests were conducted on the samples. First, a time sweep was done until an equilibrium value of storage modulus was obtained. Then, the test was followed by a frequency sweep in the range 0.1 - 100 rad/s. Finally, a strain sweep test was performed from 1 to 5,000 %. For the first two tests, 10% strain was used which was within the linear viscoelastic region as found before (Fig. 4.2). From Fig. 4.15, it can be seen that the slopes of log G' vs. log

ω were less than 2 which confirms a formation of a cross-linked network (te Nijenhuis 1996). **Fig. 4.15** also illustrates that G' is a weak function of frequency at low frequency (0.1- 10 rad/s). For the strain sweep shown in **Fig. 4.16**, at PAM/PEI of (5/0.3) wt%, as strain increases from 1 to 10% the stress increases linearly (from 7.9 to 77.8 Pa) with a slope of ~ 7.8 which changed to ~ 5.3 at a strain of 117%. The gel breakage occurred at a strain of 159% with a stress of 886 Pa. The same trend for stress-strain relationship was noted for 7/0.3 (PAM/PEI) wt%. A linear increase in stress (from 8.1 to 1,687 Pa) was observed as strain increases from 1 to 250% with a slope of 6.7. Further increase in strain changed the slope to 0.6 and the gel breakage took place at a strain of $\sim 4,000\%$ with a stress of 4,544 Pa. Depending on the stress-strain relationship, the yield stresses of PAM/PEI at (7/0.3) & (5/0.3) wt% are 77.8 and 1,786 Pa, respectively.

For a gel with a stress of τ_y to extrude through a fracture, the pressure gradient is inversely proportional to the fracture width (Broseta et al. 2000). This relationship can be written as follows (Liu and Seright 2001):

$$\frac{dp}{dl} = \frac{2\tau_y}{w_0}$$

where w_0 represents the effective size for the opening (fracture) during extrusion. Assuming a fracture width of 0.1 cm and using the above equation with the yield stresses concluded from **Fig. 4.16**, the pressure gradient is predicted to be ~ 155.5 kPa/m (55.2 psi/m) and 3,572 kPa/m (518 psi/m) for (PAM/PEI) (5/0.3) and (7/0.3) wt% respectively. Additional experimental work should be performed to further confirm these pressures gradients in porous media. However, it is expected that the trends will remain the same where the yield pressure will increase with increasing polymer concentration.

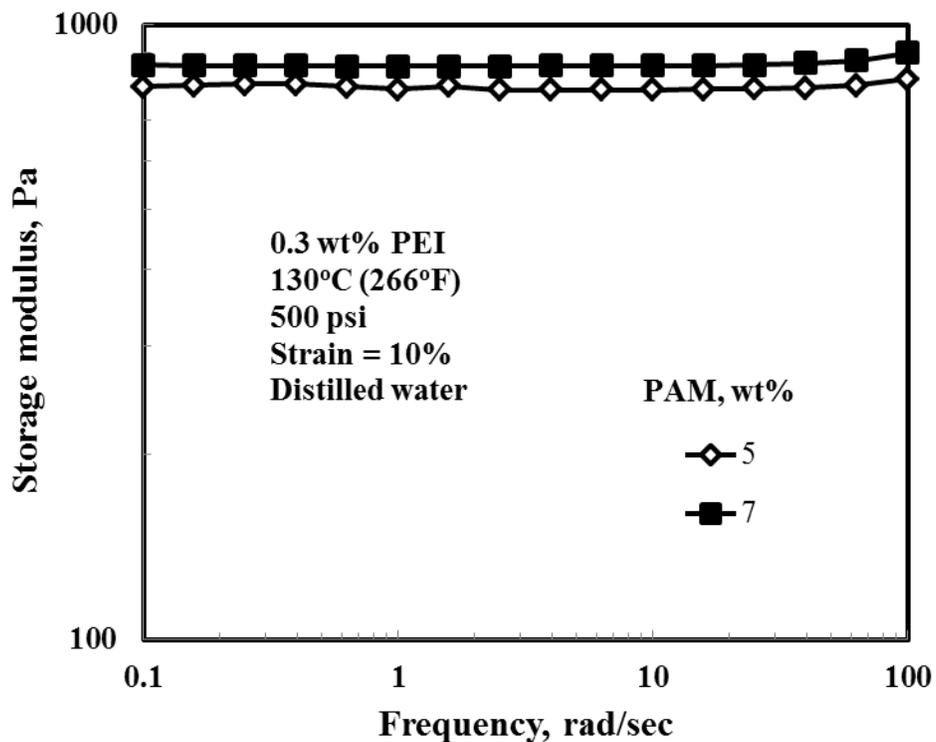


Figure 4. 15: Frequency sweeps for gel samples with different PAM concentrations

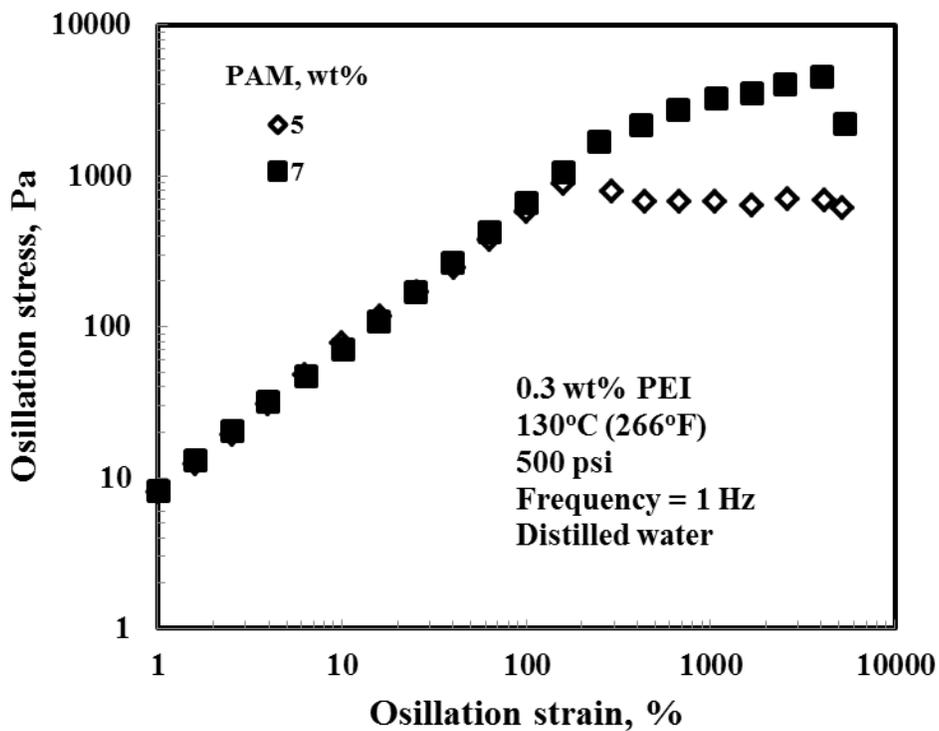


Figure 4. 16: Yield Stress determination of PAM/PEI at 130°C (266°F)

4.4 Conclusions

The influence of temperature, polymer and cross-linker concentrations, salinity of mixing water, pH, and salts on gel strength of PAM / PEI system was studied at high temperatures (>100°C). The gel strength was measured using dynamic shear measurements. Overall, PAM/PEI showed high elastic modulus compared with what was reported earlier for inorganic gels (PHPA/Cr⁺³) as well as organic gels (PAtBA/PEI). At PAtBA / PEI (7/0.3) wt% cured at 150°C (302°F), the room-temperature measured G_e' was reported to be ~ 800 Pa (Al-Muntasheri et al., 2007), whereas, it was increased to ~ 1087 Pa when PAM was used instead of PAtBA (present work). G_e' of PHPA/Cr⁺³ was measured at low temperatures. In a paper by Liu and Seright (2001), G_e' was ~ 100 Pa measured at 20°C (68°F) for PHPA/Cr⁺³ (12/1) wt% aged at 41°C (105.8°F) for 24 hours. Although PAM/PEI system was evaluated in core-flooding systems at 50°C (122°F) (Al-Muntasheri et al. 2010b) and 90°C (194°F) (Al-Muntasheri et al. 2008) and showed a high efficiency in shutting-off water. But the performance at of this system at temperatures higher than 100°C is a matter of interest to the oil industry to expand the applicability of this system to elevated reservoir temperatures. The main results of this study are summarized as follows:

- (1) The elastic modulus of the PAM / PEI (7/0.3) wt% system was found to increase by about 35% upon increasing the temperature from 120°C (248°F) to 130°C (266°F). However, no considerable increase in strength was noted above 130°C (266°F).
- (2) The elastic modulus was found to follow an exponential relationship on both PAM and PEI concentrations ($G_e' = 168 e^{0.22 [PAM]}$),
($G_e' = 931 e^{0.23 [PEI]}$)
- (3) In general, elastic modulus decreased in the presence of salts. However, the impact of different retarders (salts) is different. High water salinities resulted in low gel strength.

- (4) High elastic modulus was observed at alkaline as well as acidic media compared to neutral media where lower G' and higher gelation times were obtained.
- (5) Retarders were found to decrease the elastic modulus and increase the gelation time.
- (6) At the same concentration, addition of NaCl caused almost no change in elastic modulus, whereas NH_4Cl resulted in around 35% decrease.
- (7) The decrease or increase in gel strength was explained through the impact of the different parameters on PAM hydrolysis.
- (8) The yield stress of PAM/PEI was estimated through strain sweep tests and it was found to increase with increasing polymer concentration. It was found to be 155.5 kPa/m (55.2 psi/m) and 3,572 kPa/m (522 psi/m) for samples containing 7/0.3 and 5/0.3 wt.% of polymers/crosslinker, respectively.

Acknowledgements

The authors would like to thank King Abdul-Aziz City for Science and Technology (KACST) for supporting this research through project # AR-30-291. King Fahd University of Petroleum and Minerals (KFUPM) and Saudi Aramco are also acknowledged for their support. Also, the authors would like to thank the technical reviewers of this paper for their useful comments.

4.5 References

Albonico, P., Bartosek, M., and Lockhart, T.P. 1994. New Polymer Gels for Reducing Water Production in High-Temperature Reservoirs. Paper SPE 27609 presented at the SPE European Production Operations Conference and Exhibition, Aberdeen, 15-17 March. DOI: <http://dx.doi.org/10.2118/27609-MS>.

Al-Muntasheri, G.A., Hussein, I.A., Nasr-El-Din, H.A. and Amin, M.B. 2007. Viscoelastic Properties of a High Temperature Cross-linked Water Shut-Off Polymeric Gel. *J. Pet. Science Eng* **55**(1-2): 56-66.

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. 2010a. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Al-Muntasheri, G.A., Zitha, P.L.J., and Nasr-El-Din, H.A. 2010b. A New Organic Gel System for Water Control: a Computed Tomography Study. *SPEJ*, **15**(1): 197-207. DOI: <http://dx.doi.org/10.2118/129659-PA> .

Al-Muntasheri, G.A., Nasr-El-Din, H.A. and Zitha, P.L.J. 2008. Gelation Kinetics and Performance Evaluation of an Organically Cross-linked Gel at High Temperature and Pressure. *SPEJ*, **13**(3): 337-345. DOI: <http://dx.doi.org/10.2118/104071-PA>.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., Peters, J.A. and Zitha, P.L.J. 2006. Investigation of a High Temperature Organic Water Shut-off Gel: Reaction Mechanisms. *SPEJ*, **11**(4): 497-504.

Baily, B., Crabtree, M., Tyrie, J., et al. 2000. Water Control. *Oilfield Review* **12** (1): 30-51.

Boye, B., Rygg, A., Jodal, C., and Klungland, I. 2011. Development and Evaluation of a New Environmentally Acceptable Conformance Sealant. Paper SPE 142417 presented at the SPE European Formation Damage Conference, Noordwijk, 7-10 June. DOI: <http://dx.doi.org/10.2118/142417-MS>.

Broseta, D., Marquer, O., Blin, N., and Zaitoun, A. 2000. Rheological Screening of Low-Molecular-Weight Polyacrylamide/Chromium(III) Acetate Water Shutoff Gels. Paper SPE 59319 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April.

Broseta, D., Marquer, O., Blin, N., Zaitoun, A., Baylocq, P., and Fery, J.J. 2000. Shear Effects on Polyacrylamide / Chromium (III) Acetate Gelation. *SPE Res Eval. & Eng* **3**(3): 204-208.

Cai, W., and Huang, R. 2001. Study on gelation of partially hydrolyzed polyacrylamide with titanium(IV). *European Polymer Journal* **37**(2001): 1553-1559.

Calvet, D., Wong, J.Y., and Giasson, S. 2004. Rheological Monitoring of Polyacrylamide Gelation: Importance of Cross-Link Density and Temperature. *Macromolecules*; **37**(20): 7762-7771.

Ghannam, M.T. 1999. Rheological Properties of Aqueous Polyacrylamide Solutions. *J Appl Polym Sci* **72**(14): 1905-1912.

Grattoni, C.A., Al-Sharji, H.H., Yang, C., Muggeridge, A.H., and Zimmerman, R.W. 2001. Rheology and Permeability of Cross-linked Polyacrylamide Gel. *J. Colloid Interface Sci.* (240): 601-607.

Hardy, M., Botermans, C.W., Hamouda, A., Valdal, J. and Warren, J. 1999. The First Carbonate Field Application of a New Organically Cross-linked Water Shut-off Polymer System. Paper SPE 50738 presented at the 1999 SPE International Symposium on Oilfield Chemistry, Houston, 16-19 February.

Hardy, M.B., Botermans, C.W., and Smith, P. 1998. New Organically Cross-linked Polymer System Provides Competent Propagation at High Temperatures in Conformance Treatments.

Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19-22 April.

Hibbeler, J. and Rae, P. 2005. The Environmental Benefits of Reducing Water Production. Paper SPE 96582 presented at the SPE Asia Pacific Health, Safety, and Environment Conference and Exhibition, Kuala Lumpur, 19-20 September. DOI: <http://dx.doi.org/10.2118/96582-MS>.

Hutchins, R.D., Dovan, H.T. and Sandiford, B.B.: "Field Applications of High Temperature Organic Gels for Water Control," paper SPE 35444 presented at the 1996 SPE/DOE Improved Oil Recovery Symposium, Tulsa, OK, 21-24 April.

Kakadjian, S., Rauseo, O., and Mejias, F. 1999. Dynamic Rheology as a Method for Quantify Gel Strength of Water Shutoff Systems. Paper SPE 50751 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 16-19 February.

Kherb, J., Flores, S.C., and Cremer, P.S. 2012. Role of Carboxylate Side Chains in the Cation Hofmeister Series. *J. of Phys. Chem. B*, (**116**): 7389-7397.

Koohi, A.D., Seftie, M.V., Ghalam, A., Moghadam, A.M., and Sabet, S.Z. 2010. Rheological Characteristics of Sulphonated Polyacrylamide/Chromium Triactate Hydrogels Designed for Water Shut-off. *Iranian Polymer Journal* **19**(10): 757-770.

Kurenkov, V.F., Hartan, H.G., and Lobanov, F.I. 2001. Alkaline Hydrolysis of Polyacrylamide. *Russian Journal of Applied Chemistry* 74 (4): 543-554.

Liang, J.T, Sun, H. and Seright, R.S. 1995. Why Do Gels Reduce Water Permeability More Than Oil Permeability? *SPE Res Eng* **10** (4): 282-286. SPE-27859-PA.

Liu, J., and Seright, R.S. 2001. Rheology of Gels Used For Conformance Control in Fractures. *SPEJ* **6**(2): 120-125. SPE-70810-PA.

Mercado, M., Acuna, J.C., Caballero, C., Vasquez, J., and Soriano, E. 2009. Successful Field Application of a High-Temperature Conformance Polymer in Mexico. Paper SPE 120966 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, 20-22 April. DOI: <http://dx.doi.org/10.2118/120966-MS>.

Moradi-Araghi, A.: "Altering High Temperature Subterranean Formation Permeability," U.S Patent 4,994,194, 1991.

Nasr-El-Din., H.A., Hawkins., B.F., Green., K.A. 1991. Viscosity behavior of Alkaline, Surfactant, Polyacrylamide Solutions Used for Enhanced Oil Recovery. Paper SPE 21028 presented at the SPE International Symposium on Oilfield Chemistry. Anaheim. California. 20 – 22 February.

Omari, A. 1995. Rheological study of the gelation kinetics of the scleroglucan-zirconium system. *Polym Journal*, **36**(4): 815-819.

Polo, R.P.O., Monroy, R.R., Toledo, N., Dalrymple, E.D., Eoff, L., and Everett, D. 2004. Field Applications of Low Molecular-Weight Polymer Activated with an Organic Cross-linker for Water Conformance in South Mexico. Paper SPE 90449 presented at the SPE Annual Technical Conference and Exhibition, Houston, 26-29 September. DOI: <http://dx.doi.org/10.2118/90449-MS>.

Romero-Zerón, L., Manalo, F., and Kantzas, A. 2008. Characterization of Crosslinked Gel Kinetics and Gel Strength by Use of NMR. *SPE Res Eval & Eng* **11**(3): 439-453. SPE-86548-PA.

Stavland, A., Andersen, K.I., Sandoy, B., Tjomsland, T., and Mebratu, A.A. 2006. How To Apply a Blocking Gel System for Bullhead Selective Water Shutoff: From laboratory to Field. Paper SPE 99729 presented at the SPE/DOE Symposium on Improved Oil Recovery Tulsa, April 22-26 April. DOI: <http://dx.doi.org/10.2118/99729-MS>.

Sydansk, R.D. 1990. A Newly Developed Chromium (III) Gel Technology. *SPE Res Eng* **5** (3): 346-352. SPE-19308-PA.

Sydansk, R.D. and Seright, R.S. 2007. When and Where Relative Permeability Modification Water-Shutoff Treatments Can Be Successfully Applied. *SPE Prod & Oper* **22** (2): 236-247. SPE-99371-PA.

Tam, K.C and Tiu, C. 1989. Steady and dynamic shear properties of aqueous polymer solutions. *J Rheolgy* **33**(2): 257-280.

te Nijenhuis, K. 1996. Calculation of Network Parameters in Thermoreversible Gels. *Polym Gels and Netw*, (4): 415-433.

te Nijenhuis, K., Mensert, A., Zitha, P.L.J. 2003. Viscoelastic behavior of partially hydrolyzed polyacrylamide/chromium(III) gels. *Rheol. Acta* **42**: 132-141.

Zaitoun, A. and Kohler, N. 1988. Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. Paper SPE 18085 presented at the SPE Annual Technical Conference and Exhibition, Houston, 2-5 October.

