

Analysis of the Factors Affecting the Gelation Time for Polycrylamide-Redox System

by

Mahmoud Abdul Raouf Muhammad

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

July, 1994

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

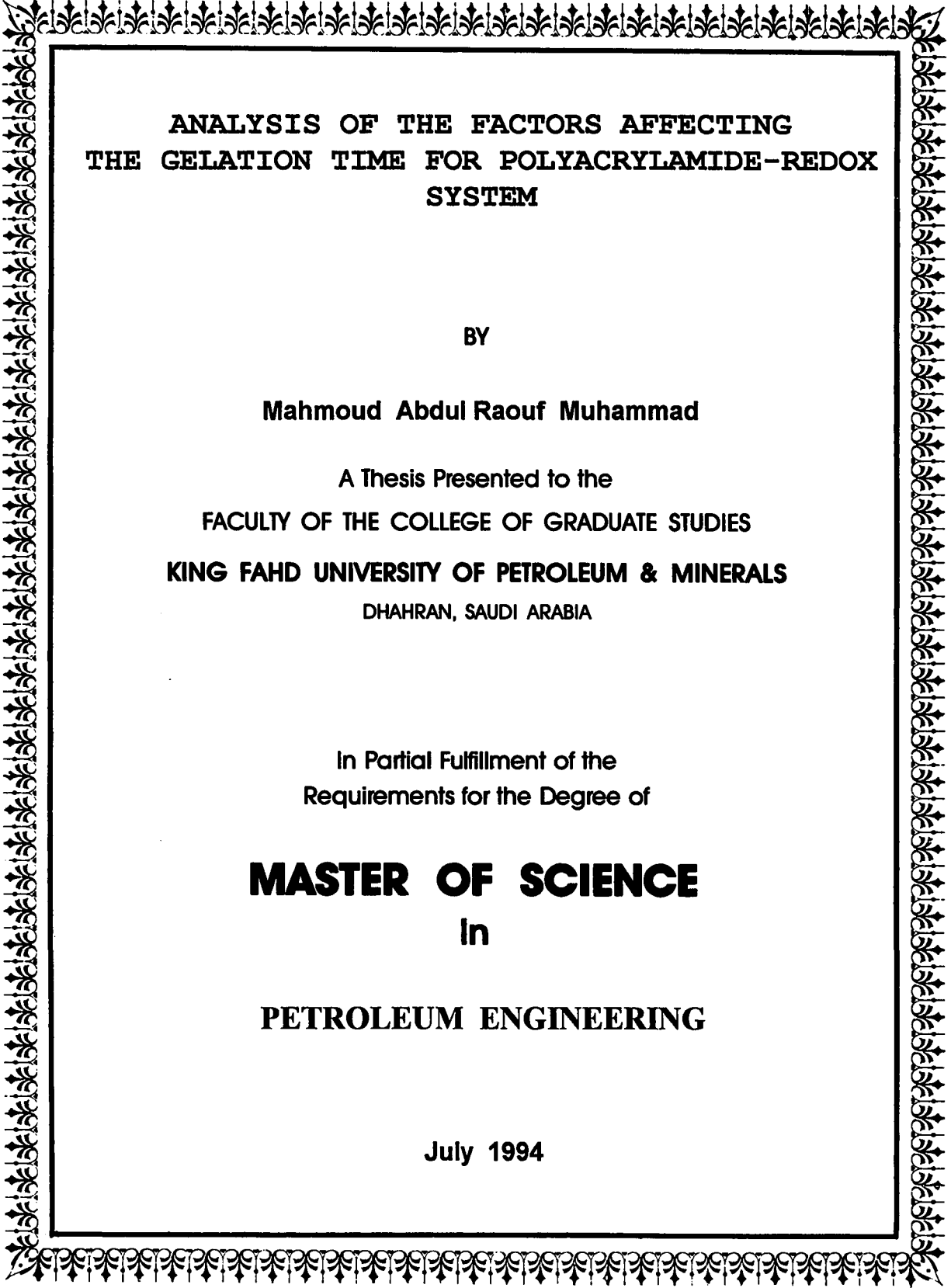
In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600



**ANALYSIS OF THE FACTORS AFFECTING
THE GELATION TIME FOR POLYACRYLAMIDE-REDOX
SYSTEM**

BY

Mahmoud Abdul Raouf Muhammad

A Thesis Presented to the
**FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA**

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

PETROLEUM ENGINEERING

July 1994

UMI Number: 1360835

**UMI Microform Edition 1360835
Copyright 1995, by UMI Company. All rights reserved.**

**This microform edition is protected against unauthorized
copying under Title 17, United States Code.**

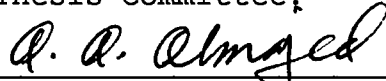
UMI
300 North Zeeb Road
Ann Arbor, MI 48103

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
DHHRAN, SAUDI ARABIA

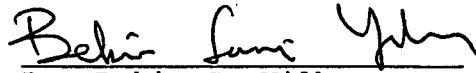
COLLEGE OF GRADUATE STUDIES

This thesis, written by Mr. Mahmoud Abdul Raouf Khan Muhammad under the direction of his Thesis Advisor and approved by his Thesis Committee, has been presented to and accepted by the Dean of the College of Graduate Studies, in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Petroleum Engineering.

Thesis Committee;



Dr. AbdulAziz A. Al-Majed
Thesis Advisor



Dr. Bekir S. Yilbas
Member



Dr. Habib Menouar
Member



Dr. Khalid Al-Fossail
Department Chairman



Dr. Ala H. Al-Rabeh
Dean, College of Graduate Studies

Date: 28/11/94



This thesis is dedicated to my beloved mother
wife, teachers, brothers, sisters, daughter, and son

ACKNOWLEDGMENT

All praise be to the Almighty, ALLAH, with whose gracious help it was possible to accomplish this work. After and after that, Acknowledgement is due to King Fahd University of Petroleum and Minerals for the support throughout my study.

I am deeply indebted to my dear teachers Dr. Abdul Aziz Al-Majed, thesis committee chairman, (Petroleum Engineering Department), Prof. Dr. Bekir Yilbas (Mechanical Engineering Department), Dr. Habib Menouar (Petroleum Engineering Department) for their able guidance throughout all phases of this work, for checking and developing the research material, for offering valuable suggestions and for their critical reading of the manuscript.

Sincere thanks are due to both Mr. Mughram Al-Houtan, Manager of Laboratory Research & Development Center at Saudi Aramco, and to Mr. AbdulHafidh Nagshabandi, Superintendent of Hydrocarbon Science Division in the Lab R & D Center (who first selected the gel project among others projects), for providing the necessary facilities and for both their moral support and continuous encouragement.

Many words of thanks are also due to my teachers Prof. Dr. Muhammed Al-Marhoun Dr. Khalid Al-Fossail, Dr. Abdulaziz Al-Kaabi, Dr. Mehmet Hastaoglu, Dr. Mohammed Aggour, Dr. Hasan Al-Hashim, Dr. Hassen Al-Yousef, Dr. Sadqi Abu-Khamsin, and Dr. Mehmet Sarbar who initiated "Gel Treatment" as the proposed topic for my Master Thesis.

Thanks go to my friends and fellow students; to faculty and staff at the Petroleum Engineering Department, KFUPM/RI Division-I, and other Departments at King Fahd University of Petroleum and Minerals; and to the staff at the Saudi Aramco, Lab R & D Center, Hydrocarbon Science Division, Chemical Fluids & Cement Unit and Petrophysics Unit.

Last but not least, I owe my beloved family, an experssion of gratitude for their patiance, encouragement, moral, and material support which made this work possible.