CHAPTER FIVE

Gelation Kinetics of PAM/PEI System: DSC Investigation

Khalid S.M. El-Karsani¹, Ghaiathan A. Al-Muntasheri^{2}, Abdullah S. Sultan³ & Ibnelwaleed A. Hussein⁴*

^{1&4}Chemical Engineering Department, King Fahd University of Petroleum & Minerals; Dhahran 31261, PO BOX 5050, Saudi Arabia

²Production Technology Team, EXPEC Advanced Research Center, Dhahran 31311, Saudi Aramco, Saudi Arabia

³Petroleum Engineering Department, and Center for Petroleum & Minerals (CPM), King Fahd University of Petroleum & Minerals; Dhahran 31261, Saudi Arabia

Abstract

Excess water production in oil and gas wells causes serious productivity and environmental problems in the oilfield. A mixture composed of a polymer, cross-linker, and water is usually injected into the reservoir to block unwanted water by forming a three dimensional structure. This transition process from solution to gel is a function of temperature, time, salinity of mixing water and concentration of the various components. The gelling solution was prepared by mixing polyacrylamide (PAM) with distilled water, and then polyethylenimine (PEI) was added as a cross-linker. The injection process was simulated and investigated by differential scanning calorimeter (DSC) over the temperature range 80° to 120°C. The DSC dynamic scan showed two consecutive peaks. An endothermic peak was observed at low temperature due to PAM alkaline hydrolysis. Another exotherm was observed at ~ 70°C which corresponds to the onset of cross-linking of PAM and PEI. It was found that high temperatures lead to high release of heat due to gelation. The effect of salts on the cross-linking was also examined. More delay in cross-linking was observed in the case of NH₄Cl compared to NaCl. The gelation kinetics was modeled using

a rate process model that relates fractional gelation with time. Further, Avrami model, usually used to study crystallization kinetics, was also used to model the gelation process. Kinetic parameters were obtained from the two different models and the results showed good agreement with experimental data. The presence of salts in sea water leads to a drop of 60-80% in the rate constant without influencing the order of the gelation reaction.

Key words: gelation, kinetics, DSC, polymeric gel, water shut-off

*Corresponding Author: ihussein@kfupm.edu.sa; Tel/Fax +966 13 860 2235/4234

5.1 Introduction

Excess water produced from matured oil and/or gas wells is a serious issue in hydrocarbon production. This can impose additional operational costs (Baily et al. 2000) as well as environmental impacts. This water needs special plants to deal with which increases the production costs. In addition, this type of water may contain elements such as mercury, arsenic (Hibbeler and Rae 2005) which affects the environment with toxicity concerns if disposed without further treatment. One of the common remediate methods is the use of cross-linked polymer gels. Polymer gels have been used in different ways in oilfield industry. They were used to totally block water production zones (Alqam et al 2005; Vasquez et al 2003), reduce permeability to water (Zaitoun and Kohler 1988; Liang et al. 1995), and increase reservoir sweep efficiency in injection wells (Chang et al. 2002; Lei et al. 2011). Beside other factors such as identification of the water source, the understanding of gelation kinetics is an important factor for successful application to avoid injectivity problems.

Two types of polymer gels were developed and used worldwide. Inorganic gel systems, in which trivalent cations such as Cr^{+3} were used to cross-link the carboxylate groups on partially hydrolyzed polyacrylamide (PHPA) (Sydansk 1990; Lockhart 1994). This cross-linking is believed to be through coordination covalent bonds. The second type was based on organic cross-linkers with polyacrylamide-based polymers (Morgan et al. 1997; Moradi-Araghi 2000). Organically cross-linked gels are preferable at high temperatures due to their higher thermal stability compared to inorganic gels. An example is polyacrylamide (PAM)/ polyethylenimine (PEI) gel system.

Polymer gels are based on a mixture of a polymer, cross-linker, and water. This mixture is referred to as gelant. When injected in the target zone, the gelant forms a 3-dimensional (3D) structure which works as a physical barrier to water flow. The transition process from gelant (solution) to polymeric gel is a function of temperature, time, salinity of mixing water, and the concentration of various components. The gelation time is a key factor for gelant placement. Thus, longer gelation times are required for high temperature reservoirs. Salts like NaCl and NH_4Cl were used to retard the gelation and delay the cross-linking process. Most of the previous gelation kinetics studies have focused on rheological techniques (Al-Muntasheri et al. 2006,2008; Liu, and Seright 2000; Huang, and Cai 2001) and Nuclear Magnetic Resonance (NMR) spectroscopy (Romero-ZerØn et al. 2008; Fong and Kowalski 1993).

In this research, we would like to explore the use of differential scanning calorimetry (DSC) in studying the gelation kinetics of PAM/PEI system which is quite uncommon. DSC was widely used before in studying crystallization kinetics (Wang and Zhang 2013; Dou and Shi 2013; Hussein 2008). The main reason for extending the use of DSC to study the gelation kinetics is the similarity of the two processes. If we look into the crystallization and gelation

phenomena, one can realize that in both cases heat is released as a result of cooling and heating, respectively. In crystallization, heat is released due to the formation of solid crystals when a liquid is cooled. In gelation, heat is released due to cross-linking reactions and 3-dimensional (3-D) gels are formed when solutions are heated. Therefore, due to the similarity of the physics of the gelation and crystallization processes, we proposed to study the gelation kinetics using the same earlier techniques used in studying crystallization kinetics. The DSC could be an effective tool in studying the gelation kinetics which would help in understanding the gelation mechanism as well as investigating the influence of different parameters and conditions. Hence, the objective of this work is to study the gelation process and its kinetics using DSC. Moreover, the influence of different parameters such as gelation temperature, water salinity, and impact of some salts on the gelation time was studied. Further, two different approaches were used to model the gelation kinetics and kinetic parameters were extracted and related to gel composition and gelation conditions.

Gelation Kinetics

Classical reaction rate equations were used previously to analyze the isothermal regime of polyacrylamide hydrogels (Singhal et al. 2002). All samples were kept at the specified temperature for a time after which no heat change was observed in the DSC curves. The total heat released in the isothermal part was used as a basis to calculate the fractional gelation at time t . The fractional conversion, x , was defined as the ratio of the heat released up to time t to the total heat released during the whole gelation process. Hence, isothermal scans can be analyzed with a reaction rate equation in the form:

$$\frac{dx}{dt} = k(T) (1 - x)^n \quad (1)$$

where $\frac{dx}{dt}$ is the rate of conversion, x is the fractional conversion, $k(T)$ is the specific rate constant at absolute temperature T (K), and n is the reaction order. The rate constant can be related to temperature through Arrhenius equation as follows:

$$k(T) = k_o e^{-E/RT} \quad (2)$$

where E is the Activation energy (J mol⁻¹), k_o is the Arrhenius frequency factor (min⁻¹), and R is the gas constant (8.314 J mol⁻¹ K⁻¹). By substituting equation 2 in 1 and taking the logarithms of both sides yields the following rate model:

$$\ln\left(\frac{dx}{dt}\right) = \ln k_o - \frac{E}{RT} + n \ln(1 - x) \quad (3)$$

To study the gelation kinetics in the isothermal regime, the conversion x at different times was calculated. The fractional gelation was obtained as the ratio of the area under the curve up to time t to the total area. Each isothermal gelation kinetics test was performed at a constant temperature and the test was repeated at different temperatures. Equation (3) was fitted by the linear least squares method using Mathematica software to obtain the values of n , k_o , and E .

On the other hand, we proposed to use the well-known models used in studying crystallization kinetics due to the similarity of both processes as stated earlier. One of the common methods for studying the crystallization kinetics is the Avrami equation which is given elsewhere (Hussein 2008). This equation can be used in the linear form as follows (Hargis and Grady 2006):

$$\ln[-\ln[1 - x_t]] = \ln k_t + mlnt \quad (4)$$

where x_t is the fractional gelation, m is an exponent related to the order, t is the time during gelation, and k_t is the rate constant. A plot of $\ln[-\ln[1 - x_t]]$ versus $\ln t$ gives a straight line with a slope of m and intercept of $\ln k_t$. Hence, the cross-linking rate constant k_t , and the exponent m can be determined. In the non-isothermal part, the total heat released was found by integrating the area under the whole gelation curve and used for calculating the fractional gelation x_t . The fraction gelation x_t was obtained as the ratio of heat released up to time t to total heat.

Earlier, rheology was widely used in studying gelation kinetics [Al-Muntasheri et al. 2007; El-karsani et al. submitted for publication]. In another publication, DSC was coupled with different techniques to characterize PAM hydrogels (Alves et al. 2011) and the authors are aware of only one study that used DSC to study gelation using the above rate model (equation 3) to analyze the gelation process (Singhal et al. 2002). Here, we used the same rate model and we proposed, for the first time, another model (equation 4) to study the gelation kinetics.

5.2 Materials and sample preparation

Two polymer solutions were used in this study. PAM was used as an aqueous solution obtained from SNF Floerger. It has a 20 wt% activity, about 250,000 to 500,000 g gmol^{-1} molecular mass and a pH of ~ 4.0 . PEI is also provided as a solution with a pH of about 11.7, a molecular mass of 70,000 g gmol^{-1} , and activity of 30 wt%. These polymer solutions were used without further treatments. The samples were prepared by adding a predetermined amount of PAM to water (either distilled or sea water) while stirring for about 2 minutes. Then the required amount of cross-linker (PEI) was added in drops while continuous stirring was performed for an extra 10 minutes to obtain a homogenous polymer solution. This mixture is referred to as gelant.

5.3 Differential Scanning Calorimetry (DSC)

All measurements were carried out in a TA Q1000 instrument. This machine is equipped with a refrigerating cooling system (RCS) in which nitrogen is used to purge the instrument at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The gelant was poured in aluminum hermetic pan and sealed with a lid in a compression tool. An empty aluminum hermetic pan was used as a reference. All samples were equilibrated at 30°C for 5 minutes, and then ramped at $1.5^\circ\text{C min}^{-1}$ to a specific final temperature of 80° , 100° , and 120°C . The sealed pan was weighed after the experiment and in all cases the same original mass was obtained. This confirms that the pan is well sealed and no water has escaped. As reported by the manufacturer these pans can operate up to 140°C without any leak. After that the final temperature was kept constant for about 2 hours to complete the gelation process. The heating rate was chosen to mimic the field application. It was reported that typical gelant placement needs 55 minutes to reach the target zone (Al-Muntasheri et al. 2010). In the field, the temperature increases from 40°C at the surface to about 120°C at the wellbore and the injection time was about 55 minutes in a typical injection. Therefore, to simulate this injection process and achieve the same injection time assuming linear increase in temperature the gelant was heated at $\sim 1.5^\circ\text{C min}^{-1}$ ($80^\circ\text{C}/55 \text{ min}$). The DSC was calibrated at the same heating rate. Another advantage for using this low heating rate is the low thermal lag.

5.4 Results and Discussion

The gelation kinetics of PAM/PEI system was studied by heating the samples from 40°C at a rate of $1.5^\circ\text{C min}^{-1}$ to a final temperature of 80° , 100° , or 120°C . A DSC scan of a gelant containing PAM/PEI at a mass ratio of 9/1 is shown in **Fig. 5.1** below. The gelant was heated to 120°C , and then kept at this temperature until no thermal change was noticed to ensure complete gelation. Initially, the DSC curve in **Fig. 5.1a&b** shows a strong endotherm which ends at a temperature

of ~ 60°C followed by an exotherm. This suggests that multiple reactions are taking place during the heating of PAM/PEI system including both endothermic and exothermic processes. The pH of PEI is ~ 11.7 which make the gelant alkaline solution. The endothermic reaction is a result of the well-known hydrolysis of PAM under alkaline conditions. In the hydrolysis of PAM, PAM amide groups are converted to carboxylates [Kurenkov et al. 2001; Caulfield et al. 2002] (**Fig. 5.2**).

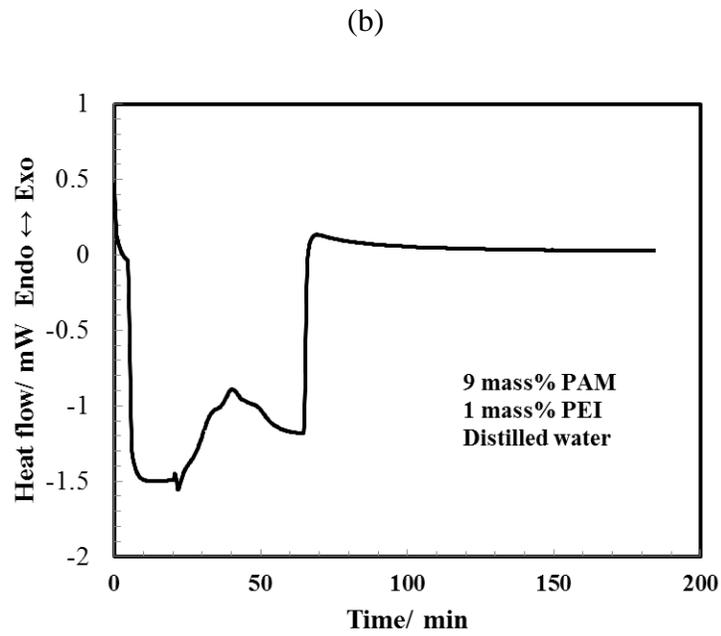
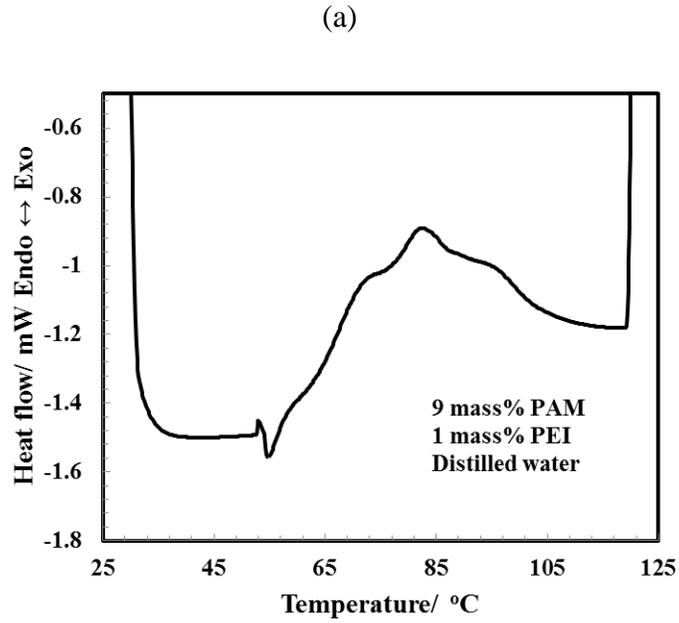


Figure 5. 1: Dynamic DSC scan of PAM/PEI system (9/1) mass ratio and final heating temperature of 120°C (a) Heat flow vs. temperature, (b) Heat flow vs. time

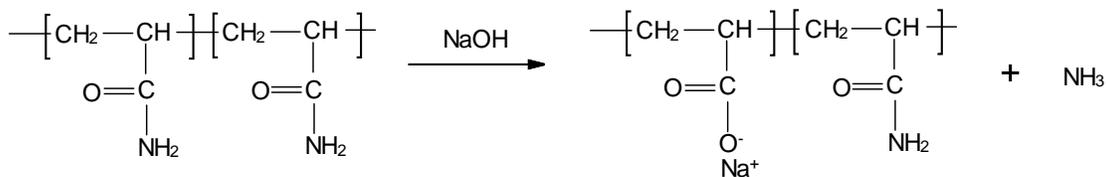


Figure 5. 2: Alkaline hydrolysis of PAM groups (Al-Muntasheri et al. 2007; El-karsani et al, submitted for publication)

In order to confirm this endothermic peak, the pH of PAM only was adjusted to 10 by adding few drops of NaOH (1M). The sample was equilibrated at 30°C, and then the temperature was suddenly increased to 120°C. The curve in **Fig. 5.3** showed only endothermic peak which starts immediately with the sample ramping and it ends at around 70°C.

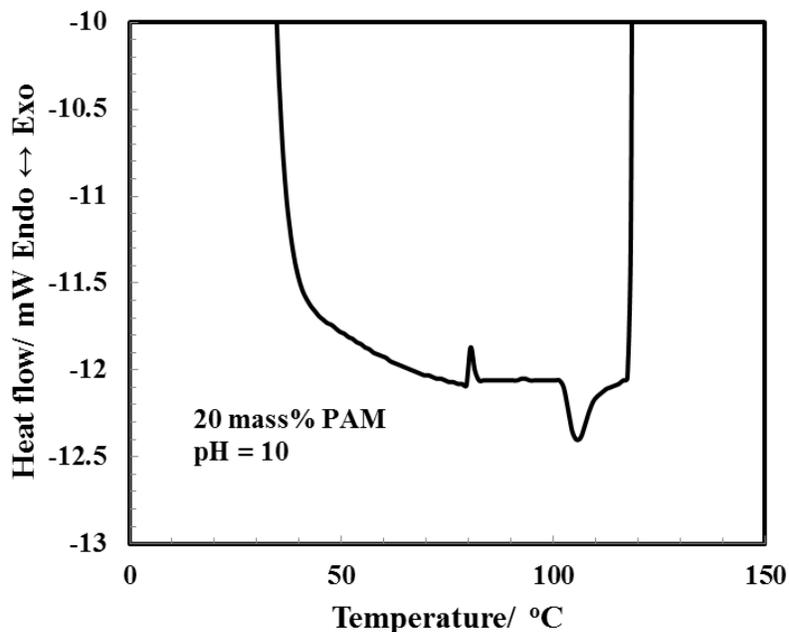


Figure 5. 3: Dynamic DSC scan of PAM up to 120°C (20 mass % activity)

The program of studying the kinetics of cross-linking of PAM with PEI was composed of non-isothermal and isothermal parts to mimic the actual injection process when the system is applied in oilfields for water control. Therefore, each regime was analyzed separately. A sample containing 9 mass % of PAM, 1 mass % PEI was prepared in distilled as well as in sea water and subjected to the above thermal program up to 80°, 100°, 120°C. The experimental data showed a good fit to the above model (equation 3) as shown in **Fig. 5.4**. The total heat released in the isothermal part was used as a basis for analysis (equation 3).

For the rate model, the values of n , k_0 , and E were found to be 0.5, $0.062 \times 10^{-4} \text{ min}^{-1}$, and 3.1 kJ mol^{-1} . The value of the rate constant k was $0.023 \times 10^{-4} \text{ min}^{-1}$. This indicates that the gelation process is slow. The sample prepared in sea water gives almost the same value of n . However, E and k_0 increased to 4.7 kJmol^{-1} and $0.065 \times 10^{-4} \text{ min}^{-1}$, respectively. The rate constant, k , decreased from $0.023 \times 10^{-4} \text{ min}^{-1}$ in distilled water to $0.067 \times 10^{-4} \text{ min}^{-1}$ in sea water which represents about 60% drop. The increase in E is likely due to the high salinity of sea water (57 g lit^{-1}) where the reaction is retarded by the presence of salts. Hence, more energy is needed to achieve the same conversion. The same data for distilled water was analyzed by Avrami method presented in equation 4.