TABLE OF CONTENTS

	Page
List of Tables	v
List of Figures	vii
Abstract in Arabic	ix
Abstract in English	x
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: LITERATURE REVIEW	9
2.1 POLYMER CHEMISTRY	10
2.1.1 Polymer definition	11
2.1.2 Polymer solution	14
2.1.3 Polymer viscosity	15
2.1.4 Polymer rheology	17
2.2 GEL AND GELATION TIME	18
2.2.1 Gel description	18
2.2.2 Gel manufacture	19
2.2.3 Gelling polymer systems	20
2.2.4 Gel stability	22

2.2.5	Gelation time	25
2.3	POLYACRYLAMIDE/CHROMIUM GELATION	27
2.3.1	Chromium chemistry	27
2.3.2	Reduction of chromium(+6)	28
2.3.3	Chromium(+3)	30
2.3.4	Polyacrylamide/chromium gel formation	31
CHAPTER 3: REQUIREMENTS OF GEL APPLICATIONS AND PARAMETERS AFFECTING GELATION TIME		33
3.1	NECESSITY IN THE FIELD APPLICATIONS	34
3.2	PARAMETERS AFFECTING GELATION TIME	41
CHAPTER 4: MATHEMATICAL MODELING		51
4.1	CHEMICAL USED FOR THIS STUDY	52
4.1.1	Preparation of the polymer solution	54
4.1.2	Data used of the gelling polymer systems	57
4.2	FACTORIAL ANALYSIS	60
4.2.1	Factorial design and F-test	62
4.3	MULTIPLE REGRESSION ANALYSIS	64
4.3.1	Coefficients of multiple determination	68
4.4	DIMENSIONAL ANALYSIS TECHNIQUES.....	71
4.4.1	Methods of developing dimensionless groups	73
4.4.1.1	The step-by-step method	73
4.4.1.2	The exponent method	74

4.5 PROCESS OF DIMENSIONAL ANALYSIS	74
4.6 POWER RELATION	78
CHAPTER 5: RESULTS AND DISCUSSIONS	91
CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS	125
NOMENCLATURE	130
REFERENCES	133
Appendix-A :	140
Appendix-B :	144
Appendix-C :	149

LIST OF TABLES

<u>Tables</u>	<u>page</u>
4.1 Some properties of the polymers used in this study	52
4.2 The chemical system for gelation tests	54
4.3 Average gelation time for system-1	85
4.4 Average gelation time for system-2	85
4.5 Average gelation time for system-3	86
4.6 Average gelation time for system-4	86
4.7 Temperature effects on gelation time for system-4	87
4.8 Average gelation time for system-5	87
4.9 Polymer properties and their level	88
4.10 Factors examined	88
4.11 Average gelation time for system 1-5 at different initial polymer and redox concentrations	89
4.12 Average gelation time for system 1-5 at different non-dimensional of initial polymer and redox concentrations	90

5.1	Factorial design analysis results	117
5.2	Values of coefficients for equation (5.1)	118
5.3	Values of coefficients for equation (5.2)	119
5.4	Values of coefficients for equation (5.3)	120
5.5	Variation of the coefficients with CR/CR ₀ and polymer types for systems 1-5	121
5.6	Variation of the coefficients with polymer types after obtaining final polynomial equations (5.6 - 5.10) for systems 1-5	122
5.7	Relative errors of the gelation time for system 1-5 at different initial polymer and redox concentrations	123
5.8	Critical values of initial polymer concentration at redox concentrations of 3103 and 2414 ppm	124

LIST OF ILLUSTRATIONS

<u>Figures</u>	<u>Page</u>
3.1 Gelation time versus initial polymer concentration at constant redox concentration	46
3.2 Gelation time versus redox concentration at constant initial polymer concentration	47
3.3 Reciprocal of gelation time versus reciprocal of initial polymer concentration at constant redox concentration	48
3.4 Log of gelation time versus reciprocal of temperature at constant redox and initial polymer concentrations	49
3.5 Gelation time versus temperature at constant redox and initial polymer concentrations	50
5.1 Variation of estimated and measured values of gelation time using Equation (1)	102
5.2 Variation of relative error with the number of data points using Equation (1)	103
5.3 Variation of estimated and measured values of gelation time using Equation (2)	104
5.4 Variation of relative error with the number of data points using Equation (2)	105
5.5 Variation of estimated and measured values of gelation time using Equation (3)	106
5.6 Variation of relative error with the number of data points using Equation (3)	107
5.7 Variation of constants in equations corresponding to different type of polymers	108

5.8	Variation of coefficients of (CI/CI_0) with the number of equations corresponding to different type of polymers	109
5.9	Variation of coefficients of $(CI/CI_0)^2$ with the number of equations corresponding to different type of polymers	110
5.10	Relative errors of the gelation time versus initial polymer concentration at constant redox concentration for system-1	111
5.11	Relative errors of the gelation time versus initial polymer concentration at constant redox concentration for system-2	112
5.12	Relative errors of the gelation time versus initial polymer concentration at constant redox concentration for system-3	113
5.13	Relative errors of the gelation time versus initial polymer concentration at constant redox concentration for system-4	114
5.14	Relative errors of the gelation time versus initial polymer concentration at constant redox concentration for system-5	115
5.15	Critical value of the initial polymer concentration versus system numbers	116

ملخص الرسالة

- اسم الطالب الكامل : محمود عبدالرؤف محمد
عنوان الرسالة : دراسة تحليلية للعوامل المؤثرة على زمن تكون الهلام لأنظمة البولي
أكريلاميد- ريدوكس
محل التخصص : هندسة البترول
تاريخ الشهادة : يوليو ١٩٩٤ م .

لقد إزداد إستخدام البوليمر الجلّي (الهلامي) كعامل تحكم في إنسياب السوائل داخل المكامن من أجل تحسين نسبة إنتاج الماء إلى الزيت في طرق الغمر بالماء . وبالرغم من وجود كثير من الطرق والمعلومات في المراجع والأبحاث العلمية إلا أنه من الصعب معرفة تأثير العوامل المختلفة على عمليات تكون الهلام ولذا كان من الضروري القيام بدراسة رياضية لمعرفة التأثير النسبي لكل عامل وأهميته وكذلك إستنباط العلاقات الرياضية بينها . واهتمت هذه الدراسة بالتحديد على إختبار تأثير أربعة عوامل على عملية تكوين الهلام . وأهم هذه العوامل هي نوع البوليمر ، التركيز الأولي للبوليمر ، التركيز الأولي لمخيلط ريدوكس بالاضافة إلى درجة الحرارة .

ولقد تم إستخدام التحاليل الاحصائية لمعرفة تأثير كل عامل على زمن تكون الهلام . ولتطوير العلاقة الرياضية التقريبية التي تربط بين العوامل السابقة وزمن تكون الهلام تم إستخدام العلاقة الأسية . ولايجاز ذلك تمت دراسة البيانات والمعلومات المتوفرة في البحوث العلمية وكذلك إعداد الجداول اللازمة التي توضح تأثير كل من العوامل السابقة . واستخدمت الطرق الاحصائية للتعرف على أهم تلك العوامل المؤثرة بالاضافة إلى تطبيق طرق التحليل الارتدادي المتعدد لايجاد العلاقة بين زمن تكون الهلام والعوامل المختلفة بالاضافة إلى استخدام طريقة التحليل البعدي لاستنتاج العلاقات الأسية والتي تم توظيفها في عمليات التطبيق (الاستخدام) الأمثل .

درجة الماجستير

جامعة الملك فهد للبترول والمعادن

الظهران ، المملكة العربية السعودية

يوليو ١٩٩٤ م

THESIS ABSTRACT

Name of Student : Mahmoud Abdul Raouf Khan Muhammad
Title of the Study : ANALYSIS OF THE FACTORS AFFECTING
THE GELATION TIME FOR POLYACRYLAMIDE-
REDOX SYSTEMS
Major Field : PETROLEUM ENGINEERING
Date of Degree : July 1994

Gelled polymers are being applied increasingly as a reservoir flow control agent to improve the water to oil ratio in water flooding. Having so much data and so many methods available in the literature, it is difficult to explicitly judge the effect of various parameters on the gelation process. Therefore, a mathematical approach for determining the relative importance of each parameter and to derive the empirical relation between process variables is needed. Specifically, the present study examines the effect of four parameters on the gelation process. These are the polymer type, the initial polymer concentration and redox concentration, and the temperature.

A factorial analysis was carried out to identify the influence of each factor on gelation time. Power relation was then employed to develop the empirical relation between the gelation time and the affecting parameters. To achieve this goal, the data available in the literature were studied and relevant tables were produced for the factors and their responses. Statistical analysis was carried out to identify the most affecting parameters, multiple regression analysis was employed to relate the gelation time to the affecting parameters, and dimensional analysis method was introduced to develop the power relations, which were then, utilized for the optimization process.

MASTER OF SCIENCE

KING FAHD UNIVERSITY OF PETROLEUM AND MINERALS
Dhahran, Saudi Arabia

July 1994

CHAPTER 1

CHAPTER 1

INTRODUCTION

During the early exploitation of a petroleum reservoir, the hydrocarbon (i.e., oil and/or gas) is produced using the natural energy available in the reservoir. Sources of natural reservoir energy are fluid and rock expansion, solution gas drive, gravity drainage, and the influx of water from aquifers. When this energy is used up, the production is commonly continued by injection of a fluid to displace the oil. Among the possible injection fluids, water is the most widely used. Its popularity is accounted for by its general availability, ability to spread through an oil-bearing formation, efficiency in displacing oil, and the corresponding low cost [1,2].

Ideally, the amount of oil recovered during water flooding and enhanced oil recovery processes is proportional to the volume of the reservoir that is swept by the displacing fluid. However, poor sweep efficiencies are encountered in many reservoir zones having significant permeability contrasts. Displacement fluids preferentially flow through the zones of relatively high permeability and by-pass the less permeable zones.

A practical method to control the flow of a displacement fluid when this situation exists is the application of gel treatments. One such treatment consists of injecting a mobile gel solution into the high permeability zones. After a period of time known as the gelation time, the gel components react to produce a relatively immobile gel which increases the flow resistance. When water injection is resumed, the injected fluid is diverted to previously unswept portions of the reservoir thereby recovering additional oil.

The gelation time is a very important and critical parameter because knowledge of it is necessary to place a chemical system at a desired location in a reservoir before the system reacts to form an immobile gel. Gelation time is known to be a function of the concentration of the reactants as well as the polymer type and the reducing agent type [3].

The gel treatments, if applied correctly, will definitely reduce water-oil ratios in producing wells and improve the sweep efficiency of water injection wells [4-6]. In addition, gel treatments have been applied to reduce channeling in high-pressure gas floods and to reduce water production from gas wells [7].

The two factors that determine the success of a gel treatment are: proper choice of the gelling system as well as proper placement of the gel in the treated zone.

The former factor depends mainly on the reservoir characteristics. Chemical interaction between various chemical species present in the formation brine and gel components is a major factor that determines the success of gel treatment. Reservoir temperature determines, among other factors, gelation time and gel stability. The latter factor depends on well logs and zone isolation. Improper placement of the gel can plug the pay zone which results in a significant decline in the productivity of the well [7,8].

As of today, the three main types of gels that exist are: water-soluble polymers and cross linkers, phenol formaldehyde resins, and silica gels [9].

Water-soluble polymers, particularly polyacrylamide, have shown to be the most promising. This is due to a natural selectivity to flow in areas of high permeability and high water saturation. Also, it provides a reduction in the permeability of those zones. Another property of polyacrylamides which makes them attractive is that these polymers have a high affinity for water. This means that the

permeability of a reservoir rock matrix to water markedly decreases while only slightly reducing the permeability to oil [10].

The gel system under consideration in this study includes a polyacrylamide polymer, a reducing agent (sodium bisulfate) and a metal ion (sodium dichromate). In order to obtain a stable polyacrylamide / chromium gel, the chromium ion must not be in a form readily available to react with polymer. Basic chemistry principles suggest that reducing a chromium(+6) compound by a reducing agent releases chromium(+3) in a controllable way. The process in which polyacrylamide/chromium gel is used as a means to reduce formation permeability has been reported in literature [11]. It usually involves two steps in which a polymer slug containing chromium(+6) is injected into a reservoir. This slug is followed by the second slug of polymer containing a reducing agent. Upon mixing in the reservoir, the reducing agent reacts with sodium dichromate to produce chrome(+3), which reacts with the carboxylate groups of polyacrylamide to produce a three-dimension structure, i.e., gel [12].

There are so much data and so many methods available in the literature, that it is difficult to explicitly judge the effect of all the parameters in the gelation process.

Therefore, a mathematical approach determining the relative importance of parameters and to derive the empirical relation between process parameters is needed. Consequently, the present study examines the mathematical relation between the gelation time and the affecting parameters. These parameters include polymer type, initial polymer concentration, redox concentration, and temperature. Here, redox concentration is defined as the sum of the concentration of the reducing agent and the source of the chrome (+6). It should be noted that the data used in this study covers the existing parameters and corresponding gelation time in the open literature. Also, It is worth to mention that the data used in this work are extracted from the experimental studies which have been carried out in the laboratory conditions, i.e., no field data are available in the open literature.

The objectives of the present work are as follows:

- (1) Carrying out a statistical analysis to identify the most affecting parameters.

- (2) Introducing a dimensional analysis to develop dimensionless groups by employing the affecting parameters.

(3) Developing an empirical formulation between the dimensionless groups and the gelation time using a multiple regression technique.

To achieve these goals, the data developed by the previous investigators [3,12,13] are studied and relevant tables are produced for the gelation time and corresponding levels of the affecting parameters.

A statistical analysis (factorial design) based on the factorial analysis is introduced [15]. A statistical program available for PC's is utilized. Using the results of statistical analysis, an F-test is introduced to identify the significant levels of the factors and their interactions.

Having identified the most affecting factors, the dimensional analysis is introduced to develop dimensionless groups using Buckingham's π rule [16]. Once the groups are developed, multiple regression technique is introduced to develop an empirical relation between the groups, which are related to the most affecting parameters, and the gelation time. These groups are then used to develop empirical formulas and later the constants and powers of the empirical formulas are determined.

After obtaining the empirical formulation , an optimization technique is employed to calculate the values of initial polymer and redox concentrations, which determines the maximum and minimum values of the gelation time. This provides the limits of the applicability of the empirical equation. In this case, once the maximum and/or minimum points appear in the resulting gelation time curve, described by the empirical equation, then the resulting empirical equation is not valid to represent the gelation time (i.e., the trend of the gelation time changes). This is due to the fact that the data extracted from the open literature do not produce the maximum and/or minimum points of gelation time. Consequently, the actual data may not be consistent with the empirical predictions beyond these points.

CHAPTER 2

CHAPTER 2

LITERATURE REVIEW

This study concerns a gelled polymer system that is being applied to control and/or plug the high permeability zones in petroleum reservoirs. The chemical system consists of a polyacrylamide polymer, a chromium(+6) compound, and a reducing agent. The analysis of the factors affecting the gelation process to be conducted involves a knowledge or understanding of the chemical solution injected into porous media to create a gel. Therefore, the literature survey is directed to the following three main categories. These are: polymer chemistry, gel and gelation time, and polyacrylamide/chromium gelation process.