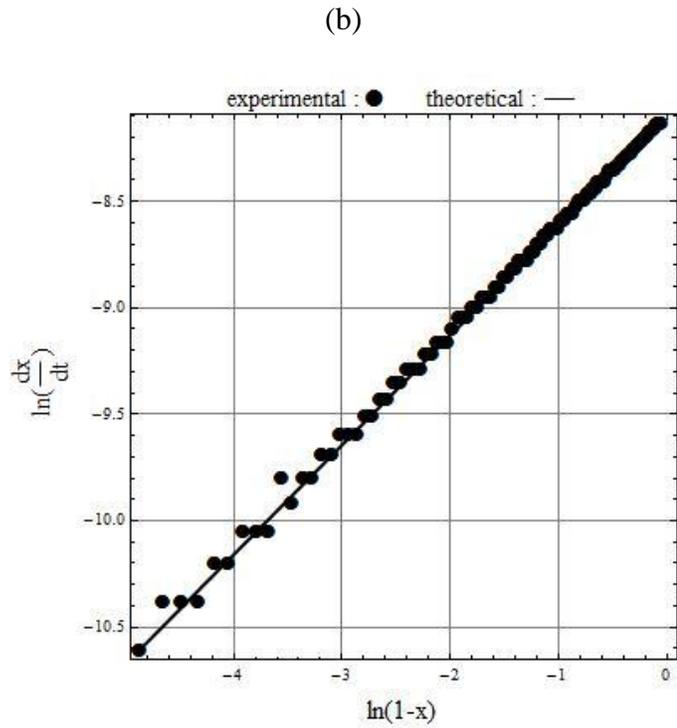
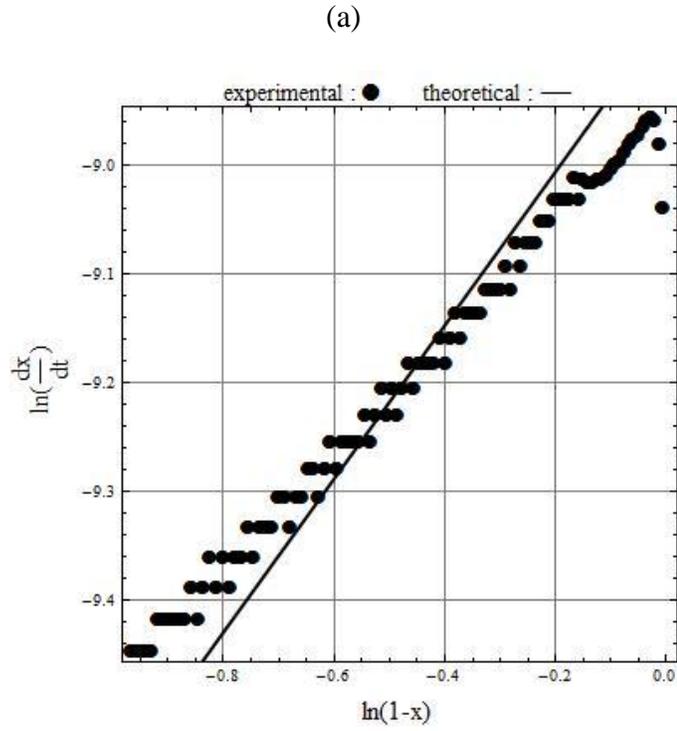


Figure 5. 4: Experimental data versus predicted data (Rate model) for PAM/PEI (9/1) mass ratio and heating temperature up to 120°C in (a) distilled water, (b) sea water

For Avrami model, the values of m and k_t were calculated for distilled water as 1.2 and $0.0183 \cdot 10^{-4} \text{ min}^{-1}$, respectively. The analysis of PAM/PEI in sea water resulted in a value of $0.003 \cdot 10^{-4} \text{ min}^{-1}$ for k , whereas, the value of m was 1.4. It should be noted that in the rate model the value of n is related to the order of the reaction while m in Avrami model is related to the nucleation (here gelation) mechanism and growth dimensions. However, the values of k and k_t in the two models relate to the rate of the gelation process. Therefore, we do not expect exact match in the two values of n and m and k and k_t obtained from the two different models. Irrespective of the model used, the two models agree that the values of n obtained from the rate model or m from Avrami model are almost the same in distilled and sea water. However, the rate parameters (k and k_t) dropped by 60-80% as a result of the presence of salts. Therefore, both models agree that salts retard the gelation process. These results show how this well-known fact in the field can be revealed by a simple DSC test.

Furthermore, the retardation of gelation in sea water was analyzed once more by considering the whole gelation process using equation 5. This was achieved by integrating the area under the curve that corresponds to the gelation in both isothermal and non-isothermal regimes. The fractional gelation was calculated by the following equation:

$$x_t = \frac{\text{Total heat released up to time } t}{\text{Total heat released for the isothermal and nonsothermal regime}} \quad (5)$$

The results in **Fig. 5.5** show that x_t is higher when distilled water is used instead of sea water. This is another confirmation for the retardation effect of sea water. For example 10% of gelation was achieved after ~ 20 minutes in distilled water. In the case of sea water, this time increased to ~ 50 minutes. At higher conversions, this observation is still valid. The time needed

to complete 90% of the gelation was ~ 114, and 167 minutes for distilled and sea water, respectively.

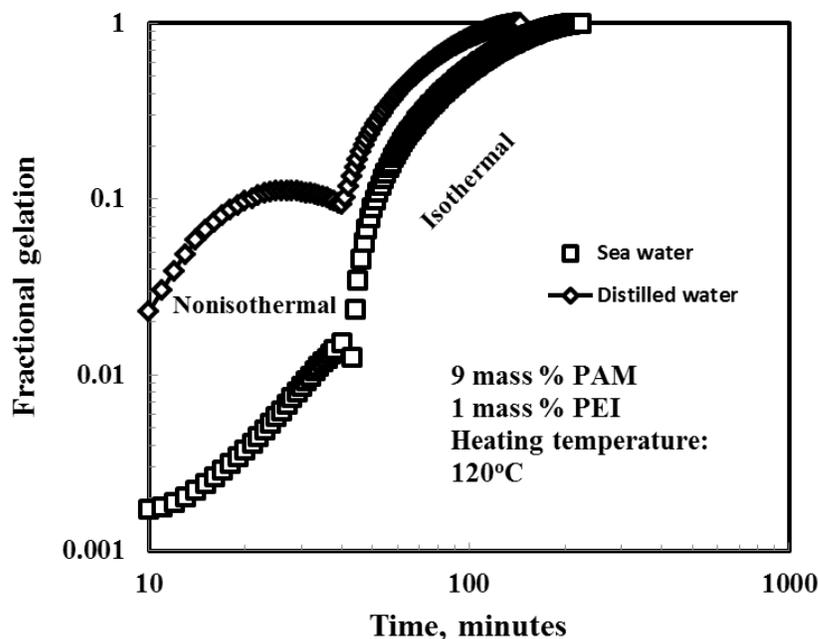


Figure 5. 5: Fractional conversion as a function of time for the gelation of PAM/PEI (9/1 mass ratio) at different salinities

The effect of salts on the isothermal gelation kinetics was examined by adding NaCl and NH₄Cl. These salts are used in the oilfield industry to retard the gelation. Two samples of gelants with a formulation of PAM/PEI of (9/1) mass ratio were prepared in distilled water by adding 1.2 g lit⁻¹ of the two salts and the previous thermal program was applied up to 120°C. Equation 1 was used to analyze the isothermal gelation data. The value of *n* was observed to be almost the same in NaCl (0.51) and in NH₄Cl (0.50). The rate constant, *k*, decreased from 0.0195*10⁻⁴ in the case of NaCl to 0.002*10⁻⁴ min⁻¹ in NH₄Cl (~ 90% drop). Therefore, NH₄Cl is a very efficient retarder for the gelation of PAM/PEI in comparison with NaCl. These findings are in agreement with

previous results obtained from rheological measurements (Al-Muntasheri et al. 2007). The retardation of gelation due to the presence of salts was also examined by considering both the isothermal and non-isothermal data. 1.2 g lit⁻¹ (0.021 moles) of NaCl and 1.2 g lit⁻¹ (0.022 moles) of NH₄Cl were used. **Fig. 5.6** shows the influence of NaCl and NH₄Cl on the gelation process. Salt-free water showed higher values of fractional gelation at any time which is retarded by the presence of NaCl and NH₄Cl. At all times, NH₄Cl showed stronger retardation effect in comparison with NaCl. Therefore, the different models and methods of data analysis confirm the retardation of gelation due to the presence of salts.

To investigate the effect of temperature on the gelation kinetics two samples of PAM/PEI (9/1 mass ratio) were prepared in distilled water and subjected to the same thermal

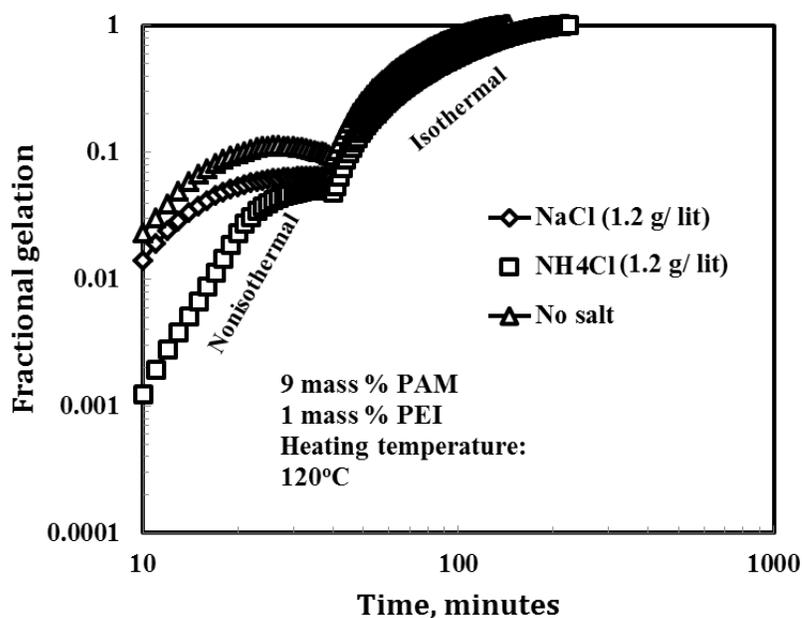


Figure 5. 6: Effect of salts (1.2 g/L) on fractional gelation of PAM/PEI (9/1 mass ratio) for a final temperature of 120°C

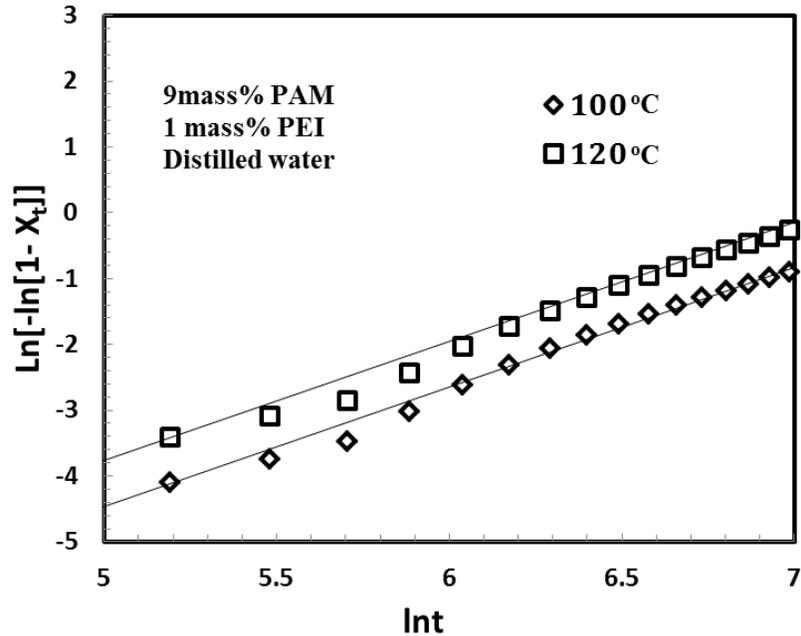


Figure 5. 7: Avrami plots for PAM/PEI at different temperatures for the non-isothermal regime

program. Two different final temperatures of 100° and 120°C were used. The results of Avrami analysis for the non-isothermal regime are shown in Fig. 5.7. The gelation rate constants were found to be $0.015 \cdot 10^{-6}$ and $0.001 \cdot 10^{-6} \text{ min}^{-1}$ at 120° and 100°C, respectively. This illustrates that the rate of gelation in distilled water at 120°C is almost 15 times faster than the rate at 100°C.

5.5 Conclusions

The gelation kinetics of PAM with PEI was studied by the use of DSC. The gelation kinetics was analyzed using well-known crystallization kinetics models. The summary of this study is:

- (1) The DSC is an effective tool for studying the cross-linking (gelation) kinetics of PAM with PEI gel system used for water shutoff in petroleum reservoirs.

- (2) The DSC curves revealed that the cross-linking of PAM/PEI gel system is associated with endothermic as well as exothermic processes. The endotherm was characterized to be due to the hydrolysis of PAM which is endothermic in nature, whereas, the exotherm is a result of the gelation reaction.
- (3) The rate of PAM/PEI gelation in distilled water at 120°C is almost 15 times faster than the rate at 100°C.
- (4) Irrespective of the model used, the two models agree that the value of n is almost the same in distilled and sea water.
- (5) Sea water and salts were found to elongate the gelation time by shifting the onset of cross-linking. However, the reaction rates are lowered by adding salts.
- (6) NH_4Cl is a stronger than NaCl in the retardation of the gelation process.
- (7) The presence of salts in sea water leads to a drop of 60-80% in the rate constant without influencing the order of the gelation reaction.
- (8) The DSC proved to be a promising technique for studying the gelation reactions.

Acknowledgements

The authors would like to thank King Abdul-Aziz City for Science and Technology (KACST) for supporting this research through project # AR-30-291. King Fahd University of Petroleum and Minerals (KFUPM) and Saudi Aramco are also acknowledged for their support. Thanks also to Dr. Housam Binous for his help with Mathematica software.

5.6 References

Baily, B., Crabtree, M., and Tyrie, J. Water Control. *Oilfield Review*. 2000. **12** (1): 30-51.

Hibbeler, J. and Rae, P. The Environmental Benefits of Reducing Water Production. Paper SPE 96582 presented at the SPE Asia Pacific Health, Safety, and Environment Conference and Exhibition, Kuala Lumpur. 2005, 19-20 September. DOI: <http://dx.doi.org/10.2118/96582-MS>.

Alqam, M.H., Nasr-El-Din, H.A. and Lynn, J.D. Treatment of super K-Zones Using Gelling Polymers. Paper SPE 64989 presented at the International Symposium on Oilfield Chemistry, Houston. 2001, 13-16 February.

Vasquez, J., Civan, F., Shaw, T.M., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Brown, D. Laboratory Evaluation of High-Temperature Conformance Polymer Systems. Paper SPE 80904 presented at the SPE Production and Operations Symposium, Oklahoma City. 2003, 22-25 March. DOI: <http://dx.doi.org/10.2118/80904-MS>.

Zaitoun, A. and Kohler, N. 1. Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. Paper SPE 18085 presented at the SPE Annual Technical Conference and Exhibition, Houston, 2-5 October 1988. DOI: <http://dx.doi.org/10.2118/18085-MS>

Liang, J.T., Sun, H. and Seright, R.S. Why Do Gels Reduce Water Permeability More Than Oil Permeability? *SPE Res Eng J* . 1995; 10 (4): 282-6.

Chang, K.T., Frampton, H., and Morgan, J.C. Composition and Method for Recovering Hydrocarbon Fluids from A Subterranean Reservoir. 2002. US Patent No. 6,454,003.

Lei, G., Li, L., and Nasr-El-Din, H.A. New Gel Aggregates To Improve Sweep Efficiency During Waterflooding. SPE Res Eng J. 2011; 14(1): 120-8.

Sydansk, R.D. A Newly Developed Chromium (III) Gel Technology. SPE Res Eng J. 1990; 5 (3): 346-52.

Lockhart, T.P. Chemical Properties of Chromium/Polyacrylamide Gels. SPE Advanced Technology Series. 1994. 2 (2): 199-205. SPE-20998-PA.

Morgan, J.C., Smith, P.L., and Stevens, D.G. Chemical Adaptation and Deployment Strategies for Water and Gas Shut-off Gel Systems. Paper presented at the 1997 Royal Chemistry Society's Chemistry in the Oil Industry International Symposium, Ambleside. 1997, April 14-17.

Moradi-Araghi, A. A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production. Journal of Petroleum Sci and Eng. 2000. 26 (1-4): 1-10.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha, P.L.J. Gelation Kinetics and Performance Evaluation of an Organically Crosslinked Gel at High Temperature and Pressure. SPE J. 2008. 13 (3): 337-45. DOI: <http://dx.doi.org/10.2118/104071-PA>.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha, P.L.J. Investigation of a High Temperature Organic Water-Shutoff Gel: Reaction Mechanisms. SPE J. 2006. 11 (4): 497-504. DOI: <http://dx.doi.org/10.2118/97530-PA>.

Liu, J., Seright, R.S. Rheology of Gels Used For Conformance Control. Paper SPE 59318 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April, 2000. <http://dx.doi.org/10.2118/59318-MS>.

Huang, R., Cai, W. Study on gelation of partially hydrolyzed polyacrylamide with titanium (IV). *European Polym J.* 2001;(37):1553-9.

Romero-ZerØn, L., Manalo, F., and Kantzas. Characterization of Cross-linked Gel Kinetics and Gel Strength by Use of NMR. *SPE Res Eval & Eng J.* 2008; 11(3): 439-53. <http://dx.doi.org/10.2118/86548-PA>.

Fong, D.W, Kowalski, D. An Investigation of the cross-linking of polyacrylamide with Formaldehyde Using ¹³C Nuclear Magnetic Resonance Spectroscopy. *J Polym Sci. Part A: Polym. Chem.* 1993; 31, 1625-7.

Wang, S., and Zhang, J. Non-isothermal crystallization kinetics of high density polyethylene / titanium dioxide composites via melt blending. *J Therm Anal Calorim.* Published online 8 June 2013.

Dou, Q., and Shi, Y.H. Non-isothermal crystallization kinetics of β -nucleated isotactic polypropylene. *J Therm Anal Calorim.* 2013; (112): 901-11.

Hussein, I.A. Nonisothermal Crystallization Kinetics of Linear Metallocene Polyethylenes. *J of Applied Polym Sci.* 2008; Vol (107): 2802-9.

Singhal, R., Sachan, S., and Rai, J.S.P. Study of Cure Kinetics of Polyacrylamide Hydrogels by Differential Scanning Calorimetry. *Iranian Polymer J.* 2002; (3):143-9.

Hargis, M.J., Grady, B.P. Effect of sample size on isothermal crystallization measurements performed in a differential scanning calorimeter: A method to determine Avrami parameters without sample thickness effects. *Thermochimica Acta*. 2006; 443, 147-58.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Hussein, I.A. A rheological investigation of a high temperature organic gel used for water shut-off treatments. *J of Pet Sci & Eng*. 2007; 59: 73-83.

El-karsani, K.S.M., Al-Muntasheri, G.A., Sultan, A.S., and Hussein, I.A. Gelation of a Water shut-off Gel at High Pressure and High Temperature: Rheological Investigation. Submitted for publication. SPEJ.