2.1 POLYMER CHEMISTRY

In this section, the literature survey is mainly concerned with polymer structure and properties, with an emphasis on polyacrylamide-type polymer.

2.1.1 POLYMER DEFINITION

It is instructive to start with the definition of polymers that are used in gelling process. The term "polymer" is derived from the Greek words *polys* meaning many and *meros* meaning parts or units. Normally, polymer substances result from the generation of the entire molecular structure through repetition of one or more elementary units. These units are called monomers. The number of monomer units in a polymer may vary from two to millions. In case the polymer contains less than ten units, the term *oligomer* is often used. As the number of units becomes very large, the term *high polymer* is used. The number of monomer units in a polymer is referred to as the degree of polymerization. Polymers containing repeat units of only one chemical composition are termed *homopolymers* while those with two or more chemically different types of repeating units are termed *copolymers* [17,18].

A polymer is a mixture of many molecules with different numbers of repeating units. As the *molecular weight* is applied for a polymer, it is always implicitly taken to be an average molecular weight of all the macromolecules in the sample. Properties such as solubility, viscosity, modulus of elasticity, and strength are affected not only by the

molecular weight but also by molecular weight distribution and the interconnections between units [19,20].

At the present, the most employed water-soluble polymers utilized for oil field applications are polyacrylamides and biopolymers [21].

Purified acrylamide is a white crystalline solid and melting point of 84 to 85°C. It is soluble in water and slightly soluble in hydrocarbon solvents. Acrylamide monomer may be polymerized or copolymerized to produce water-soluble polymers. The polymerization is accomplished by means of a catalyst, light sensitive dyes, or ultrasonic waves [22].

Polymers produced through the homopolymerization of acrylamide are neutral, water-soluble, and essentially nonionic in character. Partially hydrolyzed polyacrylamide, a derivative from polyacrylamide in which some amide groups are transformed to carboxyl groups, is derived by heating the homopolymer with dilute sodium hydroxide. The degree of hydrolysis is designated as the ratio of the amount of carboxyl groups along the backbone to the summation of carboxyl groups and amide groups. Partially hydrolyzed polyacrylamide can also be prepared through a copolymerization of acrylamide and acrylic acid. In addition to

acrylic acid, acrylamide is capable of being copolymerized with a large variety of monomers. The ionic derivatives could be prepared from homopolyacrylamide through the chemically reactive amide groups. Poly-acrylamides and their copolymers are of extremely high molecular weight, commonly ranging from 1 million to 10 millions [17,19,22].

Biopolymers such as xanthan gum are produced by a fermentation process. Xanthan gum is an extra-cellular heteropoly-saccharide produced by the bacterium *xanthomonas campestris*. The primary structure of xanthan consists of a backbone of glucose monomers (cellulose-like chain) and trisaccharide side chains. The backbone consists of glucose residues connected by β (1 to 4) glycosidic linkages. A side chain that contains the sequence mannose/glucuronic acid/mannose is attached to every other glucose unit. In each side chain an O-acetyl group is usually attached to the mannose closest to the polymer backbone. The terminal mannose may contain a ketal-linked pyruvate group. The percentage of side chains that contain pyruvate groups varies from 0 to 100%, depending on the bacterial strain and the fermentation conditions. The presence of carboxylate groups in the side chains gives the polymer its ionic character [17,19,23,24,26].

2.1.2 POLYMER SOLUTION

A polymer molecule dissolved in water may be visualized as a long, continuous, twisted chain in a random orientation. Water-soluble polymers increase the viscosity of the aqueous phase by many orders of magnitude. Water molecules penetrating into the coil are held to the polymer and thereby immobilized. This is supported by an observation that the polymer coil could not be separated from water (i.e., bound to the polymer chain) during a sedimentation run in an ultracentrifuge [17].

In a dilute solution, polymer molecules as a random statistical coil has become saturated with solvent. The coils of several macromolecules are separated from each other by pure solvent and each molecule acts like a micro sponge. The conformation of a polymeric chain depends primarily on the nature of the solvent. If the solvent is a good one, the polymer segments prefer to be surrounded by solvent molecules rather than by other segments. If the solvent is poor, the polymer molecules tend to minimize the area of contact with the solvent molecules [18].

In concentrated solutions, the solute molecular domains overlap and contacts between segments of different polymer

molecules become as possible as contacts between segments of the same polymer chain. In other words, the solutions are macroscopically homogeneous. The polyacrylamide concentration necessary for the transition from a diluted solution to a concentrated one could be correlated to polymer molecular weight [25].

2.1.3 POLYMER VISCOSITY

The main solution property which is of interest in polymer flooding application is the viscosity of the polymer. Polymers are added to the injection brine in the waterflooding in order to increase the viscosity of the drive fluid, which in turn improves the oil-water mobility ratio. This leads to improve areal and vertical sweep efficiency.

The viscosity of a polymer solution is related to the size and extension of the polymer molecule in that particular solution, larger molecular species are generally associated with higher solution viscosities. Also, as the polymer size is reduced, the viscosity decreases. For a given type of polyacrylamide polymer, the solution viscosity increases

with polymer concentration. In addition, as the temperature is raised, the viscosity decreases [20,26].

Mungan [33] and Sparlin [35] found that a lower solution pH gives a lower viscosity. Montgomery [36], however, reported that the viscosity of nonionic polyacrylamide did not change markedly within a pH range of 1 to 10. When stored at pH above 10, however, the viscosity of polymer solution increases. He attributed this to the hydrolysis of polymer molecules. Also, he observed that the increase of the viscosity was time dependent and suggested that hydrolysis proceeded gradually. Furthermore, at a higher degree of hydrolysis, the viscosity was larger [37].

The solution viscosity of partially hydrolyzed polyacrylamide decreases in the presence of salt. This is due to neutralization of negatively charged carboxyl groups, which in turn decreases electrostatic repulsion among the polymer segments. Unlike polyacrylamide, biopolymers undergo thermal transition where they lose most of their solution viscosity. In general, any factor that affects the configuration of the polymer molecules in solution would affect the viscosity [26].

2.1.4 POLYMER RHEOLOGY

The solutions of most polymers are non-Newtonian fluids. They also exhibit pseudoplastic viscosity behavior. Pseudoplastic fluids are those fluids whose viscosities decrease with increasing rate of shear (i.e., shear thinning). The pseudo-plasticity of polymer solutions was further investigated in the work of Nouri and Root [38]. They found that the power law model could fit quite well the rheological behavior of eighty-eight solutions of twelve different polymers frequently used by the petroleum industry [20].

The flow of polyacrylamide solutions through porous media requires effective viscosities needed for use in Darcy's equation. The prediction of viscosity of a polymer solution in porous media has been attempted by many researchers. Hirasaki and Pope [39] noted that rheological behavior of polymer solutions was quite complicated. It was Newtonian at low flow rates, pseudoplastic at intermediate rates and viscoelastic at high rates. The pseudoplastic fluids acting like Newtonian fluids at low shear rate have also been observed by Kulicke et al. [22] and Gogarty [40].

2.2 GEL AND GELATION TIME

2.2.1 GEL DESCRIPTION

Gels are easy to recognize but difficult to define. As a commonly accepted concept, the term gel is broadly used to describe any chemical system that has suddenly lost its mobility. The gels usually comprise two components, the one being a solid-like material and the other a liquid. They may be defined more strictly as "a physical state with properties intermediate between those of solid and liquid phases" [52]. The gels vary widely both in chemical composition and in the nature of the chemical bonds and/or physical forces which give them coherence. The properties such as elasticity and rigidity are sometimes used to characterize gels, but no particular property has been found to uniquely distinguish gelled systems.