Alves, T.V.G., Tavares, E.J.M., Aouada, F.A., Oliveira, M.E.C., Negrão, C.A.B., and Ferreira da Costa, C.E. Thermal analysis characterization of PAAm-co-MC hydrogels. 2011; *J Therm Anal Calorim*, (106): 717-24.

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 2010, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Kurenkov, V.F., Hartan, H.G., and Lobanov, F.I. Alkaline Hydrolysis of PAM. *Reviws. Russian J of Applied Chemistry*. 2001; 74(4), 543-54.

Caulfield, M.J., Qiao, G.G., and Solomon D.H. Some Aspects of the Properties and Degradation of Polyacrylamides. American Chemical Society. *Chem Rev*. 2002, 102, 3067-83. DOI: <http://pubs.acs.org/doi/pdf/10.1021/cr010439p>.

CHAPTER SIX

Evaluation of PAM / PEI Gel System for Water Shut-Off at High Temperature and Pressure: Laboratory Study

Khalid S.M. El-Karsani¹, Ghaiathan A. Al-Muntasheri^{2}, Abdullah S. Sultan³ & Ibbelwaleed A. Hussein⁴*

^{1&4}Chemical Engineering Department, King Fahd University of Petroleum & Minerals; Dhahran 31261, PO BOX 5050, Saudi Arabia

²Production Technology Team, EXPEC Advanced Research Center, Dhahran 31311, Saudi Aramco, Saudi Arabia

³Petroleum Engineering Department, and Center for Petroleum & Minerals (CPM), King Fahd University of Petroleum & Minerals; Dhahran 31261, Saudi Arabia

Abstract

A polymer gel is one of the common remediate methods to either reduce or totally block excessive water production in oilfields. Some systems demonstrated an excellent performance in treating the problem like polyacrylamide tert-butyl acrylate (PAtBA) / polyethylenimine (PEI). But this system showed some compatibility concerns with high salinity reservoirs in addition to its high cost in comparison with polyacrylamide (PAM) homopolymers. Hence, PAM was used as an alternative to PAtBA. Dynamic rheology as well as core-flooding experiments were used to evaluate PAM / PEI gel system at high temperatures. The injectivity of the PAM/PEI in high temperature formations required the use of a retarder to elongate the gelation time of the subject gel in order to achieve a successful placement. NaCl and NH₄Cl were evaluated for gelation time delay at different concentrations. Dynamic oscillatory measurements were conducted by using these retarders to find an accepted gelation time with a higher strength. NH₄Cl was found to be a good candidate for application to be used with PAM/PEI system for its effectiveness in

elongating the gelation time. Core-flooding tests were conducted in sandstone and carbonate cores. The subject polymer gel was injected at low rates similar to those in the field. The injectivity of PAM/PEI was tested in Berea sandstone cores with initial permeability of ~ 45 mD. The post treatment of the system showed a permeability reduction of ~ 94%. The injectivity in low permeability (~6.5 mD) (tight) carbonate cores required more retardation compared to the injectivity in sandstone cores. NH_4Cl concentration was increased from 6,000 to 36,000 mg/L in the gel recipe formulation implemented in Indiana limestone (carbonate) cores. The gel reduced the permeability to brine in Indiana limestone core by a percentage of 99.8%.

6.1 Introduction

The excessive water production is a serious issue facing the petroleum industry. This occurs during the lifetime of oil/ and or gas wells, especially when they get matured. Different technical, economical, and environmental problems are associated with the increase in water production (Bailey et al., 2000). The water produced may cause corrosion and scale in the operation tools. In addition, this water needs to be lifted, separated from oil, and re-injected which require special plants which will add more costs. Consequently, excessive water production reduces profitability. Some environmental concerns exist if the produced water is disposed by a large amount without treatment. This is because this water may contain toxic elements such as mercury and arsenic (Hibbeler and Rae, 2005). Eventually, early end of the economic life of the well may take place if the problem is not treated.

Different mechanical and chemical methods were used in the oilfield to deal with the unwanted water production. The use of polymer gels was considered as one of the remediated chemical techniques to overcome the problem. The application of polymer gels for water control is referred to as conformance improvement treatments (CITs) (Sydansk 1990). The technology of

polymer gels is based on a low viscous flowable mixture of a polymer and a cross-linker referred to as gelant (Seright 1996). Both, the polymer and the cross-linker are water soluble. The gelant is prepared on the surface and then injected into the target zone needs to be treated. Then, with time and temperature the gelant is converted to 3-dimensional (3-D) network structure via a cross-linking reaction between the polymer chains. Polymer gels are categorized into two main groups; inorganic and organic, depending on the nature of the cross-linker. In inorganic gels, a metal ion is used to cross-link the polymer through a bonding believed to be coordination covalent bond. The most common element is the trivalent chromium ion (Cr^{+3}). An example of inorganic cross-linked gels is the partially hydrolyzed polyacrylamide (PHPA)/ Cr^{+3} (Seright 1999). On the other hand, organically cross-linked gels are based on a polyacrylamide-based polymer and an organic cross-linker such as polyacrylamide tert-butyl acrylate (PAtBA)/polyethylenimine (PEI) gel system (Morgan et al., 1997; Hardy et al., 1998; Urlwin-Smith 1998, 2001; Van Eijden et al., 2004, 2005; Vasquez et al., 2005; Eoff et al, 2007; Dalrymple et al., 2008; Deolarte et al., 2009, Al-Muntasheri et al., 2010; Reddy et al., 2012). A detailed review of the chemistry and field applications of PAtBA/PEI gel system can be found elsewhere (El-karsani et al., 2013).

The application of chromium cross-linked gels was limited to low temperature reservoirs. This is due to their low gelation times at high temperatures. Moreover, different technical concerns were associated with chromium cross-linked gels such thermal stability, propagation into the target zone as well as toxicity (Hardy et al., 1998).

The widely used organically cross-linked gel is PAtBA/PEI. It was applied in different parts around the globe. Although it exhibited high performance for water control at high temperatures but it showed some compatibility problems with some field mixing water when a

retarder is used for delaying gelation time (Al-Muntasheri et al., 2010). At the same time, recent research indicated that low cost homo polymers of PAM can be used instead of PAtBA to form polymeric gels (Al-Muntasheri et al. 2008). PAM/PEI showed a permeability reduction of 100% using Berea sandstone cores at 90°C for one month. But some reservoirs have a temperature higher than 90°C. Hence, evaluation of PAM/PEI gel system at higher temperatures is needed to recommend the system for higher temperature applications. Hence, the objectives of this study are to optimize a formulation of PAM/PEI with a compatible retarder to delay the gelation time. Retarders such as NaCl and NH₄Cl were studied through dynamic rheology measurements. Then core-flood experiments were used at high temperatures (150°C) to evaluate the long term water shutoff effectiveness of the system.

6.2 Experimental Studies

6.2.1 Materials

Two polymer solutions were used in this study. Polyacrylamide (PAM) was provided by SNF Floriger as an aqueous solution and used without further treatment. PAM solution was 20 wt% active and has a molecular weight within the range 250 to 500 kg/mol (as disclosed by the supplier). Polyethylenimine (PEI) was used as a cross-linker in a solution form. Its activity and molecular weight were 30wt% and 70 kg/mol, respectively. Salts used in this study include Sodium chloride (NaCl), ammonium chloride (NH₄Cl), and potassium chloride (KCl). All these salts were ACS grade.

Berea sandstone and Indiana limestone cores were used to assess the core-flooding experiments. Their properties are given in **Table 6.1**. XRD analysis revealed that Berea sandstone core contains 99 wt% Quartz and the balance is Kaolinite (1 wt%), whereas, Indiana limestone core contains 99 wt% Calcite and 0.8 wt% Coasite. The elemental analysis of the was

characterized by XRF and the results are shown in **Table 6.2**. Two Indiana limestone cores were tested to evaluate the polymer gel system in carbonate lithology.

Table 6. 1: Specifications of the cores used for polymer gel evaluation

Core Type	Diameter, cm	Length, cm	Pore Volume, cm ³	Porosity, %	Initial Permeability to Brine, mD
Berea Sandstone	3.8 (1.49 in)	7.48 (2.5 in)	13	15	44.45
Indiana limestone	3.76 (1.48)	7.67 (3.03 in)	7.5	8.9	2.98
Indiana limestone	3.59 (1.41)	7.55 (2.97 in)	11	13.89	6.5

Table 6. 2: Elemental analysis of Berea sandstone and Indiana linstone cores

Element	Content, wt%	
	Berea sandstone	Indiana limestone
Si	49.73	0.1772
Al	4.103	0.616
P	0.3871	0.7011
K	1.443	0.08895
Ti	0.379	0.00674
Fe	1.447	0.1486
Ca	1.185	57.91

6.2.2 Procedure

For the dynamic rheology measurements samples of PAM/PEI (9/1) wt% were prepared at room temperature. A specified amount of salt (retarder) was mixed with field water first, then the required amount of PAM was added while stirring for one minute, and then the cross-linker was added with 10 minutes extra stirring time. Then, the sample was loaded to the pressure cell mounted on the rheometer. All tests were done at a temperature of 116°C (240.8°F), a pressure of 500 psi (34.47 bar), a frequency of 1 Hz, and a strain of 10%. The selection of the temperature (116°C) was based on a previous reported simulation study. The down-hole temperature (150°C) of the reservoir was expected to drop by 30.1°C during the pre-flush (2 wt% KCl) injection. Hence, all rheology and injectivity of the polymer gel system will be done at 116°C. The formation brine was prepared according to the concentrations reported in **Table 6.2**. The pre-flush fluid was prepared by adding 2 wt% KCl to the field mixing water. The chemical analysis

of this water is given elsewhere (Al-Muntasheri et al. 2010). Note that the field mixing water was collected from a close field.

Table 6. 3: Chemical analysis of the formation brine

Ion	Concentration, mg/L
Na	59,300
Ca	23,400
Mg	1,510
SO ₄	110
Cl	137,000
HCO ₃	353
Total Dissolved Solids (TDS)	221,673

The effectiveness of PAM/PEI system was tested in a core-flow setup. Berea sandstone core was first saturated with formation brine given in **Table 6.1**. Nine pore volumes brine were injected to determine the initial permeability of core by using Darcy law. Then, 2 wt% KCl prepared in field mixing water was forwarded through the core to displace the formation brine (two pore volumes were injected). Six pore volumes of the gelant were injected at 1 cm³/min. All the previous steps were done at 116°C, under a back pressure and overburden pressure of 1000 and 2500 psi, respectively. To examine the polymer gel system in Indiana limestone cores, the core-flow set-up was slightly modified to simulate the real injectivity in the field. According to a recent study (Al-Muntasheri et al. 2010), the residence time for the system inside the tubing before reaching the formation was 55 minutes. A coiled tubing was added to the core-flow

system such that the dead volume to be about 9 cm^3 . This volume was heated in the tubes inside the oven before hitting the core face. Therefore, the injection rate was adjusted to $0.15 \text{ cm}^3/\text{min}$ for gelant placement. A total of 15 pore volumes were injected. This includes 6 pore volumes of formation brine at different flow rates to make a base for the core permeability to brine. Then, 3 pore volumes of a pre-flush were injected at $0.15 \text{ cm}^3/\text{min}$ to cool down the core followed by 6 pore volumes of the gelant at $0.15 \text{ cm}^3/\text{min}$ to make sure that the core is saturated by the gelant.

6.2.3 Equipment

The dynamic shear tests were assessed in a Discovery Hybrid Rheometer (DHR) provided by TA Instrument. This machine is equipped with a high pressure cell in which the gelation experiments were performed. The pressure cell has a cup and bob diameters of 28 and 26 mm, respectively. All experiments were conducted at a temperature of 116°C and a pressure of 500 psi. The pressure cell has a torque range of $100 \mu\text{N}\cdot\text{m}$ to $0.2 \text{ N}\cdot\text{m}$ and a maximum working temperature of 150°C . It should be mentioned that the viscosity of the gelant was measured by using concentric cylinder geometry at room temperature (25°C).

The core-flow experiments were assessed with a high pressure and high temperature core-flood system. Two Isco Syringe pumps were used with maximum injection pressure of 7500 psi. A Memmert oven was used with an upper temperature limit of 200°C to simulate the temperature in the reservoir. The set-up was equipped with a back pressure regulator running at 1000 psi to keep the liquid in solution as well as to prevent gases from escaping from the core. Two Transducers (5-66-Model) were used having range from zero to 5000 psi. The system was connected to a data acquisition system capable of recording data every second.

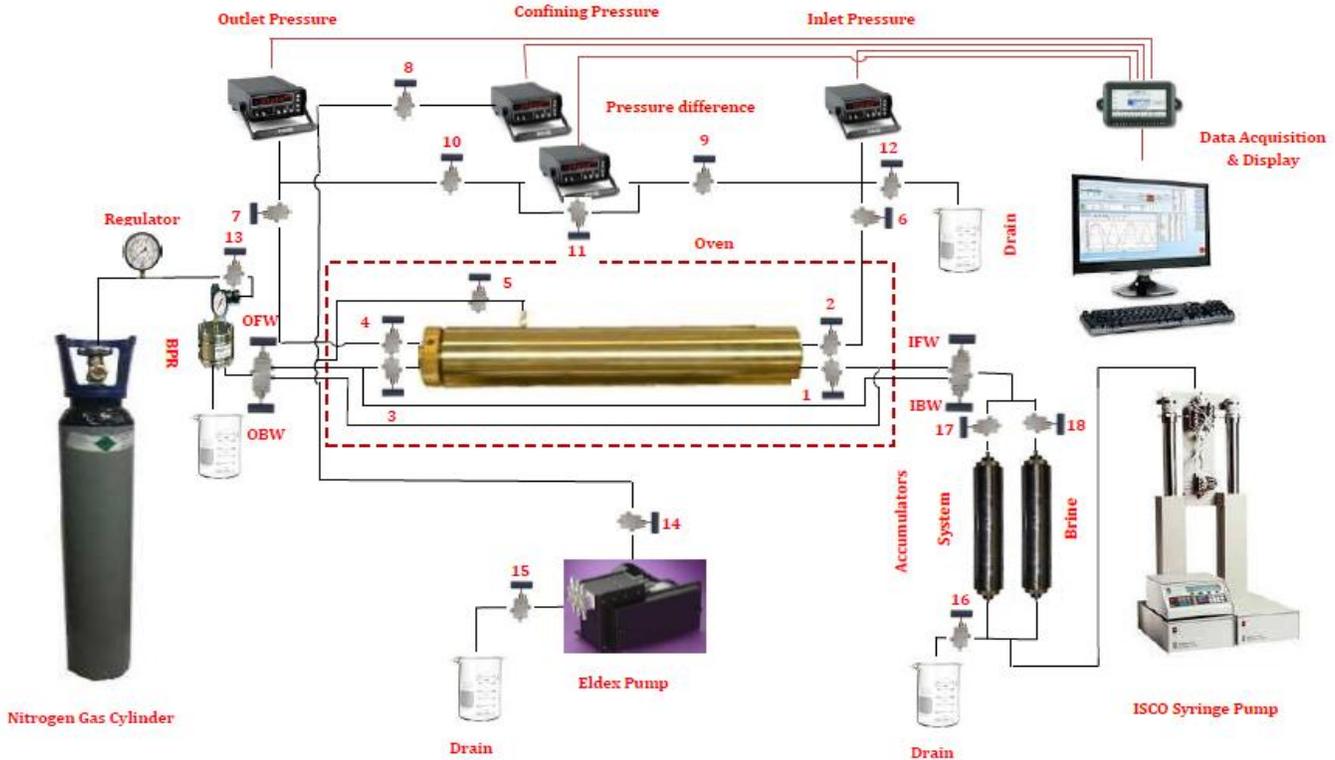


Figure 6. 1: A schematic diagram of core-flooding apparatus

6.3 Results and Discussion

6.3.1 Gelation of PAM/PEI System with Retarders

From the thermal stability test which was done through the bulk testing method, it was found that the most thermally stable formulation of the polymer gel at 150°C (302°F) is 9/1 wt% (PAM/PEI). So, it is proposed to use this formulation to examine the stability in porous media through the core-flooding setup. However, the gelation time of 9/1 wt% (PAM/PEI) at 150°C (302°F) is less than half an hour as reported in chapter three (**Figure. 3.2**). This time is not sufficiently enough for field applications to place the gelling solution safely without prior gelation before reaching the target zone. The time needed for gelling solution placement was reported to be about 55 minutes (Al-Muntasheri et al., 2010). Thus some dynamic rheological experiments were performed prior the core-flooding experiments to come up with acceptable formulation with sufficient gelation time and high strength.

Different retarders were examined at 116°C (240.8°F) to identify a formulation with a low viscosity and an acceptable gelation time. This can be accomplished by adding a suitable retarder with the optimum concentration. At the same time, the retarder concentration should not reduce much the final gel strength of the polymer gel. From the gelation study in chapter four, it was found that sodium chloride (NaCl) and ammonium chloride (NH₄Cl) can increase the gelation time depending on the concentration. However, gels prepared in presence of NH₄Cl showed lower strength compared with NaCl at the same time of testing and longer times are required to reach the same equilibrium value.. Thus, it is required to optimize the formulation taking into account the gelation time as well as the gel strength (storage modulus).

Sodium chloride and ammonium chloride were added initially at a concentration of 100 lb/ 1000 gal (12,000 mg/l). As can be seen from **Figure 6.2**, the gelation time was about 70

minutes only in the case of NaCl which was lower than the target (more than 120 minutes). When NH_4Cl was added at the same concentration, the gelation time was increased to around 295 minutes, but the plateau gel strength was very weak as the storage modulus was about 690 Pa only. It should be mentioned that after about 200 minutes, the sample with NaCl began to reach the plateau value (700 Pa), whereas, the sample with NH_4Cl exhibited only about 18 Pa. Thus, it was planned to examine either the combination of the two salts or to increase the concentration.

A sample was prepared by adding 50 lb/ 1000 gal (6,000 mg/l) from the two salts, the gelation time and the storage modulus were observed to be about 189 minutes and 910 Pa, respectively. In another tests, the concentration of NaCl was increased to 250 lb/ 1000 gal (30,000 mg/l) and the concentration of NH_4Cl was decreased to 50 lb/ 1000 gal (6,000 mg/l). The results from **Figure 6.3** show that the option of using NH_4Cl at a concentration of 50 lb/ 1000 gal (6,000 mg/l) is the optimum one since the gelation time is about 150 minutes and the storage modulus is 1017 Pa. The gelation time and the plateau storage modulus for PAM/PEI system at 116°C (240.8°F) in field water were extracted and reported in **Table 6.2**.

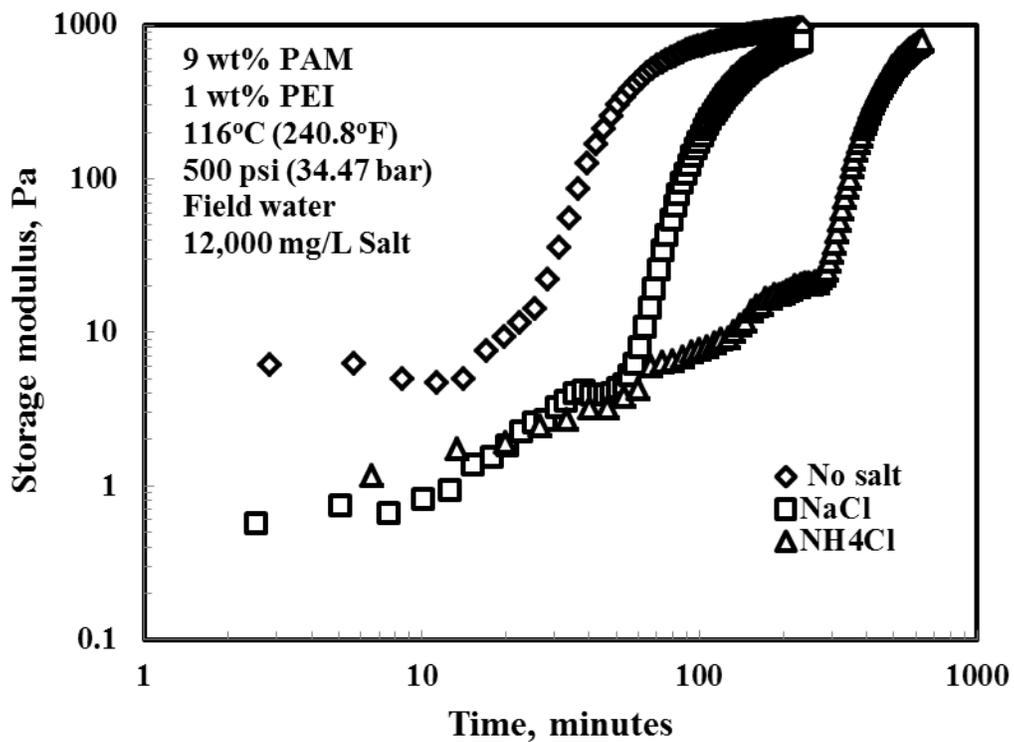


Figure 6. 2: Effect of retarders on gelation time and storage modulus of PAM/PEI (9/1) wt% gel system

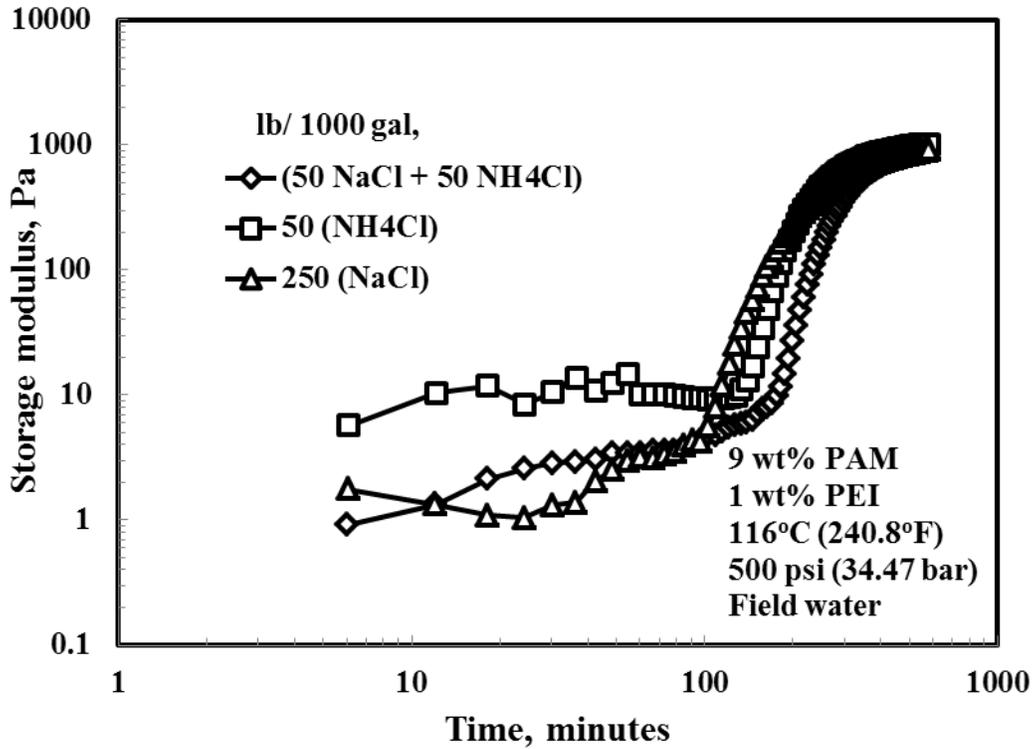


Figure 6. 3: Effect of retarders on gelation time and storage modulus of PAM/PEI (9/1) wt% gel system at different salt concentration

Table 6. 4: Storage modulus and gelation time for PAM/PEI (9/1) wt% gel system at 116°C (240.8°F) after 10 hours with different retarder concentration

Retarder, mg/l	Gelation time, minutes	Equilibrium storage modulus, Pa
NaCl (6,000) + (6,000) NH ₄ Cl	189	910
NaCl (30,000)	115	903
NH ₄ Cl (6,000)	150	1017

Based on the above results, it was decided to use NH_4Cl with 50 lb/ 1000 gal (6,000 mg/L) in the evaluation of the polymer gel for water shut-off. The viscosity of the gelling solution which contains NH_4Cl was measured by using a concentric cylinder geometry. The viscosity was found to be about 40 cP in the range from 1 to 2500 1/s as shown in **Figure 6.4**.

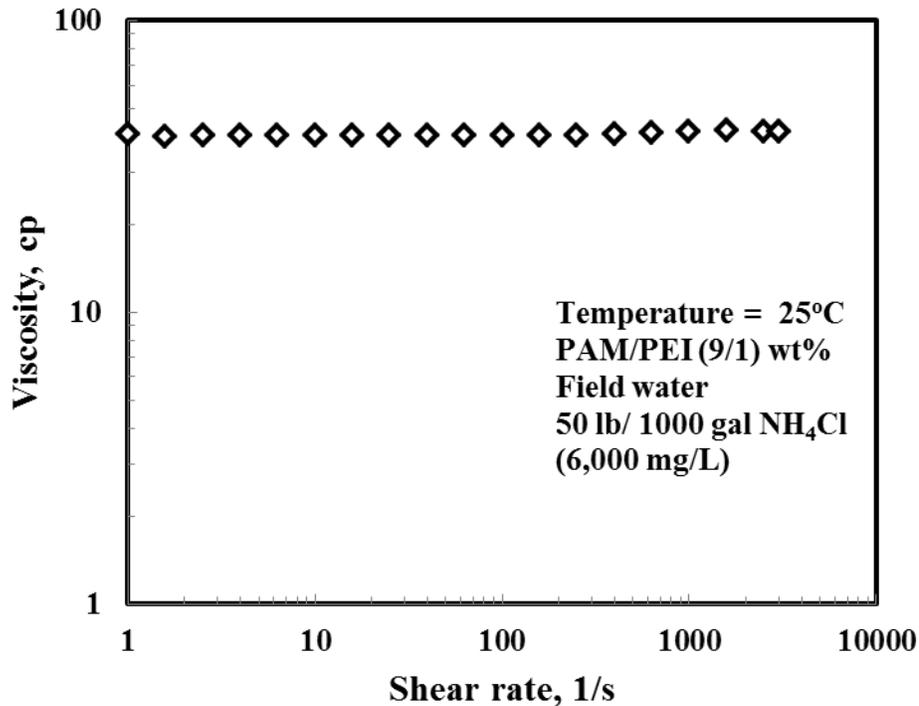


Figure 6. 4: Viscosity vs. shear rate for the 9/1 PAM/PEI gelant at 25°C

6.3.2 Efficiency of PAM/PEI System in Porous Media

Berea Sandstone Core

From the previous rheology results, 6,000 mg/l NH_4Cl was chosen to elongate the gelation time of PAM/PEI. At this salt concentration, the expected gelation time and storage modulus are ~ 2.5 hours and ~ 1017 Pa, respectively. Berea sandstone core was used to examine the injectivity of

the gelant. After saturating the core with brine, the initial permeability to brine was found to be 45.45 mD. Then, the brine was displaced by 2 wt% KCl prepared in field mixing water. After that, a gelant containing 9 wt% PAM, 1 wt% PEI, 6,000 mg/l NH₄Cl, 2 wt% KCl was injected through the core. All the previous steps were done at 116°C. A sample was collected from the core effluent in a high thermal resistant tube. This tube was put inside the oven to make sure that the gel did form inside the core. The pressure drop across the core during the injectivity of brine and gelant is shown in **Figure. 6.5**. As can be seen, the pressure drop increased during gelant placement in comparison with brine injection. This is due to the fact that gelant viscosity is higher than brine viscosity. The pressure drop versus time during gelant placement is given in **Figure. 6.6**. The placement time is about 1.36 hours after which the temperature was increased to 150°C. Then, the core was shut-in for 5 days to mature the gel in the core. The sample in the tube showed a rigid gel (**Figure. 6.7**). After the shut-in time (5 days), 2 wt% KCl was injected in the backward direction to simulate the production in the field. A constant pressure of 2050 psi was maintained in the pump. Within 2 minutes, the inlet pressure was increased from 1050 to 2000 psi. Hence, the pressure drop across the core was maintained at 1000 psi (86.95 Bars). No flow was initiated through the core. The PAM/PEI (9/1) wt% showed a high efficiency in shutting-off water in Berea sandstone cores. The reduction in permeability to brine was calculated using the following formula:

$$R_k = 100 * (1 - k_{\text{after}}/k_{\text{before}})$$

As shown in **Table 6.3**, the system reduced the permeability to brine by ~ 94%.

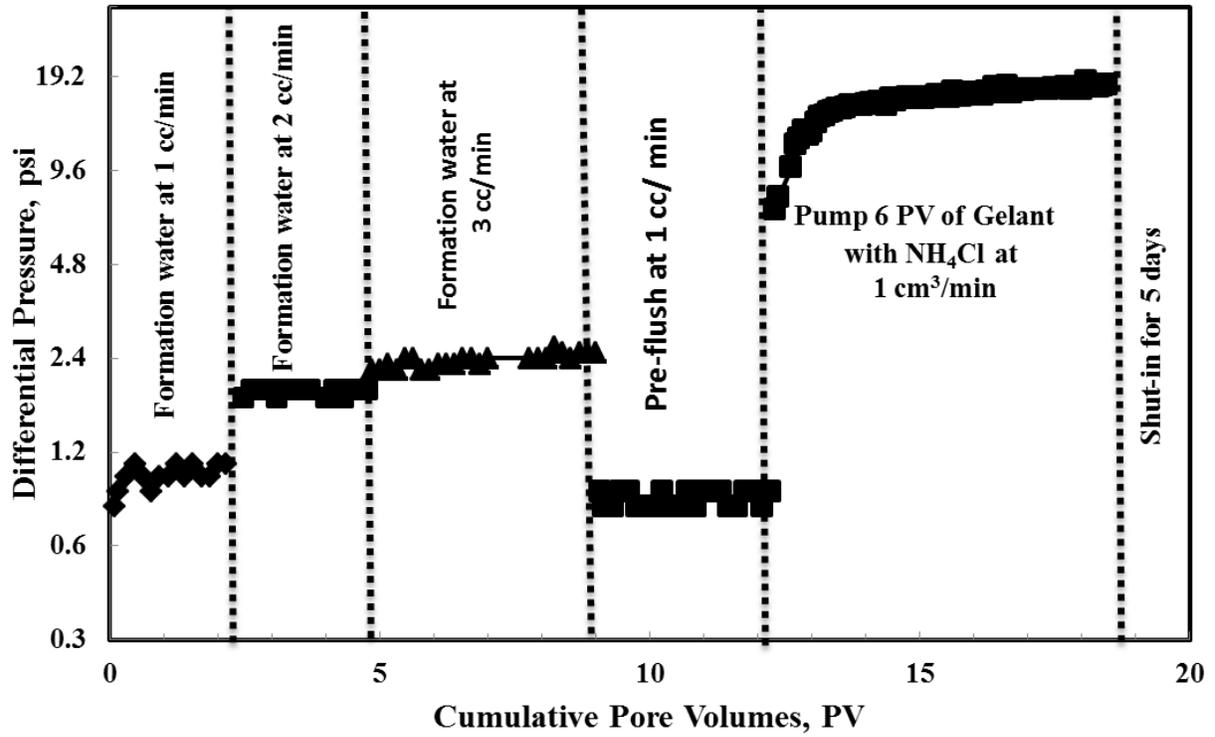


Figure 6. 5: Pressure drop as a function of pore volumes in a core-flow experiment

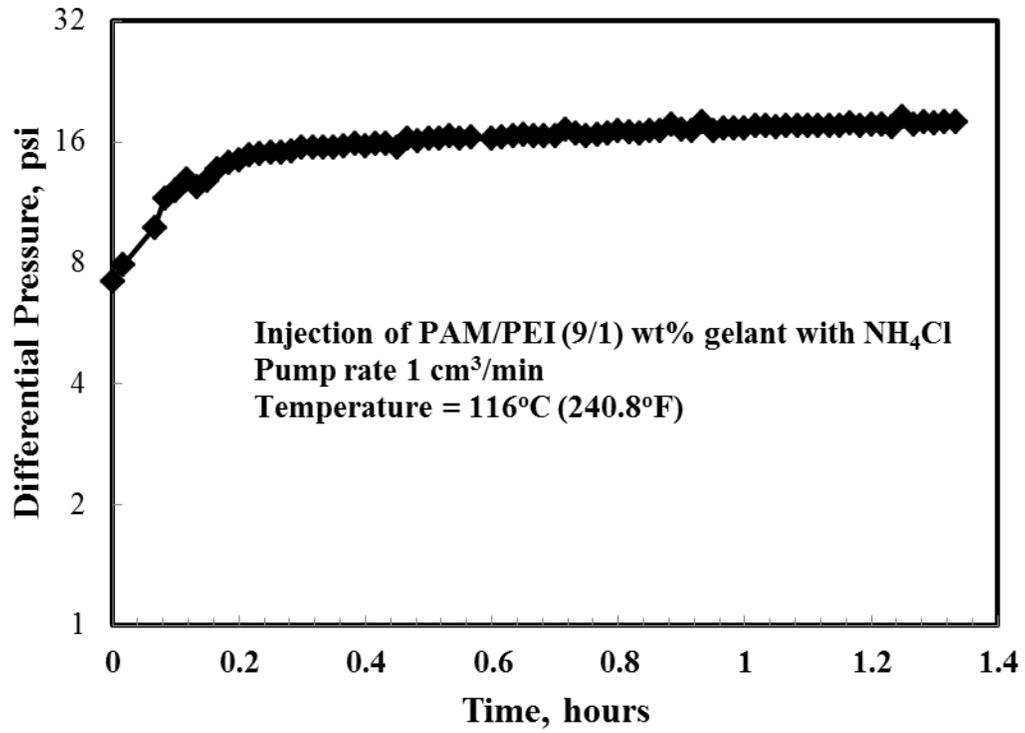


Figure 6. 6: Pressure drop as a function of time during gelant placement in Berea sandstone core



Figure 6. 7: Sample from Berea sandstone core effluents ((PAM/PEI) 9/1 wt% with 6,000 mg/l NH_4Cl) aged beside the core-holder for 5 days

Table 6. 5: Percent permeability reduction (R_k) in Berea sandstone core at 150°C (302°F)

Time, days	Permeability after treatment, mD	Permeability Reduction R_k, %
0.04	0.005	100
0.21	0.025	100
1	0.029	99
2	0.087	98
3	0.087	98
4	0.087	98
5	0.101	98
6	0.12	97
7	0.12	97
8	0.12	97
9	0.156	96
10	0.156	96
11	0.156	96
12	0.207	95
13	0.207	95
14	0.246	94
15	0.246	94

Indiana Limestone Core

Indiana limestone cores were used to examine the effectiveness of the developed gel system in carbonate formations. One core was saturated with formation brine first, and then the initial permeability was measured to be 2.98 mD by injecting different flow rates. A gelant containing 9 wt% PAM, 1 wt% PEI, 50 lb / 1000 gal NH_4Cl was prepared in 2 wt% field mixing water, and then forwarded to the core at $0.15 \text{ cm}^3 / \text{min}$. The injectivity was conducted at a temperature of 116°C , 2500 psi confining pressure, 1000 psi back pressure. **Figure. 6.8** shows that during the gelant injection the differential pressure across the core was higher than that of brine. The high gelant viscosity is the reason behind this observation (see **Figure. 6.4**). However, the differential pressure continued to increase more than 1000 psi and some valves leaked since it reached its maximum allowable pressure and the injection was terminated. This is an indication of the gel formation inside the core. Approximately 2 pore volumes were injected in about 120 minutes as shown in **Figure. 6.9**. This finding confirms that more retardation is needed to place and saturate the core with more pore volumes. Consequently, it was decided to increase the retarder (NH_4Cl) concentration in a second trial.

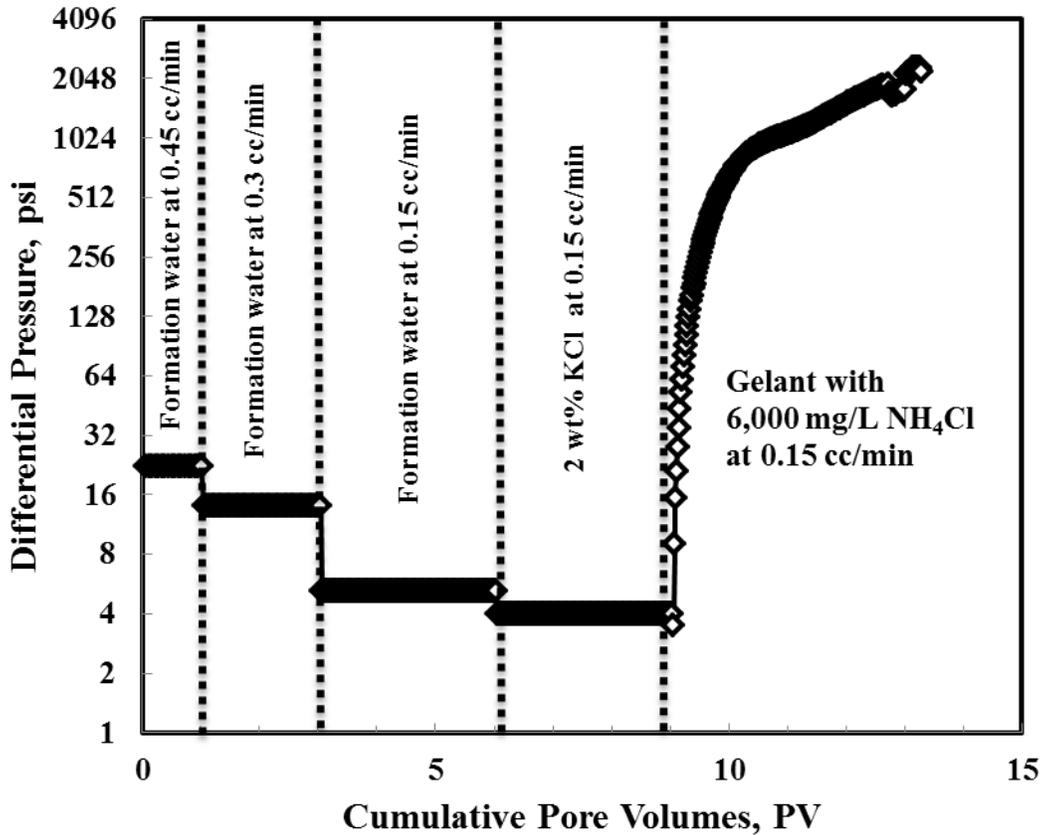


Figure 6. 8: Pressure data as a function of pore volumes injected in Indiana limestone core with initial permeability to brine of 2.98 mD

Another Indiana limestone core was selected which has initial permeability to brine of about 6.5 mD. The same previous injectivity plan was implemented by increasing the concentration of NH_4Cl to 300 lb / 1000 gal (36,000 mg/L). This concentration resulted in sufficient retardation when a copolymer was used with PEI in a previous study (Al-Muntasheri et al. 2010). The differential pressure during the gelant injectivity at 116°C was increased to a plateau value of about 50 (a factor of 11.1) as shown in **Figure. 6.10**. The stable differential pressure during the injectivity of the gelant is a proof for the retardation feature of the new

concentration of NH_4Cl . It should be mentioned that the gelant injectivity took about 8 hours where about 6 pore volumes were placed. After that, the core was shut-in for 5 days for the gel to mature. When the shut-in period was completed, 2 wt% KCl was injected in a back flow direction. The differential pressure increased to more than 1000 psi without any flow through the core (**Figure. 6.10**). This is an indication for the efficiency of the gel to reduce the water production. Few drops were observed after one day of treatment. From **Table 6.5**, the post-treatment showed a permeability reduction by about 99.8%.