Gels are crosslinked networks of molecules which have a rubbery consistency. Examples are the fruit flavoured gels and aspic gels common in cookery. Polyacrylamide based gels are formed by linking together the molecules of acrylamide based water soluble polymers through use of crosslinking agents. Multivalent metal ions, for example Aluminium,

Chromium and Zirconium ions, can link together the acrylate groups on acrylamide. Other crosslinking agents can be used but the basic mechanism remains the joining together of molecules to form a network.

2.2.2 GEL MANUFACTURE

Gels may be formed either from a solution or from a xerogel. The xerogel is a solid macromolecular substance capable of absorbing solvents such as water. Silica gel is an example of this type [20].

Formation of a gel from a solution is induced when the solubility of a colloidal suspension or solution is reduced to the extent that some solid phase is produced. The solid phase should be allowed to suspend in the solution as a continuous pattern or frame work of colloid fineness. Techniques for gel formation cover a physical transformation such as change in temperature or a chemical transformation, such as adding substances to induce a reaction [26].

Addition of chemical substances to induce gelation is very common in synthetic polymer chemistry. Formation of a gel in this type is caused by the occurrence of macroscopic

branched molecules. These molecules are of a size commensurate with the dimensions of the system [17-19].

Another example of a chemical transformation that causes gelation is adding a salt to neutralize charged colloidal particles. The colloidal particles are originally held in suspension due to electric repulsion between the charged surfaces.

Neutralization may produce a gel or a precipitate, depending upon the interaction between the neutralized particles and the solvent. If water is the solvent and the particles are hydrophobic, the neutralization causes agglomeration and then precipitation. On the other hand, if the particles are hydrophilic, a gel is likely to form because the particles have an affinity for water, which causes the particles to suspend [19,20,42].

2.2.3 GELLING POLYMER SYSTEMS

As of today, the three commercially available gelling systems are: water-soluble polymers and crosslinkers, phenol-formaldehyde resins, and silica gels [9,43-48].

In the first gelling system, a polyvalent cation $\text{Cr}(+3)$ or $\text{Al}(+3)$ is used to cross link the molecules of a water-soluble polymer to form a gel. Water-soluble polymers that can be used include polyacrylamides, biopolymers, and ligno-sulphonates [9]. In this gelling system, the gelling components are injected into the reservoir in a liquid form. Then, the polyvalent ions cross link the polymer molecules to form a three dimensional structure, i.e., a gel. The gelation time in this type of gels can be controlled by changing the concentrations of the reactants [4]. Another method to control the gelation time is to use $\text{Cr}(+6)$ and a reducing agent [3]. The gels that are formed by cross linking a polymer and a polyvalent cation can be removed by using a bleach (sodium hypo chlorite) [31].

In the second gelling system, a polyphenolic material, e.g., lignin, is dissolved in sodium hydroxide solution. Then, the phenolic groups of lignin react with formaldehyde to form a rigid resin [9,26,46]. The gels formed from this reaction has a high yield stress and good mechanical properties. Once this gel is set, it is very hard to remove. This gel is very resistant to acids and the only way to remove it is by using alkaline solutions [9].

In the third gelling system, a dispersion of sub-micron silica particles is injected into the formation. The surface charge of these particles is negative at high pH values and can be varied by changing the pH or the salinity of the solution [19,47]. A gel in this system can be formed by changing the surface charges of the particles where silica particles coagulate to form the gel. Unlike the previous two types of gels, this one is formed by a physical process where the silica particles coagulate due to Van-der Waals attraction forces. This gel can be removed by changing pH or salinity [49,50].

2.2.4 GEL STABILITY

The stability of polymer solutions is important since the polymers are expected to retain their integrity as they travel through the reservoir. Gel stability is a very important factor that should be carefully examined when choosing the gelling systems. Many gels undergo syneresis, which means a decrease in the gel volume with the time [38,39]. This change in the gel volume is not desirable because when the gel volume decreases it creates channels where injected fluids can flow. As a result, the efficiency

of the gel in blocking and/or diverting the treated zones decreases [26].

Recent studies have shown that gel syneresis is a function of gel type, temperature, and gel compositions. All gels undergo syneresis but to a different extent. The polyacrylamide and phenol formaldehyde gels showed better stability at high temperatures [26].

The gel stability is also a function of the mechanical properties of the parent polymer. Mechanical degradation of polymer solutions occurs when the fluid stresses, developed during flow or deformation, become large enough to break the polymer molecular chains. Under ordinary conditions polyacrylamides are not degradable. Because the energy required to sever a carbon-carbon bond is quite large, on the order of 80 kcal/mole [27]. However, the most polyacrylamide solutions degraded when they are strongly stirred. Also, the degradation becomes marked at high flow velocity [28].

Maerker [29] found that the shear degradation was more severe in high salinity brine. In addition, he noted that the presence of calcium ion was especially detrimental.

The presence of dissolved oxygen has been proven to be harmful to solution stability. The disintegration of molecular aggregates by rehydration of crosslinks, or rupture of carbon-carbon bonds are due to oxidation. Also, this effect became more pronounced at higher temperatures. Knight [30] found the same effects and recommended the use of formaldehyde to prevent degradation caused by oxygen. Shupe [31] suggested that formaldehyde plus methanol was slightly better than formaldehyde alone.

Polyacrylamide solutions are also degraded by biological decomposition. In many cases, this decomposition could be reduced or completely eliminated by addition of proper chemical stabilizers [30-32].

Thermal degradation of polyacrylamide has been observed in the temperature range of 120°C to 150°C [33]. Because most oil-field applications do not involve temperatures in this range, this type of decomposition is of limited practical interest. Polyacrylamides are also degraded due to exposure to light and aging [34]. Unlike polyacrylamides, biopolymers are susceptible to bacterial degradation and a biocide should be added when they are used.

2.2.5 GELATION TIME

Gelation time is a very important parameter that should be considered when working with certain gelling systems. Several techniques have been developed for the determination of gelation time which is the time necessary for a gel to form in a chemical system. The experimental techniques are dependent on the definition of a gel point based either on an increase in viscosity or on the on-set of rigidity.

Experimentally, each of them involves the continuous monitoring of an appropriate property. The gel point is located via examining a sudden change in that property. Obviously, the location of the gel point is quite subjective, for the abrupt change usually covers a period of time. This is because the gelation process starts very slowly, sweeps through a maximum of activity, and then continues but tapers off into a final hardening or setting stage [18,19,20,26,51]. As an example, the gel point in the viscosity measurement method has been defined as the point of maximum rate of increase of viscosity which corresponds to an infinitely large viscosity [52].

Therefore, gelation time could also be defined as the time required for the gelling components to form a gel. In

other words, it is the time required to convert the gelling mixture from the liquid state to a solid-like state. Gelation time can be measured accurately using a conventional viscometer. In this case, the gel mixture is placed in the viscometer at the desired temperature and the solution viscosity is measured frequently. A steep increase in viscosity indicates the on-set of gelation [26]. The gelation time is a function of the gelling polymer type, initial polymer and redox concentrations, temperature, pH, salinity, and hardness.

During the buildup of a three-dimensional gel network, any shearing imposed on the sample tends to break down the network being formed. To remedy this drawback in the rheological method, an oscillation technique [53] was developed in which the sample is subjected to only small sinusoidal shear deformation. Thus during measurement, the gel network structure remains intact. The analysis of gelation is based on the fact that the build-up of a network causes a change in the storage modulus, which is defined as the elastic part of the stress in the sample. Once the gel point is reached, the storage modulus becomes independent of oscillating frequency.