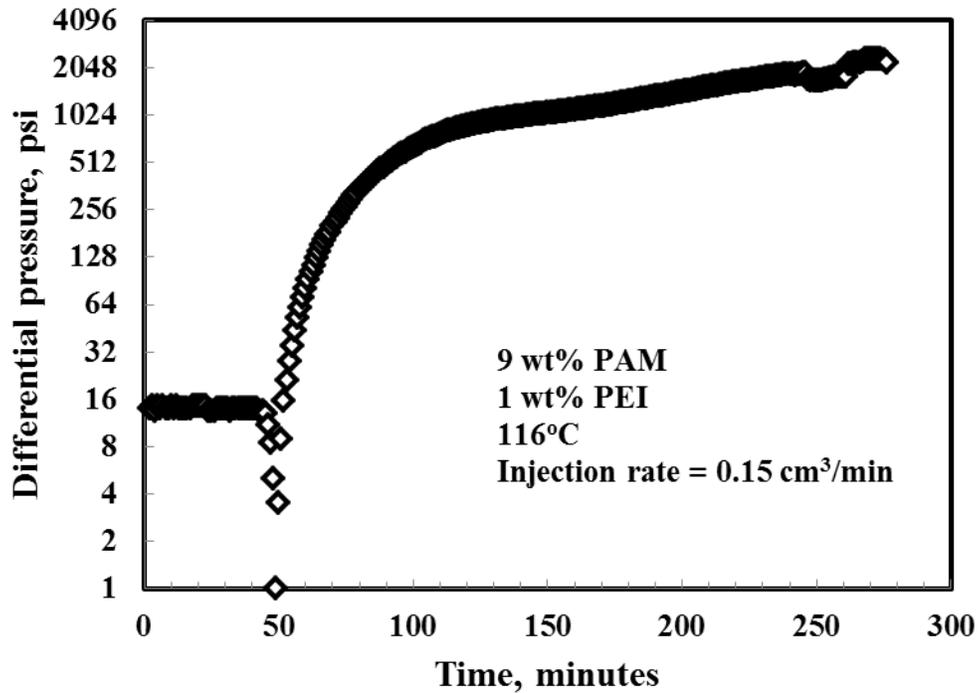


Figure 6. 9: Pressure data vs. time during gelant placement in Indiana limestone core (with initial permeability to brine of 2.98 mD)

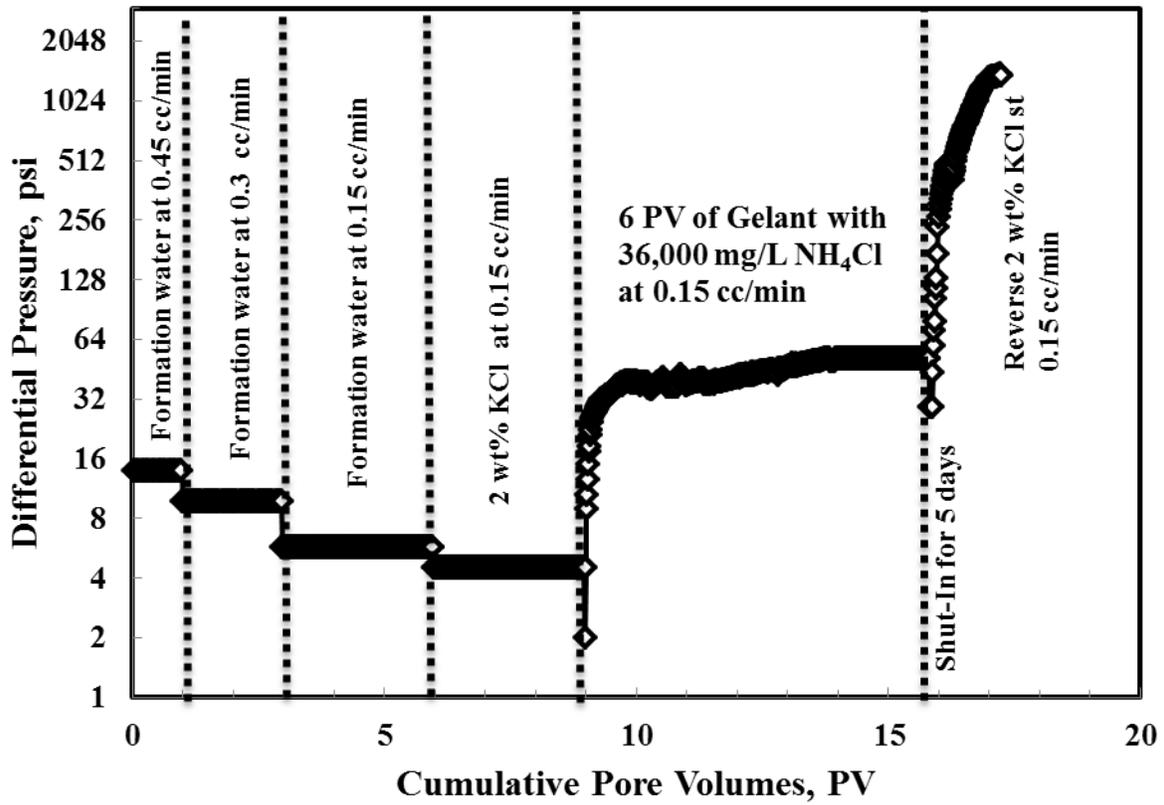


Figure 6. 10: Pressure data as a function of pore volumes injected in Indiana limestone core with initial permeability to brine of 2.98 mD

Table 6. 6: Percent permeability reduction (R_k) in Indiana limestone core at 150°C (302°F)

Time, days	Permeability after treatment, mD	Permeability Reduction R_k, %
0.04	0	100
0.21	0	100
1	0.009	99.8
2	0.009	99.8
3	0.009	99.8
17	0.009	99.8
18	0.009	99.8
21	0.009	99.8
22	0.009	99.8
35	0.009	99.8
48	0.009	99.8
62	0.009	99.8

6.4 Conclusions

Lab tests were conducted for PAM/PEI gel system as an alternative for PAAtBA/PEI. Dynamic rheology as well as core-flooding measurements were performed. A thermally stable formulation of PAM/PEI (9/1) wt% at 150°C (302°F) was used. Compatible retarders (NaCl and NH₄Cl) with PAM/PEI at a salinity of the target reservoir were chosen for gelation time delay to perform

successful placement of the system. PAM/PEI was evaluated in a core-flooding system at 150°C (302°F) using Berea sandstone core with initial permeability of ~ 45 mD. The following conclusions can be drawn from this study:

- (1) At the same salt concentration, NH₄Cl is more efficient in delaying gelation compared to NaCl.
- (2) During the cross-linking PAM with PEI, the gel with NH₄Cl showed lower strength compared with NaCl at the same time of comparison and the addition of NH₄Cl needs longer times to reach higher values of storage modulus.
- (3) The combination of NaCl and NH₄Cl resulted also in decreasing the gel strength. This means that any addition of NH₄Cl will delay gelation and decrease the gel strength at any given time but the ultimate gel strength will remain almost the same.
- (4) NH₄Cl was chosen for retardation at a concentration of 50 lb/ 1000 gal (6,000 mg/l) where it exhibited strength of ~ 1017 Pa with acceptable gelation time (> 2 hours).
- (5) PAM/PEI was injected successfully in Berea sandstone core with initial permeability to brine of ~ 45 mD.
- (6) The post treatment in Berea sandstone core at 150°C (302°F) showed a reduction in permeability to brine of ~ 94%.
- (7) Gelant placement in tight carbonate cores requires long retardation time. Hence, higher concentrations of retarders will be used.
- (8) The post-treatment in Indiana limestone cores showed a reduction in permeability of ~ 99.8%.

Acknowledgements

The authors would like to thank King Abdul-Aziz City for Science and Technology (KACST) for supporting this research through project # AR-30-291. King Fahd University of Petroleum & Minerals (KFUPM) and Saudi Aramco are also acknowledged for their support.

6.5 References

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. 2010. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha, P.L.J. Gelation Kinetics and Performance Evaluation of an Organically Crosslinked Gel at High Temperature and Pressure. SPE J. 2008. 13 (3): 337-45. DOI: <http://dx.doi.org/10.2118/104071-PA>.

Baily, B., Crabtree, M., Tyrie, J., et al. 2000. Water Control. *Oilfield Review* **12** (1): 30-51.

Dalrymple, D., Eoff, L., Vasquez, J., and Van Eijden, J. 2008. Shallow Penetration Particle-Gel System for Water and Gas Shutoff Applications. Paper SPE 114886 presented at the SPE Russian Oil & Gas Technical Conference and Exhibition, Moscow, 28-30 October. DOI: <http://dx.doi.org/10.2118/114886-MS>.

Deolarte, C., Vasquez, J., Soriano, E., and Santillan, A. 2009. Successful Combination of an Organically Cross-linked Polymer System and a Rigid-Setting Material for Conformance Control in Mexico. *SPE Prod & Opera* **24**(4): 522-529. DOI: <http://dx.doi.org/10.2118/112411-PA>.

El-Karsani, K.S.M., Al-Muntasheri, G.A., and Hussein, I.A. 2013. Polymer Systems for water Shutoff and Profile Modification: A review Over the Last Decade. *SPE Journal*. Published online: May, 7, 2013.

Eoff, L.S., Dalrymple, E.D., Everett, D., and Vasquez, J. 2007. Worldwide Field Applications of a Polymeric Gel System for Conformance Applications. *SPE Prod & Oper* **22** (2): 231-235. SPE-98119-PA. DOI: <http://dx.doi.org/10.2118/98119-PA>.

Hardy, M.B., Botermans, C.W., and Smith, P. 1998. New Organically Cross-linked Polymer System Provides Competent Propagation at High Temperatures in Conformance Treatments. Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19-22 April.

Hibbeler, J. and Rae, P. 2005. The Environmental Benefits of Reducing Water Production. Paper SPE 96582 presented at the SPE Asia Pacific Health, Safety, and Environment Conference and Exhibition, Kuala Lumpur, 19-20 September. DOI: <http://dx.doi.org/10.2118/96582-MS>.

Morgan, J.C., Smith, P.L., and Stevens, D.G. 1997. Chemical Adaptation and Deployment Strategies for Water and Gas Shut-off Gel Systems. Paper presented at the 1997 Royal Chemistry Society's Chemistry in the Oil Industry International Symposium, Ambleside, April 14-17.

Reddy, B.R., Crespo, F., and Eoff, L. 2012. Water Shutoff at Ultralow Temperatures Using Organically Crosslinked Polymer Gels. Paper SPE 153155 presented at the Eighteenth SPE Improved Oil Recovery Symposium, Tulsa, April, 14-18.

Seright, R.S. 1996. A review of gel placement concepts. PRRC, 96-21.

Seright, R.S. 1999. Mechanism for gel propagation through fractures. Paper SPE 55628 presented at the SPE Rocky Mountain Regional Meeting, Wyoming.

Sydansk, R.D. 1990. A Newly Developed Chromium (III) Gel Technology. *SPE Res Eng* **5** (3): 346-352. SPE-19308-PA.

Urlwin-Smith, P.L. 1998. Oil and Gas Field Chemicals. US Patent No. 5, 836, 392.

Urlwin-Smith, P.L. 2001. Blocking Composition for Use in Subterranean Formation. US Patent No. 6, 192, 986.

Van Eijden, J., Arkesteijn, F., Akil, I., Vliet, J., van, Batenburg, D., and McGinn, P. 2004 Gel-Cement, a Water Shut-Off System: Qualification in a Syrian Field. Paper SPE 88765 presented at the International Petroleum Exhibition and Conference, Abu Dhabi, 10-13 October.

Van Eijden, J., Arkesteijn, F., Van Batenburg, D., and Van Vliet, J. 2005. Development and Field Application of a Shallow Perforation Shutoff System for HP/HT Oil Wells. Paper SPE 94518 presented at the SPE European Formation Damage Conference, Sheveningen, 25-27 May. DOI: <http://dx.doi.org/10.2118/94518-MS>.

Vasquez, J., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Civan, F. 2005. Development and Evaluation of High Temperature Conformance Polymer Systems. Paper SPE 93156 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, 2-4 February. DOI: <http://dx.doi.org/10.2118/93156-MS>.

CHAPTER SEVEN

Conclusions and Future Work

7.1 General Conclusions

In this thesis, the possibility of using a cost-effective polymer gel system for water control in petroleum reservoirs with high temperature applications was investigated. The proposed polymer gel system was based on a homopolymer of polyacrylamide (PAM) and polyethylenimine (PEI) as a cross-linker. PAM/PEI was developed to replace the existing commercial systems like PAtBA/PEI. This development is expected to reduce the cost of the application since PAtBA is more expensive (\$7/kg) compared to PAM (2 to 4 \$/kg). Moreover, PAtBA showed technical problems with some field mixing waters when a retarder (NaCO_3) was used to elongate the gelation time of PAtBA cross-linked with PEI. In this research, extensive literature review on water production in oil fields and the use of the polymer gel systems was provided with focus on the last decade. Then, the effect of retarders (salts) on PAM hydrolysis and its impact on the gelation time was studied intensively by using different experimental techniques. The strength of the developed gel was also studied through high temperature / high pressure rheology taking into account different parameters. Gelation kinetics was also investigated by differential scanning calorimetry (DSC). Importantly, the efficiency of PAM/PEI gel in reducing water permeability in different lithologies was examined at high temperature (150°C) in core-flooding set-up. The general conclusions from this research are summarized in the following sections.

A thorough review during the last decade revealed that the development of polymer systems can be categorized into two groups. The first type is either organically or inorganically cross-linked polymer gels used to totally block water near the wellbore area. The second type

deals with deep treatment of water injection wells. Here, the fluid is diverted away from high permeability zones referred to as thief zones. These thief zones take most of the injected water during water-flooding leaving a large amount of hydrocarbons unrecovered. Different past decade developments in inorganically as well as organically cross-linked polymer gels were captured. For inorganically cross-linked gels, nanoparticles were introduced to elongate the gelation time of PHPA / Cr^{+3} (Cordova et al. 2008; Berkland et al. 2010). In addition, foam gel was used to block wormholes by cross-linking partially hydrolyzed polyacrylamide (PHPA) with Cr^{+3} in the presence of a surfactant. Colloidal dispersion gels (CDGs) were also developed as aggregates for thief zones blocking. The propagation of CDGs into the formation is still questionable. Copolymers of PAM were also cross-linked with Cr^{+3} . For organically cross-linked gels, research has focused on PAtBA / PEI gel. The application of PAtBA / PEI was extended to high temperatures (160°C) by elongating the gelation time. This was achieved by modifying the cross-linker (PEI), adding polyamino acid, as well as using different retarders (salts). Furthermore, the strength of PAtBA / PEI gel was increased by adding some materials such as cement, silica flour and rigid setting materials. For the second type, two systems were developed for deep water profile modification. An elastic cross-linked microgel was formulated in the form of microspheres with controllable sizes for pores blockage. Other thermally activated microparticles known as Bright Water were also developed for deep wells treatment to modify their injection profiles. The developed microgels and Bright Water have a density similar to water enabling them to penetrate deeply into the reservoir formation.

Elongating the gelation time of the cross-linked gel by using inorganic salts is evident. Sufficient amount of gelants should be injected into the target zones without any blockage to the tubing. Polymer degree of hydrolysis was reported to play a major role in the thermal stability of

the formed gel. Hence, the effect of retarders (salts) on the degree of hydrolysis was investigated. Compatibility tests indicated that NaCl and NH₄Cl were compatible with PAM / PEI gel when representative field water was used. However, Na₂CO₃ which is an effective retarder showed a white precipitate with the subject gel and was ruled out form further investigation. At the same molar concentration, NH₄Cl increased the degree of hydrolysis of PAM significantly compared to NaCl as revealed by ¹³C NMR. Dynamic rheology experiments revealed that NH₄Cl has an efficient retardation feature compared to NaCl. NH₄Cl extended the gelation time more compared to NaCl. Moreover, it is compatible with field mixing water. PAM solutions containing NH₄Cl showed lower viscosity than PAM-NaCl samples. The drop in viscosity is correlated to the hydrolyzed PAM structure (shrinkage). Now, although there are more carboxylate groups as a result of the addition of NH₄Cl, but these groups are not accessible to the cross-linker (PEI) due to the shrinkage of PAM chains. For the effect of salts on gelation time, the delay is suggested to be due to the charge shielding effect rather than a result of the decrease in the degree of hydrolysis. . The DSC confirmed the ¹³C NMR results as well as rheology results. The onset of gelation shifted from 68°C in the case of NaCl to 80°C in the case of NH₄Cl. Long term bulk thermal stability tests revealed that sea water produced more stable gels compared to field and distilled waters.

In any polymer gel treatment in oilfield it is extremely important that the strength of the gel should be high enough to withstand the high pressures exerted by water in the formations. For the first time, high temperature high pressure rheology was conducted to investigate the strength of the gel by studying different parameters like temperature, PAM and PEI concentrations, initial pH of the polymer mixture, salinity, and salts. The elastic modulus increased by 35% when the temperature was increased from 120°C to 130°C. However, no

appreciable increase was observed beyond 130°C. Moreover, the elastic modulus was increased by increasing PAM and PEI concentration. NH₄Cl is efficient in elongating the gelation time and longer times are needed to reach equilibrium plateau values of gel strength. The strength of the polymer gel was noted to be high at acidic as well as alkaline media, however, with lower associated gelation times.

Gelation kinetics of PAM / PEI gel was studied by the use of DSC. In general, the DSC dynamic scans showed two consecutive peaks. An endothermic peak was observed at a low temperature which was correlated to PAM alkaline hydrolysis. The second peak was exothermic occurring at ~ 70°C and explained as the onset of the cross-linking of PAM and PEI. Results showed that high temperatures lead to higher heat release which indicates high degree of gelation and consequently higher strength. The effect of salts which was investigated earlier by rheology is also confirmed by the use of DSC. More delay was observed when NH₄Cl was mixed with the gelant. Gelation kinetics was modeled by using different methods, a rate process model and Avrami model. Modeling showed a good agreement with the experimental data.

The evaluation of PAM / PEI gel in porous media at high temperatures and high pressures is very important for field applications. The success of the polymer gel system in oilfields requires sufficient gelation time for placement and long term thermal stability for considerable economic application period. The effectiveness of PAM / PEI was examined in a core-flooding set-up simulating the same process in the field. Dynamic rheology experiments (to measure the gelation time and strength) were performed on a thermally stable formulation (9/1 wt%) (PAM / PEI) along with NaCl and NH₄Cl. Results revealed that NH₄Cl is a good choice for field application. PAM / PEI gel was evaluated in Berea sandstone as well as in Indiana limestone (carbonate) cores at 150°C (302°F). The post treatment results showed a permeability

reduction in Berea sandstone cores by 94% for a period of two weeks, whereas, it was 99.8% for more than three weeks in Indiana limestone cores. This finding supports the recommendation for the application of PAM / PEI in the field.

Finally, this research showed that the cost-effective PAM is a potential candidate for replacing the expensive PAtBA in water shut-off oilfield applications. Also, this research has shown that ammonium chloride is a good retarder and can be used with PAM/PEI system. Further, the different techniques used in this study described the gelation kinetics and shed some light on the gelation mechanisms. For the first time, high temperature (150°C) high pressure rheology as well as core-flooding experiments were used for evaluating PAM/PEI system. The core-flooding experiments showed that the new system has a potential for use in water shut-off applications in both sandstone and carbonate formations.

7.2 Future Work

Although considerable work was performed throughout this research, but still there are some areas that need to be explored. The following points summarize the recommendations for future research:

- Depending on the results of this research, PAM / PEI gel system should be tested in the field.
- There is a need to study the yielding of gelled PAM / PEI systems in porous media and compare these measurements to data from rheometers
- Despite the fact that inorganic and organic cross-linkers were applied globally, still there is a need for acceptable environmentally friendly organic cross-linker for high

temperature applications in off-shore environment. This can direct research towards cross-linkers from natural sources.

References

Al-Assi, A.A., Willhite, G.P., Green, D.W., and McCool, C.S. 2009. Formation and Propagation of Gel Aggregates Using Partially Hydrolyzed Polyacrylamide and Aluminum Citrate. *SPEJ* **14**(3): 450-461. SPE-100049-PA.

Albonico, P., Bartosek, M., and Lockhart, T.P. 1994. New Polymer Gels for Reducing Water Production in High-Temperature Reservoirs. Paper SPE 27609 presented at the SPE European Production Operations Conference and Exhibition, Aberdeen, 15-17 March. DOI: <http://dx.doi.org/10.2118/27609-MS>.

Al-Dhafeeri, A.M., Nasr-El-Din, H.A., and Al-Harith, A.M. 2008. Evaluation of Rigless Water Shutoff Treatments to be Used in Arab-C Carbonate Reservoir in Saudi Arabia. Paper SPE 114331 presented at the CIPC/SPE Gas Technology Symposium Joint Conference, Calgary, 16-19 June.

Allison, J.D. and Purkale, J.D. 1988. Reducing Permeability of Highly Permeable Zones in Underground Formations. US Patent No. 4,773,481.

Al-Muntasheri, G.A. 2008. Polymer Gels for Water Control: NMR and CT Scan Studies. PhD thesis, Delft University of Technology, Delft, The Netherlands (September 2008).

Al-Muntasheri, G.A. and Zitha, P.L.J. 2009. Gel Under Dynamic Stress in Porous Media: New Insights Using Computed Tomography. Paper SPE 126068 presented at the SPE Saudi Arabia Section Technical Symposium and Exhibition, AlKhobar, 9-11 May. DOI: <http://dx.doi.org/10.2118/126068-MS>.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., and Zitha, P.L.J. 2006. Gelation Kinetics of an Organically Cross-linked Gel at High Temperature and Pressure. Paper SPE 104071 presented at the First International Oil Conference and Exhibition, Cancun, 31 August-2 September. DOI: <http://dx.doi.org/10.2118/104071-MS>.

Al-Muntasheri, G.A., Sierra, L., and Bakhtiyarov, A. 2011. Ammonium Halide as Gelation Retarder for Cross-linkable Polymer Compositions. U.S. Patent Application WO 2011/ 107744.

Al-Muntasheri, G.A., Sierra, L., Garzon, F., Lynn, J.D., and Izquierdo, G. 2010. Water Shut-Off with Polymer Gels in A High Temperature Horizontal Gas Well: A Success Story. Paper SPE 129848 presented at the SPE Improved Oil Recovery Conference, Tulsa, 24-28 April. DOI: <http://dx.doi.org/10.2118/129848-MS>.

Al-Tolaihy, M. and Bukhari, D.O. 2010. Study on the Optimization of De-Scaling Operations in Saudi Arabian Khuff Gas Wells. Paper NACE 10271 presented at the NACE International Corrosion Conference, San Antonio, 14-18 March.

Asghari, K., Taabbodi, L., and Dong, M. 2005. A New Gel-Foam System for Water Shut-off Purposes in Wormhole Reservoirs. Paper SPE 97765 presented at the SPE/PS-CIM/CHOA International Thermal Operations and Heavy Oil Symposium, Calgary, 1-3 November. DOI: <http://dx.doi.org/10.2118/97765-MS>.

Assem, I., and Zhu, H. 2007. Chromium-Toxicological Overview. Institute of Environment and Health. Version 1. http://www.hpa.org.uk/webc/HPAwebFile/HPAweb_C/1194947362170.

Bai, B., Hung, F., Liu, Y., Seright, R.S., and Wang, Y. 2008. Case Study on Preformed Particle Gel for In-Depth Fluid Diversion. Paper SPE 113997 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19-23 April.

Bai, B., Li, L., Liu, Y., Liu, H., Wang, Z., and You, C. 2007b. Preformed Particle Gel for Conformance Control: Factors Affecting Its Properties and Applications. *SPE Res Eval & Eng* **10**(4): 415-422. DOI: <http://dx.doi.org/10.2118/89389-PA>.

Bai, B., Liu, Y., Coste, J.-P., and Li, L. 2007a. Preformed Particle Gel for Conformance Control: Transport Mechanism Through Porous Media. *SPE Res Eval & Eng* **10**(2): 176-184. DOI: <http://dx.doi.org/10.2118/89468-PA>.

Baily, B., Crabtree, M., Tyrie, J., et al. 2000. Water Control. *Oilfield Review* **12** (1): 30-51.

Barclay, D.A., Lawson, K., Mullins, B., and Cardno, B. 2006. Stand-Alone Coiled-Tubing Water Shutoff Operations Reinstates Well on a Normally Unattended Installation. Paper SPE 100132 presented at the SPE/ICoTA Coiled Tubing and Well Intervention Conference and Exhibition, The Woodlands, 4-5 April. DOI: <http://dx.doi.org/10.2118/100132-MS>.

Berkland, C., Cordova, M., Liang, J.T., and Willhite, P. 2010. Polyelectrolyte Complexes as Delayed Gelling Agents for Oil and Gas Applications. US Patent No. 7,644,764.

Bjørsvik, M., Høiland, H., and Skauge, A. 2008. Formation of colloidal dispersion gels from aqueous polyacrylamide solutions. *Colloids and Surfaces A: Physicochem. Eng. Aspect* 317 (2008) 504-511.

Botermans, C.W., Dalrymple, E.D., Dahl, J., and Smith, D. 2001. Chemical Systems for Water and Gas Control: Terminology, Evaluation Methods, Candidate Selection, and Expectations. Paper SPE 65415 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 13-16 February. DOI: <http://dx.doi.org/10.2118/65415-MS>.

Boye, B., Rygg, A., Jodal, C., and Klungland, I. 2011. Development and Evaluation of a New Environmentally Acceptable Conformance Sealant. Paper SPE 142417 presented at the SPE European Formation Damage Conference, Noordwijk, 7-10 June. DOI: <http://dx.doi.org/10.2118/142417-MS>.

Chang, H.L., Sui, X., Xiao, L., Guo, Z., Yao, Y., Xiao, Y., Chen, G., Song, K., and Mack, J.C. 2006. Successful Field Pilot of In-Depth Colloidal Dispersion Gel (CDG) Technology in Daqing Oil Field. *SPE Res Eval & Eng* 9(6): 664-673. SPE-89460-PA.

Chang, K.T., Frampton, H., and Morgan, J.C. 2002. Composition and Method for Recovering Hydrocarbon Fluids from A Subterranean Reservoir. US Patent No. 6,454,003.

Chauveteau, G., Omari, A., Tabary, R., Renard, M., and Rose, J. 2000. Controlling Gelation Time and Microgel Size for Water Shutoff. Paper SPE 59317 presented at the 2000 SPE/DOE Improved Oil Recovery symposium, Tulsa, 3-5 April.

Chauveteau, G., Omari, A., Tabary, R., Renard, M., Veerapen, J., and Rose, J. 2001. New Size-Controlled Microgels for Oil Production. Paper SPE 64988 presented at the 2001 SPE International Symposium on Oilfield Chemistry, Houston, 13-16 February.

Chauveteau, G., Tabary, R., Blin, N., Renard, M., Rousseau, D., and Faber, R. 2004. Disproportionate Permeability Reduction by Soft Preformed Microgels. Paper SPE 89390 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil recovery, Tulsa, 17-21 April.

Chauveteau, G., Tabary, R., Bon, C.L., Renard, M., Feng, Y., and Omari, A. 2003. In-Depth Permeability Control by Adsorption of Soft Size-Controlled Microgels. Paper SPE 82228 presented at the SPE European Formation Damage, The Hauge, 13-14 May.

Cordova, M., Cheng, M., Trejo, J., Johnson, S.J., Willhite, G.P., Liang, J.T., and Berkland, C. 2008. Delayed HPAM Gelation via Transient Sequestration of Chromium in Polyelectrolyte Complex Nanoparticles. *Macromolecules J* **41**: 4398-4404.

Coste, J.-P., Liu, Y., Bai, B., LI, Y., Shen, P., Wang, Z., and Zhu, G. 2000. In-Depth Fluid Diversion by Pre-Gelled Particles. Laboratory Study and Pilot Plant. Paper SPE 59362 presented at the 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April.

Cozic, C., Rousseau, D., and Tabary, R. 2009. Novel Insight Into Microgel System for Water Control. *SPE Prod & Opera* **24**(4): 590-601. SPE-115974-PA.

Dalrymple, D., Eoff, L., Vasquez, J., and Van Eijden, J. 2008. Shallow Penetration Particle-Gel System for Water and Gas Shutoff Applications. Paper SPE 114886 presented at the SPE

Russian Oil & Gas Technical Conference and Exhibition, Moscow, 28-30 October. DOI: <http://dx.doi.org/10.2118/114886-MS>.

Deolarte, C., Vasquez, J., Soriano, E., and Santillan, A. 2009. Successful Combination of an Organically Cross-linked Polymer System and a Rigid-Setting Material for Conformance Control in Mexico. *SPE Prod & Opera* **24**(4): 522-529. DOI: <http://dx.doi.org/10.2118/112411-PA>.

Der Sarkissian, J., Prado, M., and Rauseo, O. 2005. Lessons Learned From Four Selective Water-Shutoff Treatments in Mature Reservoirs in Maracaibo Lake. 2005. Paper SPE 96528 presented at Offshore Europe 2005, Aberdeen, 6-9 September.

Diaz, D., Somaruga, C., Norman, C, and Romero, J. 2008. Colloidal Dispersion Gels Improve Oil Recovery in a Heterogeneous Argentina Waterflood. Paper SPE 113320 presented at the 2008 SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19-23 April.

Donham, J.E. 1991. Offshore Water Injection System: Problems and Solutions. Paper OTC 6782 presented at the 23rd Annual OTC, Houston, 6-9 May. DOI: <http://dx.doi.org/10.4043/6782-MS>.

Elewaut, K., Stavland, A., Zaitoun, A., Krilov, Z., and Zitha, P.L.J. 2006. Investigation of a Novel Chemical for Bullhead Water Shutoff Treatments. Paper SPE 94660 presented at the SPE European Formation Damage Conference, Scheveningen, 25-27 May.

Eoff, L., Dalrymple, D., and Everett, D. 2006. Global Field Results of a Polymeric Gel System in Conformance Applications. Paper SPE 101822 presented at the SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, 3-6 October.

Eoff, L.S., Dalrymple, E.D., Everett, D., and Vasquez, J. 2007. Worldwide Field Applications of a Polymeric Gel System for Conformance Applications. *SPE Prod & Oper* **22** (2): 231-235. SPE-98119-PA. DOI: <http://dx.doi.org/10.2118/98119-PA>.

Feng, Y., Tabary, R., Renard, M., Bon, C.L., Omari, A., and Chauveteau, G. 2003. Characteristics of Microgels Designed for Water Shutoff and Profile Control. Paper SPE 80203 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 5-7 February.

Frampton, H., Morgan, J.C., Cheung, S.K., Munson, L., Chang, K.T., and Williams, D. 2004. Development of a Novel Waterflood Conformance Control System. Paper SPE 89391 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery, Tulsa, 17-21 April.

Grattoni, C.A., Jing, X.D., and Zimmerman, R.W. 2001. Disproportionate Permeability Reduction When a Silicate Gel is Formed In-Situ to Control Water Production. Paper SPE 69534 presented at SPE Latin American and Caribbean Petroleum Engineering Conference, Buenos Aires, 25-28 March.

Hardy, M.B. 2001. Methods and Compositions for Reducing the Permeabilities of Subterranean Zones. US Patent No. 6,196,317.

Hardy, M.B., Botermans, C.W., and Smith, P. 1998. New Organically Cross-linked Polymer System Provides Competent Propagation at High Temperatures in Conformance Treatments. Paper SPE 39690 presented at the SPE/DOE Symposium on Improved Oil Recovery, Tulsa, 19-22 April.

Hardy, M.B., Botermans, W., Hamouda, A., Valdal, J., and Warren, J. 1999. The First Carbonate Field Application of a New Organically Cross-linked Water Shut-off Polymer System. Paper

SPE 50738 presented at the SPE International Symposium on Oilfield Chemistry, Houston, 16-19 February.

Hernandez, M.I. 2012. Private Communication. March.

Hibbeler, J. and Rae, P. 2005. The Environmental Benefits of Reducing Water Production. Paper SPE 96582 presented at the SPE Asia Pacific Health, Safety, and Environment Conference and Exhibition, Kuala Lumpur, 19-20 September. DOI: <http://dx.doi.org/10.2118/96582-MS>.

Jaripatke, O. and Dalrymple, D. 2010. Water-Control Management Technologies: A Review of Successful Chemical Technologies in the Last Two Decades. Paper SPE 127806 presented at the 2010 SPE International Symposium and Exhibition on Formation Damage Control, Lafayette, 10-12 February.

Johnson, S., Trejo, J., Veisi, M., Willhite, G.P., Liang, J.T., and Berkland, C. 2010. Effects of Divalent Cations, Seawater, and Formation Brine on Positively Charged Polyethyleneimine/Dextran Sulfate/Chromium (III) Polyelectrolyte Complexes and Partially Hydrolyzed Polyacrylamide/Chromium (III) Gelation. *J of Applied polymer Science* **115**: 1008-1014.

Junesompitsiri, C., Berel, A., Curtice, R., Riyanto, L., Thouvenin, E., and Cheneviere, P. 2009. Selective Water Shutoff in Gas Well Turns a Liability into an Asset: A Successful Case History from East Kalimantan, Indonesia. Paper SPE 121182 presented at the SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, 4-6 August. DOI: <http://dx.doi.org/10.2118/121182-MS>.

Kabir, A.H. 2001. Chemical Water & Gas Shutoff Technology-An Overview. Paper SPE 72119 presented at the SPE Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, 8-9 October.

Khatib, Z. 2007. Produced Water Management: Is it a Future Legacy or a Business Opportunity for Field Development. Paper IPTC 11624 presented at the International Petroleum Technology Conference, Dubai, 4-6 December.

Kurenkov, V.F., Hartan, H.G., and Lobanov, F.I. 2001. Alkaline Hydrolysis of Polyacrylamide. *Russian Journal of Applied Chemistry* **74** (4): 543-554.

Leighton, J., Saltel, J.L., Morrison, J., Welch, R., and Pilla, J. 2001. Water Shutoff Using Inflatable Composite Sleeve Polymerized In-Situ: A Case History on Forties Delta. *SPE Prod & Fac* **16** (2): 97-105. SPE-72051-PA.

Lei, G., Li, L., and Nasr-El-Din, H.A. 2011. New Gel Aggregates To Improve Sweep Efficiency During Waterflooding. 2011. *SPE Res Eng* **14**(1): 120-128. SPE-129960-PA.

Li, M.Y., Dong, Z.X., Lin, M.Q, and Wu, Z.L. 2004. A study on Size and Conformation of Linked Polymers Coils. *Journal of Petroleum Science and Engineering* **41**(1-3): 213-219.

Liang, J., Lee, R.L. and Seright, R.S. 1993. Gel Placement in Production Wells. *SPE Prod & Fac* **8** (1): 276-284. SPE-20211-PA.

Liang, J.T, Sun, H. and Seright, R.S. 1995. Why Do Gels Reduce Water Permeability More Than Oil Permeability? *SPE Res Eng* **10** (4): 282-286. SPE-27859-PA.

Lightford, S., Pitoni, E., Burrafato, G., and Serapiglia, C.P. 2008. Solving Excessive Water Production in a Prolific Long Horizontal Open Hole Drilled in a Naturally Fractured Carbonate Reservoir. Paper SPE 113700 presented at the SPE/ICoTA Coiled Tubing and well Intervention Conference and Exhibition, The Woodlands, 1-2 April. DOI: <http://dx.doi.org/10.2118/113700-MS>.

Lockhart, T.P. 1991. Chemical and Structural Studies on Cr^{+3} /Polyacrylamide Gels. Paper SPE 20998 presented at the SPE International Symposium on Oilfield Chemistry, Anaheim, 20-22 February.

Mack, J.C. and Smith, J.E. 1994. In-Depth Colloidal Dispersion Gels Improve Oil Recovery Efficiency. Paper SPE 27780 resented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 17-20 April. DOI: <http://dx.doi.org/10.2118/27780-MS>.