2.3 POLYACRYLAMIDE/CHROMIUM GELATION

2.3.1 CHROMIUM CHEMISTRY

In this study, the criticism to the success of the in-situ gelation process is an understanding of the reaction kinetics governing both the redox and crosslinking reactions. Knowledge of the reaction kinetics would provide an effective means to control the gelation process for selective placement of the gelling agents into the reservoir.

Chromium forms three well-known series of compounds having the oxidation numbers +2, +3, and +6. The Chromium (atomic number 24) is one of the metal found effective in the crosslinking of water-soluble polymers like the polyacrylamides and xanthan polysaccharide biopolymers for gelled polymer treatments. For the in-situ gelation process, chromium in the +6 oxidation state is reduced to the +3 oxidation state to form species which will then react with the polymer.

A Chromium is derived from the Greek *chromos* meaning color. This element was first discovered about 1719 [54,55]

by the French chemist, Louis N. Vauquelin. The color of chromium compounds varies depending on the oxidation state of chromium and the ligand or group bound to the central chromium atom. The most distinctive colors are the dark green and purple Cr(+3) compounds and the bright orange to yellow Cr(+6) compounds.

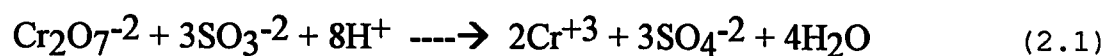
Chromium(+6) or Cr(+6) for short is strongly oxidizing, acidic, and very toxic. Cr(+6) complexes are mostly anionic generally soluble in water. Also, they appear yellow to red due to charge-transfer absorption's [22,26].

2.3.2 REDUCTION OF CHROMIUM(+6)

Chromium(+6) ions are strong oxidizing agents in acid solution. The reduction of chromium from the +6 oxidation state to the +3 state provides a method of controlling the rate of the gelation or polymer crosslinking process. Two reducing agents used for the application of this process to enhanced oil recovery are sodium bisulfite (NaHSO_3) and thiourea (NH_2CSNH_2). Sodium bisulfite provides a relatively fast redox rate [12,13] of the order of minutes to hours, whereas the thiourea provides a much slower reduction rate of the order of days to weeks for specific reaction

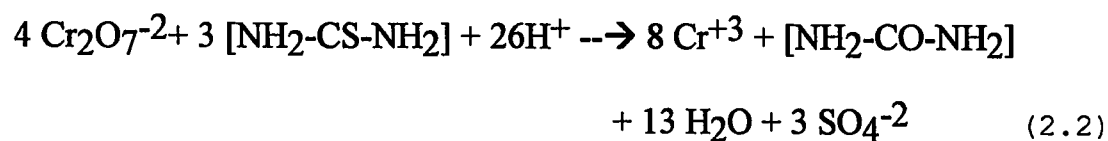
conditions. The redox rates using both species were determined in the presence of polymer by Terry [3]. It is known that Cr(+6) does not react with or crosslink the polymer.

The reduction of dichromate ion by bisulfite takes place according to



in which a color change from bright yellow to turquoise or blue-green takes place.

The reduction of dichromate by thiourea occurs by the following reaction.



This reaction is generally marked by a change in color from bright yellow to dark brown.

2.3.3 CHROMIUM(+3)

The Chromium(+3) complexes are classified as *chemically inert* and noted to undergo only slow ligand substitution reactions. The complex of the metal ion is formed when the number of ions or molecules combined with the central atom to form an entity in which the number of atoms directly attached to the central atom exceeds the normal covalence (oxidation state) of this atom. The complexes can be either neutral, cationic, or anionic. The groups that bond to the central atom are called ligands or donor molecules, which donate a pair of electrons to the central atom. The bond between the central atom and ligand is coordinate in nature [56-58]. Because the solvent, water, is a neutral ligand, chromium(+3) exists in aqueous solution as a partially to completely hydrated complex. For the in-situ gelation process, aqueous solutions of chromium salts are utilized to generate a source of chromium in the +3 valence state to crosslink the water-soluble polymers in the formation.

2.3.4 POLYACRYLAMIDE / CHROMIUM GEL FORMATION

Polyacrylamide polymers are known to form the gels in the presence of Cr(+3). The amount of Cr(+3) needed to induce gelation of the polymers varies over a wide range and depends on the molecular weight, concentration, and type of the polymer, as well as pH, temperature and salt concentration of the solution. Also, the Chromium may be introduced in the +3 valence state in the form of Cr(+3).

Gentile [59] suggested that an amount of chromium salt, calculated as Cr(+3), of from about 0.002% to as much as about 40% of the weight of the polymer may be employed.

Polyacrylamide/chromium gels may also be formed with an indirect gelling technique [60]. In this technique, the direct addition of Cr(+3) is replaced by introducing a reducing agent to convert the previously added Cr(+6) to Cr(+3). Following the conversion, the chromium ion reacts with the polymer to form a gel.

According to Clampitt et al. [60], the gels formed in this method are much more stable than those formed by directly introducing Cr(+3) into polymer solution. They recommended that the amount of the chromium(+6) compounds used be in the

range of 0.05 to 70 weight percent of the amount of polymer used, preferably 0.5 to 40 wt%.

The mechanism by which polyacrylamide or its partially hydrolyzed version forms gels due to the presence of chromium ion is not well understood. One postulate is that Cr(+3) serves as a crosslinking agent between the polymer molecules [11]. Another suggestion is that Cr(+3) forms a stable colloidal dispersion in the polymer solution, creating either a highly viscous liquid or a gel [61].

CHAPTER 3

CHAPTER 3

REQUIREMENTS OF GEL APPLICATIONS AND
PARAMETERS AFFECTING GELATION TIME

This chapter deals with the necessities in the field applications of the gelling polymer treatments as well as the affecting parameters in the gelation time. The methods of using gel systems for water shut-off treatments will first be explained [62-66]. After that, The factors affecting the gelation time considering the previous works [3,12-14] will be discussed.

3.1 *NECESSITIES IN THE FIELD APPLICATIONS
OF GEL TREATMENTS*

Most of the guidelines presented in this section are recommended by Allied Colloids Inc., a manufacturer of the gel polymers.

High production rates, especially when coupled with high water relative mobility, can lead to the formation of a watered out zone between the source of the water drive and a

production well. Once established the watered out zone dominates production and the well is usually either treated, converted into a water injector, or abandoned.

High success rates in gel treatments can not be achieved unless the problem being treated is adequately understood. Certain information is needed to determine what treatment is needed and how best to apply it. Specifically, in treating excess water production it is necessary to know where the water is coming from as well as the size and severity of the problem.

Fields which will benefit from the water shut-off treatment of wells using polymer based gels may be identified by an abnormally rapid or large rise in water production. The typical features are:

[1] High water disposal costs in fields having a dominant water drive mechanism, even though the mobility ratio is adequate and the field is new or has only produced a fraction of the estimated the original oil in the place.

[2] Excessive sand production problems associated with a medium to high water cut.

[3] A sharp rise in produced water cut relatively soon after commencing a water injection project.

All of these are symptoms of rapid water communication from the source of the water drive to the production wells. The study of the well selection criteria can identify the best candidate wells. Also, the objective of studying the wells before treatment is to confirm the source of the problem fluid.

Not all high water-cut producing wells are candidates for polymer treatment. Care must be exercised in choosing the target wells. The following well properties are useful guidelines for selection the candidates having the best chance for success.

[1] Wells displaying a high water/oil ratio, particularly where this high ratio results from water coning or from a high permeability bottom water zone.

[2] Individual wells in water drive reservoirs which initially had high oil production and little or no water production. This indicates that the production is not commingled and that a distinct zone exists through which the water reaches the well.

[3] Wells displaying a definitive water/oil contact and with a high fluid level. Water production from wells with a definitive oil/water contact below the well implies coning of water. Also, a high fluid level indicates prolific water production in excess of pump capacity. By reducing the water production, the fluid level will drop to give an increased pressure differential (drawdown) between the reservoir and the well. This leads to increase the oil production rate.

[4] Wells that have not been shut-in for a significant and recent period. The shut-in creates uncertainty about the current well performance and causes operational difficulties due to the well deterioration.

[5] Wells showing better permeability in the water zone than in the oil zone, wells where the oil/water interface lies below the producing zone and water production is from or controlled by the matrix flow.

Since these are some of the guidelines, it is not implied that each well will fit all of the criteria. In addition, it is the most important that the individual well problem and its causes are understood in order to be able to design a treatment program which addresses them specifically.

The selection of a treatment strategy consists of deciding on the economically and technically favoured options for achieving selective placement in the target zone and tailoring the size and shape of the gel plug to the problem.

Modern gel treatment formulations are designed to be robust and reliable. Such gels will set wherever they are placed and block the zones which they enter. Accordingly correct placement of the gels to achieve the desired effect is now one of the most important topics which can be addressed in the treatment planning. A number of options for achieving selectivity are currently available. The best option depends on the detailed geology of the well and many other factors such as availability of equipment.

The factors affecting the choice of methods used to achieve selective injection of gel into the target zone are: the geology of the zone to be treated; the nature of the well completion, i.e., open hole and cased well; the cost of a workover versus the budget available; and the oil price which affects the economics of the fluid balance technique.

The quantity of gel mixture required for the production well treatments can be estimated. The methods available for determining the size of bulk gel treatment required vary with the type of problem to be treated and the nature of the reservoir. One of the estimate for the treatment volume required can be made by assuming that the reservoir is homogeneous and planning a treatment penetration of up to fifteen meters radius from the production well. This is sufficient to ensure a successful treatment in the majority of cases. Also, the selection of the appropriate gel-time profile and the injected fluid viscosity allows the gel mixture to be injected into a watered-out zone.

The gel time required will vary significantly with the objective of the treatment. The gelation time of a treatment formulation can be used to control the shape of the gel barrier formed in the reservoir. The basis of the gelation time selection is to calculate how long the front of the gel treatment will take to reach the desired position, and add a margin for error. The elements contributing to the gel-slug travel time include: time in the surface equipment, wellbore transit time, and treatment zone transit time.

As the treatment progresses, it is often desirable to change the gelation time, for example to achieve directionality or

ensure uniform setting and minimum shut-in time. Consequently, the laboratory tests indicate how this can be achieved.

The following checklist can be used to assist the selection of a polymer gel system. Each of the points should be compared with the requirements decided on during planning.

[1] Is the gel system usable under the reservoir conditions? (I.e., temperature, salinity).

[2] Are the gel components acceptable under local environmental regulations?.

[3] Is the cost of the treatment acceptable? (Chemical + equipment).

[4] Can the required range of the gelation times be achieved?.

[5] Is the viscosity profile of the gel compatible with the planned process?.

[6] Is the final gel strength acceptable?.

3.2 *PARAMETERS AFFECTING GELATION TIME*

An experimental method of studying polyacrylamide/ chromium(+6) gelation was developed by many investigators [3,12,13] in an attempt to provide useful design data. They studied the effects of the concentrations and the types of reactants on the gelation time. It was based on continuous monitoring of the viscosity following addition of the chemical reactants.

The process in which polyacrylamide / chromium(+6) gel is used as a means to reduce formation permeability involves two steps in which a polymer slug containing chromium (+6) is injected into a reservoir. This slug is followed by a second slug of polymer containing a reducing agent. Upon mixing in the reservoir, chromium(+6) is reduced to chromium(+3), and a gel is created.

This process has been applied in near-wellbore treatments for both injection and producing wells. Some treatments have been successful while others have not [67]. The reasons for the mixed results are not well understood. In general, this system yielded better performance than the treatment with polymer alone.

The parameters affecting the gelation time may include polymer type, initial polymer and redox concentrations, salinity, and temperature. These affecting parameters can readily be obtained from the open literature [3,13]. The effects of these parameters are also shown in figures 3.1 through 3.5.

EFFECT OF POLYMER TYPE:

Gelation time was defined as the time required for the solution to reach a specified large viscosity. The gelation time changes with varying polymer type. In some cases, keeping the other affecting parameters such as the initial polymer concentration, redox concentration, and temperature, the gelation time varies within the range 10 to 100% such as a polymer type "Calgon 800", the reciprocal of the gelation time corresponding to the reciprocal of the initial polymer concentration is of the order of 0.10. However, in the case of polymer type "Calgon 815", it is 0.015 and this becomes 0.20 for polymer type "Calgon 825". This variation may be due to the degree of hydrolysis which is related to polyacrylamide systems, i.e., the degree of hydrolysis in the polymer types "Calgon 800", "Calgon 815", and "Calgon 825" are 0%, 15%, and 25% respectively. It should be noted that the average molecular weight of the three polymer types

is the same and equal to 3×10^6 . Therefore, the effect of the average molecular weight of the polymer type is not effective in the gelation time.

EFFECT OF INITIAL POLYMER CONCENTRATION:

Figure 3.1 shows the variation of the initial polymer concentration with the gelation time. It is evident that increasing the initial polymer concentration decreases the gelation time. This variation shows a non-linear relation that exists between the gelation time and the initial polymer concentration. It can also be seen from the Figure 3.2 that keeping the initial polymer concentration constant while decreasing the redox concentration results in increasing the gelation time. As a result, a linear relationship was found to exist between the reciprocal of the gelation time and the reciprocal of the initial polymer concentration for a given chemical system [Figure 3.3]. The slope of this linear relation varies with the degree of hydrolysis, the anionic or cationic character of the polymer, and the type of reducing agent. All of these findings were for a constant temperature and fixed brine concentration. Moreover, Their studies revealed that the gelation time became more sensitive to change in polymer

concentration as the degree of hydrolysis of the polymer increased.

EFFECT OF REDOX CONCENTRATION:

The variation of the gelation time with the redox concentration is shown in the Figure 3.2. The increasing of the redox concentration results in decreasing the gelation time. Longer gelation times are obtained as the redox concentration decreases while holding the initial polymer concentration constant. This may be explained in terms of the kinetic theory approach [3]. From the kinetic theory, for certain order of the reaction, the time required to achieve a given extent of reaction decreases with increasing the initial reactant concentration.

EFFECT OF TEMPERATURE:

Figure 3.4 shows the variation of gelation time with temperature. The gelation time was found to decrease with increasing temperature. This relation could be correlated by an Arrhenius-type plot [Figure 3.5] in which a linear relationship exists between the logarithm of the gelation time and the reciprocal of the absolute reaction temperature. This results in considerable error for high values of redox concentration.

EFFECT OF THE SALINITY:

Jordan et al. [13] showed that the gelation time varies in a parabolic form with the salinity. The gelation time is a function of NaCl concentration. The time decreases slightly with increasing salt concentration up to approximately 5,000 - 10,000 ppm and then increases as salt concentration is increased.

To sum up, the correlations are needed which would relate characteristics such as the gelation time to design parameters that include the system's chemicals composition. Moreover, the behavior of the gelling system could also be predicted if the gelation reaction is clearly understood [67,68].