Mercado, M., Acuna, J.C., Caballero, C., Vasquez, J., and Soriano, E. 2009. Successful Field Application of a High-Temperature Conformance Polymer in Mexico. Paper SPE 120966 presented at the SPE International Symposium on Oilfield Chemistry, The Woodlands, 20-22 April. DOI: <http://dx.doi.org/10.2118/120966-MS>.

Merdhah, A.B. and Yassin, A.M. 2009. Scale Formation Due to Water Injection in Malaysian Sandstone Cores. *American J. of Applied Science* **6** (8): 1531-1538.

Moradi-Araghi, A. 2000. A Review of Thermally Stable Gels for Fluid Diversion in Petroleum Production. *Journal of Petroleum Science and Engineering* **26** (1-4): 1-10.

Moradi-Araghi, A. and Doe, P. 1987. Hydrolysis and Precipitation of Polyacrylamide in Hard Brines at Elevated Temperatures. *SPE Res Eng* **2** (2): 189-198. SPE-13033-PA.

Moradi-Araghi, A., Cleveland, D.H., and Westerman, I.J. 1987. Development and Evaluation of EOR Polymers Suitable for Hostile Environments-Part II: Copolymers of Acrylamide and Sodium AMPS. Paper SPE 16273 presented at the SPE International Symposium on Oilfield Chemistry, San Antonio, 4-6 February. DOI: <http://dx.doi.org/10.2118/16273-MS>.

Morel, D., Labastie, A., Jouenne, S., and Nahas, E. 2007. Feasibility Study for EOR by Polymer Injection in Deep Offshore Fields. Paper IPTC 11800 presented at the International Petroleum Technology Conference, Dubai, 4-6 December.

Morgan, J.C., Smith, P.L., and Stevens, D.G. 1997. Chemical Adaptation and Deployment Strategies for Water and Gas Shut-off Gel Systems. Paper presented at the 1997 Royal Chemistry Society's Chemistry in the Oil Industry International Symposium, Ambleside, April 14-17.

Mustoni, J.L., Norman, C.A., and Denyer, P. 2010. Deep Conformance Control by a Novel Thermally Activated Particle System to Improve Sweep Efficiency in Mature Waterfloods of the San Jorge Basin. Paper SPE 129732 presented at the 2010 SPE Improved Oil Recovery Symposium, Tulsa, 24-28 April.

Nasr-El-Din, H.A. 2003. New Mechanisms of Formation Damage: lab Studies and Case Histories. Paper SPE 82253 presented at the SPE European Formation Damage Conference, The Hauge, 13-14 May.

Nasr-El-Din, H.A. and Taylor, K.C. 2005. Evaluation of sodium silicate / urea gels used for water shut-off treatments. *Journal of Petroleum Science and Engineering* **48** (3-4): 141- 160.

Ohm, D., McLeod, J.D., Graff, C.J., Frampton, H., Morgan, J.C., Cheung, S.K., and Chang, K.T. 2010. Incremental-Oil Success From Waterflood Sweep Improvement in Alaska. *SPE Prod & Opera* **25**(2): 247-254. <http://dx.doi.org/10.2118/121761-PA>.

Park, C.S., Lee, H.I., Son, S.M., Chung, M.K., Baek, K.K., and Chung, E.S. 2009. Premature Coating Disbonding on Ships and Offshore Structures. Paper NACE 09015 presented at the NACE International Corrosion 2009 Conference & EXPO, Atlanta, 22-26 March.

Patnaik, P. 2007. A Comprehensive Guide to the hazardous Properties of Chemical Substances. 3ed Edition. ISBN-13: 978-0-471-71458-3.

Perdomo, L., Rodriguez, H., Liamedo, M., Oliveros, L., Gonzalez, E., and Molina O. 2007. Successful Experiences for Water and Gas Shutoff Treatments in North Monagas, Venezuela. Paper SPE 106564 presented at the Latin American & Caribbean Petroleum Engineering Conference, Buenos Aires, 15-18 April.

Petrie, E.M. 2001. Adhesives Families/Handbook of Adhesives and Sealant. Page 383.

Polo, R.P.O., Monroy, R.R., Toledo, N., Dalrymple, E.D., Eoff, L., and Everett, D. 2004. Field Applications of Low Molecular-Weight Polymer Activated with an Organic Cross-linker for Water Conformance in South Mexico. Paper SPE 90449 presented at the SPE Annual Technical Conference and Exhibition, Houston, 26-29 September. DOI: <http://dx.doi.org/10.2118/90449-MS>.

Prada, A., Civan, F., and Dalrymple E.D. 2000. Evaluation of Gelation Systems for Conformance Control. Paper SPE 59322 presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 3-5 April. DOI: <http://dx.doi.org/10.2118/59322-MS>.

Prado, M., Palencia, J., Reyna, M., Fernandez, I., Espinoza, J., and Rauseo, O. 2005. Two Different Water Shutoff Applications in a Poorly Consolidated Sandstone Reservoir with Strong Water drive. Paper SPE 93060 presented at the 2005 SPE International Symposium on Oilfield Chemistry, Houston, 2-4 February.

Pritchett, J., Frampton, H., Brinkman, J., Cheung, S., Morgan, J., Chang, K.T., Williams, D., and Goodgame, J. 2003. Field Application of a New In-Depth Waterflood Conformance Improvement Tool. Paper SPE 84897 presented at the SPE International Improved Oil Recovery Conference in Asia Pacific, Kuala Lumpur, 20-21 October.

Reddy, B.R., Eoff, L., Dalrymple, E.D., Black, K., Brown, D., and Rietjens, M. 2003. A Natural Polymer-Based Cross-linker System for Conformance Gel Systems. *SPEJ* **8** (2): 99-106. SPE-84937-PA. DOI: <http://dx.doi.org/10.2118/84937-PA>.

Rousseau, D., Chauveteau, G., Renard, M., Tabary, R., Zaitoun, A., Mallo, P., Braun, O., and Omari, A. 2005. Rheology and Transport in Porous Media of New Water Shutoff /Conformance Control Microgel. Paper SPE 93254 presented at the 2005 SPE International Symposium on Oilfield Chemistry, Houston, 2-4 February.

Roussennac, B. and Toschi, C. 2010. Bright Water Trial in Salema Field (Campos Basin, Brazil). Paper SPE 131299 presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition, Barcelona, 14-17 June.

Saltel, J.L., Leighton, J.R.N., Faure, A.M., and Baaijens, T. 1999. In-Situ Polymerization of Inflatable Composite Sleeve To Reline Damaged Tubing and Shut Off Perforations. *SPE Drill & Comp* **14**(2): 115-122. SPE-56867-PA.

Seright, R.S. 2007. Are Colloidal Dispersion Gels Really a Viable Technology? New Mexico Petroleum Recovery Research Center. DOI: <http://baervan.nmt.edu/randy>.

Seright, R.S., Lane, R.H., and Sydansk, R.D. 2003. A Strategy for Attacking Excess Water Production. *SPE Prod & Fac* **18** (3): 158-169. SPE-84966-PA.

Seright, R.S., Zhang, G., Akanni, O.O., and Wang, D. 2011. A Comparison of Polymer Flooding With In-Depth Profile Modification. Paper CSUG/SPE 146087 presented at the Canadian Unconventional Resources Conference, Calgary, 15-17 November.

Shafian, S.R.M., Hassan, A.A., Ismail, S., Teng, L.K., and Irawan, S. 2010. Blocked Isocyanate Fluid System for Water Shut Off Application. Paper IADC/SPE 132813 presented at the IADC/SPE Asia Pacific Drilling Technology Conference and Exhibition, Ho Chi Minh City, 1-3 November.

Son, S.M., Chung, M.K., Shin, C.S., and Kim, K.H. 2010. Feasibility Study of Rapid Cure Anti-Corrosive Coatings for Marine Environments. Paper NACE 10016 presented at the NACE International 2010 Corrosion Conference & EXPO, San Antonio, 14-18 March.

Spildo, K, Skauge, A, Aarra, M.G., and Tweheyo, M.T. 2009. A New Polymer Application for North Sea Reservoirs. *SPE Res Evaluation & Eng* **12**(3): 427-432. SPE-113460-PA.

Stavland, A., Andersen, K.I., Sandoy, B., Tjomsland, T., and Mebratu, A.A. 2006. How To Apply a Blocking Gel System for Bullhead Selective Water Shutoff: From laboratory to Field. Paper SPE 99729 presented at the SPE/DOE Symposium on Improved Oil Recovery Tulsa, April 22-26 April. DOI: <http://dx.doi.org/10.2118/99729-MS>.

Sydansk, R.D. 1990. A Newly Developed Chromium (III) Gel Technology. *SPE Res Eng* **5** (3): 346-352. SPE-19308-PA.

Sydansk, R.D. 2007. Polymers, Gels, Foams, and Resins. *Petroleum Engineering Handbook* (2nd edition), L. W. Lake (ed.), Society of Petroleum Engineers, Richardson, Texas, Volume V (Reservoir Engineering and Petrophysics), Chapter 13: 1149-1260.

Sydansk, R.D. and Romero-zeron, L. 2011. *Reservoir Conformance Improvement*. Society of Petroleum Engineers. ISBN-10:1555633021.

Sydansk, R.D. and Seright, R.S. 2007. When and Where Relative Permeability Modification Water-Shutoff Treatments Can Be Successfully Applied. *SPE Prod & Oper* **22** (2): 236-247. SPE-99371-PA.

Sydansk, R.D. and Southwell, G.P. 2000. More than 12 Years Experience with a Successful Conformance-Control Polymer-Gel Technology. *SPE Prod & Fac* **15** (4): 270-278. SPE-55668-PA.

Sydansk, R.D., Xiong, Y., Al-Dhafeeri, A.M., Schrader, R.J., and Seright, R.S. 2005. Characterization of Partially Formed Polymer Gels for Application to Fractured Production Wells for Water-Shutoff Purposes. *SPE Prod & Fac* **20** (3): 240-249. SPE-89401-PA.

Uddin, S., Dolan, J.D., Chona, R.A., Gazi, N.H., Monteiro, K., Al-Rubaiyea, J.A., and Al-Sharqawi, A. 2003. Lessons Learned from the First Openhole Horizontal Well Water Shutoff Job Using Two New Polymer Systems-A Case History from Wafra Ratawi Field, Kuwait. Paper SPE 81447 presented at the SPE Middle East Oil Show, Bahrain, 9-12 June.

Urlwin-Smith, P.L. 1998. Oil and Gas Field Chemicals. US Patent No. 5, 836, 392.

Urlwin-Smith, P.L. 2001. Blocking Composition for Use in Subterranean Formation. US Patent No. 6, 192, 986.

Van Eijden, J., Arkesteijn, F., Akil, I., Vliet, J., van, Batenburg, D., and McGinn, P. 2004 Gel-Cement, a Water Shut-Off System: Qualification in a Syrian Field. Paper SPE 88765 presented at the International Petroleum Exhibition and Conference, Abu Dhabi, 10-13 October.

Van Eijden, J., Arkesteijn, F., Van Batenburg, D., and Van Vliet, J. 2005. Development and Field Application of a Shallow Perforation Shutoff System for HP/HT Oil Wells. Paper SPE 94518 presented at the SPE European Formation Damage Conference, Sheveningen, 25-27 May. DOI: <http://dx.doi.org/10.2118/94518-MS>.

Vasquez, J. and Eoff, L. 2010. Laboratory Development and Successful Field Application of a Conformance Polymer System for Low, Medium, and High-Temperature Applications. Paper SPE 139308 presented at the SPE Latin American & Caribbean Petroleum Engineering Conference, Lima, 1-3 December. DOI: <http://dx.doi.org/10.2118/139308-MS>.

Vasquez, J., Civan, F., Shaw, T.M., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Brown, D. 2003. Laboratory Evaluation of High-Temperature Conformance Polymer Systems. Paper SPE 80904 presented at the SPE Production and Operations Symposium, Oklahoma City, 22-25 March. DOI: <http://dx.doi.org/10.2118/80904-MS>.

Vasquez, J., Dalrymple, E.D., Eoff, L., Reddy, B.R., and Civan, F. 2005. Development and Evaluation of High Temperature Conformance Polymer Systems. Paper SPE 93156 presented at

the SPE International Symposium on Oilfield Chemistry, The Woodlands, 2-4 February. DOI: <http://dx.doi.org/10.2118/93156-MS>.

Vasquez, J., Jurado, I., Santillan, A., and Hernandez, R. 2006. Organically Cross-linked Polymer System for Water Reduction Treatments in Mexico. Paper SPE 104134 presented at the First International Oil Conference and Exhibition, Cancun, 31 August-2 September. DOI: <http://dx.doi.org/10.2118/104134-MS>.

Vega, I., Morris, W., Robles, J., Peacock, H., and Marin, A. 2010. Water Shut-off Polymer Systems: Design and Efficiency Evaluation based on Experimental Studies. Paper SPE 129940 presented at the 2010 SPE Improved Oil Recovery Symposium, Tulsa, 24-28 April.

Veil, J.A., Puder, M.G., Elcock, D., and Redweik, R.J. 2004. Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane. United States Department of Energy, National Energy Technology laboratory, Under Contract W-31-109-Eng-38, 2004.

Wang, L., Zhang, G.C., Ge, J.J., Li, G.H., Zhang, J.Q., and Ding, B.D. 2010. Preparation of Microgel Nanospheres and Their Application in EOR. Paper SPE 130357 presented at the CPS/SPE International Oil & Gas Conference and Exhibition, Beijing, 8-10 June.

Zaitoun, A. and Kohler, N. 1988. Two-Phase Flow Through Porous Media: Effect of an Adsorbed Polymer Layer. Paper SPE 18085 presented at the SPE Annual Technical Conference and Exhibition, Houston, 2-5 October.

Zaitoun, A., Tabary, R., Rousseau, D., Pichery, T., Nouyoux, S., Mallo, P., and Braun, O. 2007. Using Microgels To Shut Off Water in a Gas Storage. Paper SPE 106042 presented at the 2007 SPE International Symposium on Oilfield Chemistry, Houston, 28 February-2 March.

VITAE

Name Khalid Saad Mohamed Elkarsani

Date of Birth August 2, 1979

Place of Birth Wad Medani, Sudan

Nationality Sudanese

Education Bachelor of Science in Chemical Engineering
Technology
University of Gezira,
Wad Medani, Sudan, **March, 2003.**

Master of Science in Chemical Engineering
University of Gezira,
Wad Medani, Sudan, **December, 2007.**

Doctor of Philosophy in Chemical
Engineering
King Fahd University of Petroleum & Minerals,
Dhahran, Kindgom of Saudi Arabia, **December,
2013.**

Permenant Address House No. 5 – Block 24, Al debaga North,
Wad Medani, Sudan

Present Address King Fahd University of Petroleum & Minerals,
31261, Dhahran, Kindgom of Saudi Arabia

Email address khalid.karsani@gmail.com

PROFESSIONAL EXPERIENCE

September 2009 to December 2013

Lecturer & PhD Study

The Department of Chemical Engineering; King Fahd University of Petroleum & Minerals (KFUPM); Dhahran 31261, Kingdom of Saudi Arabia

December 2007 to September 2009

Lecturer

Faculty of Engineering & Technology

Department of Applied Chemistry & Chemical Technology

PO.Box: 2020

University of Gezira

Wad Medani

Sudan

April 2004 to December 2007

Teaching Assistant

Faculty of Engineering & Technology

Department of Applied Chemistry & Chemical Technology

PO.Box: 2020

University of Gezira

Wad Medani

Sudan

April 2003 to April 2004

Part-Time Teaching Assistant

Faculty of Engineering & Technology

Department of Applied Chemistry & Chemical Technology

PO.Box: 2020

University of Gezira

Wad Medani

Sudan

Teaching Experience:

Unit Operation Lab (University of Gezira) (several times)

- Fluid Mechanics
- Heat Transfer
- Mass Transfer (Distillation, Drying, Extraction, Humidification, Absorption)

Chemical Reaction Engineering (Reactor Design) (University of Gezira) (two times)

Process Control (University of Gezira)

Mass Transfer operations (University of Gezira)

Chemical Engineering Laboratory (CHE 309) (8 times) (King Fahd University of Petroleum & Minerals)

- Fluid Mechanics
- Heat transfer
- Mass Transfer

AWARDS

Senate Prize for Academic Excellence during the BS study

University of Gezira

Wad Medani

Sudan

PAPERS PUBLISHED IN REFEREED JOURNALS

Khalid S. M. El-Karsani, Ghaithan A. Al-Muntasheri, Ibnelwaleed A. Hussein.

“Polymer systems for Water Shutoff and Profile Modification: A Review over the last Decade,” *Society of Petroleum Engineers’ Journal*, [This paper had been accepted and published online on May,7, 2013 in Society of Petroleum Engineers Journal (SPEJ); DOI : <http://dx.doi.org/10.2118/163100-PA>]

PAPERS IN PROCESS FOR JOURNAL PUBLICATIONS

1. *Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah S. Sultan & Ibnelwaleed A. Hussein*
, “Gelation of a Water Shut-off Gel at High Pressure and High Temperature: Rheological Investigation”, SPEJ, revised **version was submitted**.

2. *Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah S. Sultan, Ibnelwaleed A. Hussein*
, “Gelation Kinetics of PAM/PEI System: DSC Investigation, **submitted to J. Thermal Analysis and calorimetry**.

3. **Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah, S. Sultan & Ibbelwaleed A. Hussein** “Retardation of Polyacrylamide Crosslinking with Polythyleneimine: New Insights Using C¹³ NMR, DSC and Rheology “, **to be submitted to a Polymer Journal.**

4. **Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah, S. Sultan & Ibbelwaleed A. Hussein** “Evaluation of PAM / PEI Gel System for Water Shut-Off at High Temperature and Pressure: Laboratory Study”, **under preparation for publication.**

PAPERS PUBLISHED IN CONFERENCE PROCEEDINGS

1. **Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah, S. Sultan & Ibbelwaleed A. Hussein**, “Gelation Kinetics of PAM/PEI System: DSC Investigation”, 41st NATAS Conference, Kentucky, August, 4-7, 2013.

2. **Khalid S.M. El-Karsani, Ghaithan A. Al-Muntasheri, Abdullah, S. Sultan & Ibbelwaleed A. Hussein**, “Effect of Salts On Polyacrylamide Hydrolysis and Cross-Linking With Polyethylenimine at Elevated Temperatures”, AICHE Annual Meeting, San Francisco, 2-9 November, 2013.

Research Interest:

- Polymers science and engineering
- Rheology of Polymers
- Water soluble polymers for Enhanced Oil Recovery
- Polymeric gels for water shutoff in petroleum reservoirs
- Polymeric gels for Enhanced Oil Recovery
- Polymer structure-properties relationships
- Fluid Mechanics

APPLIED TECHNOLOGY WORKSHOP Attended

Laser Application in Chemical Analysis & oil industry
Laser Institute
Sudan University of Science & Technology
27 to 28 April. 2008