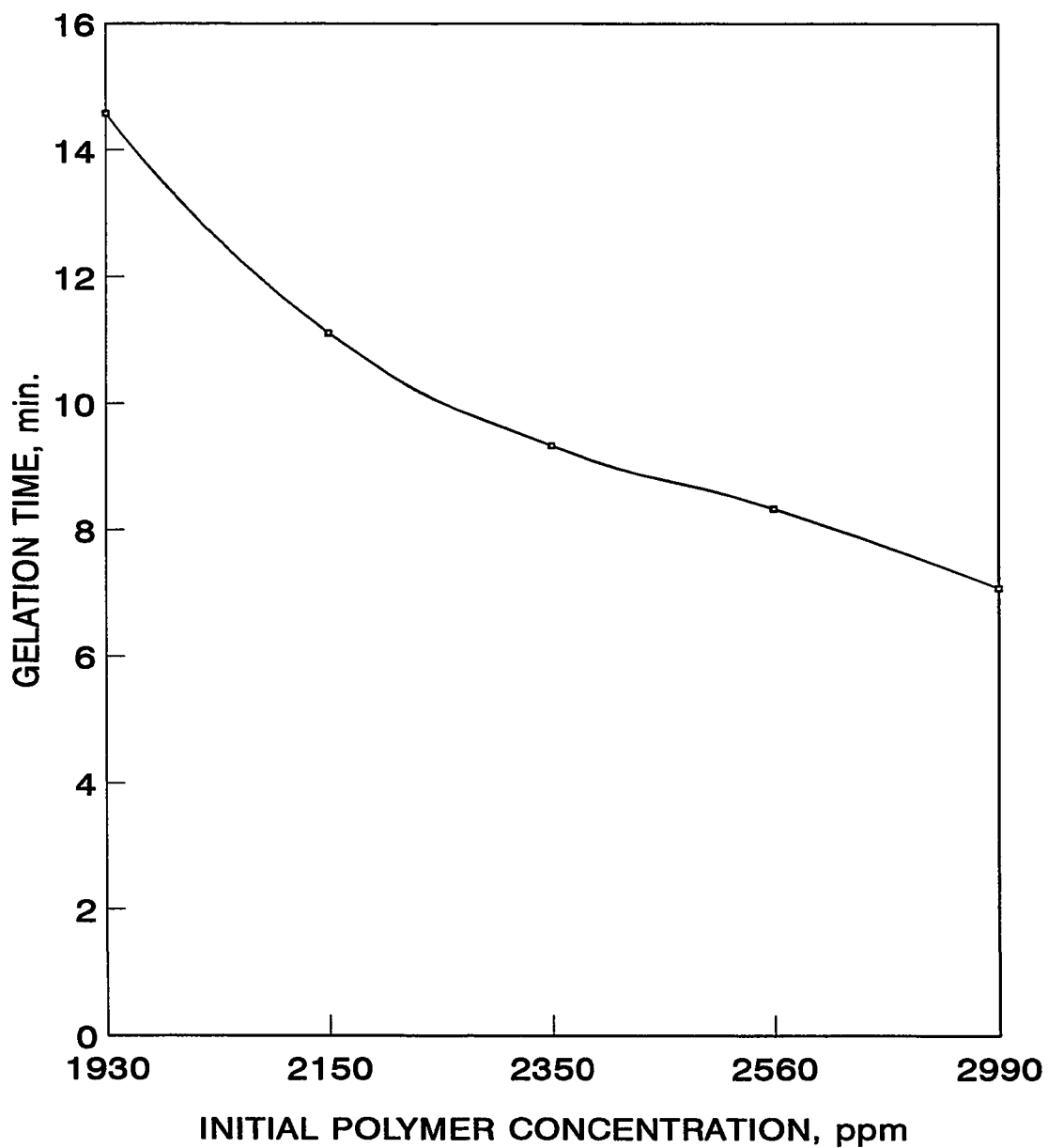


Figure 3.1 Gelation time versus initial polymer concentration at constant redox concentration for polymer type "Calgon 800" (similar trend for the other polymer types), by Terry et al. 1981

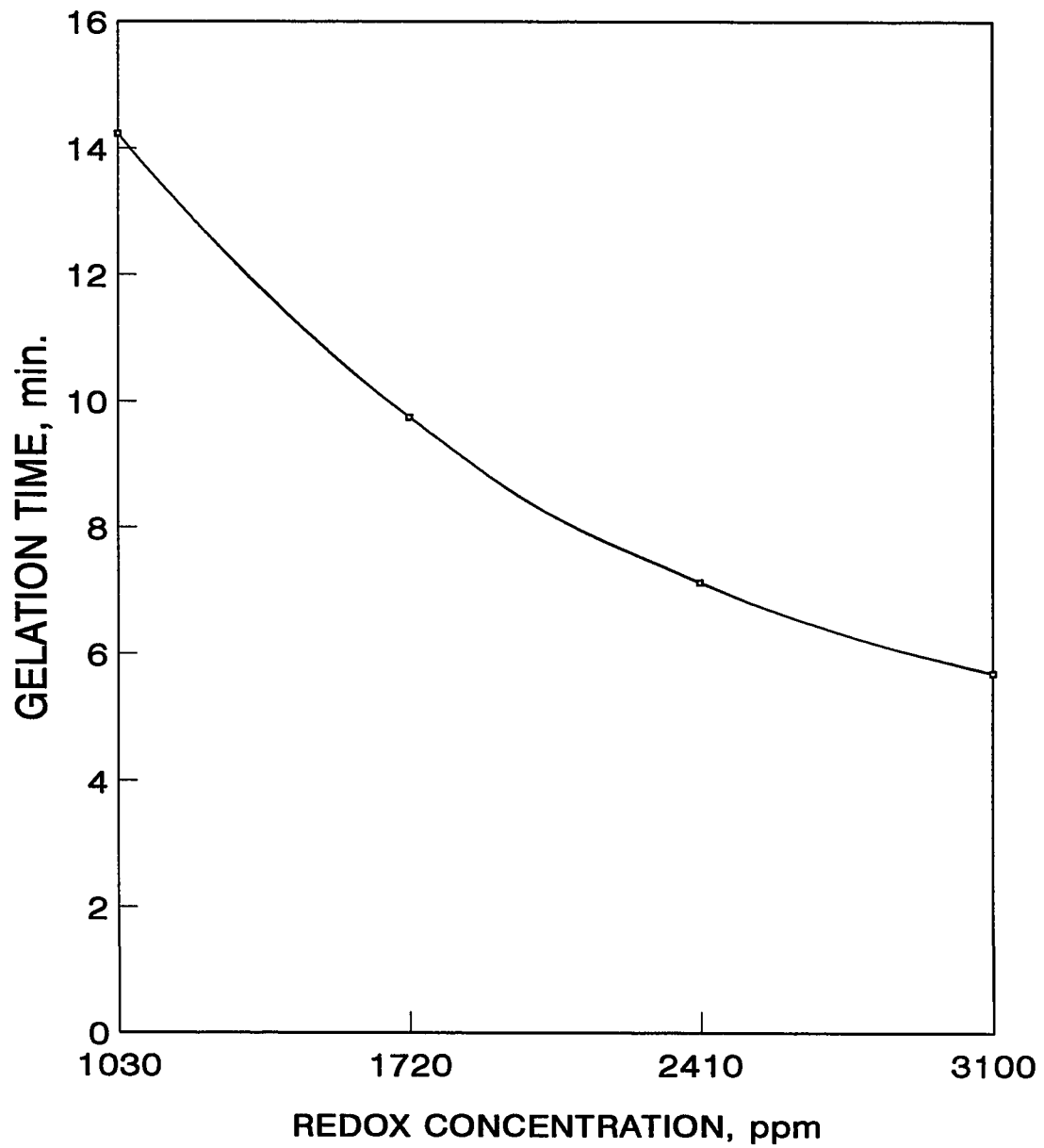


Figure 3.2 Gelation time versus redox concentration at constant initial polymer concentration for polymer type "Calgon 800" (similar trend for the other polymer types), by Terry et al. 1981

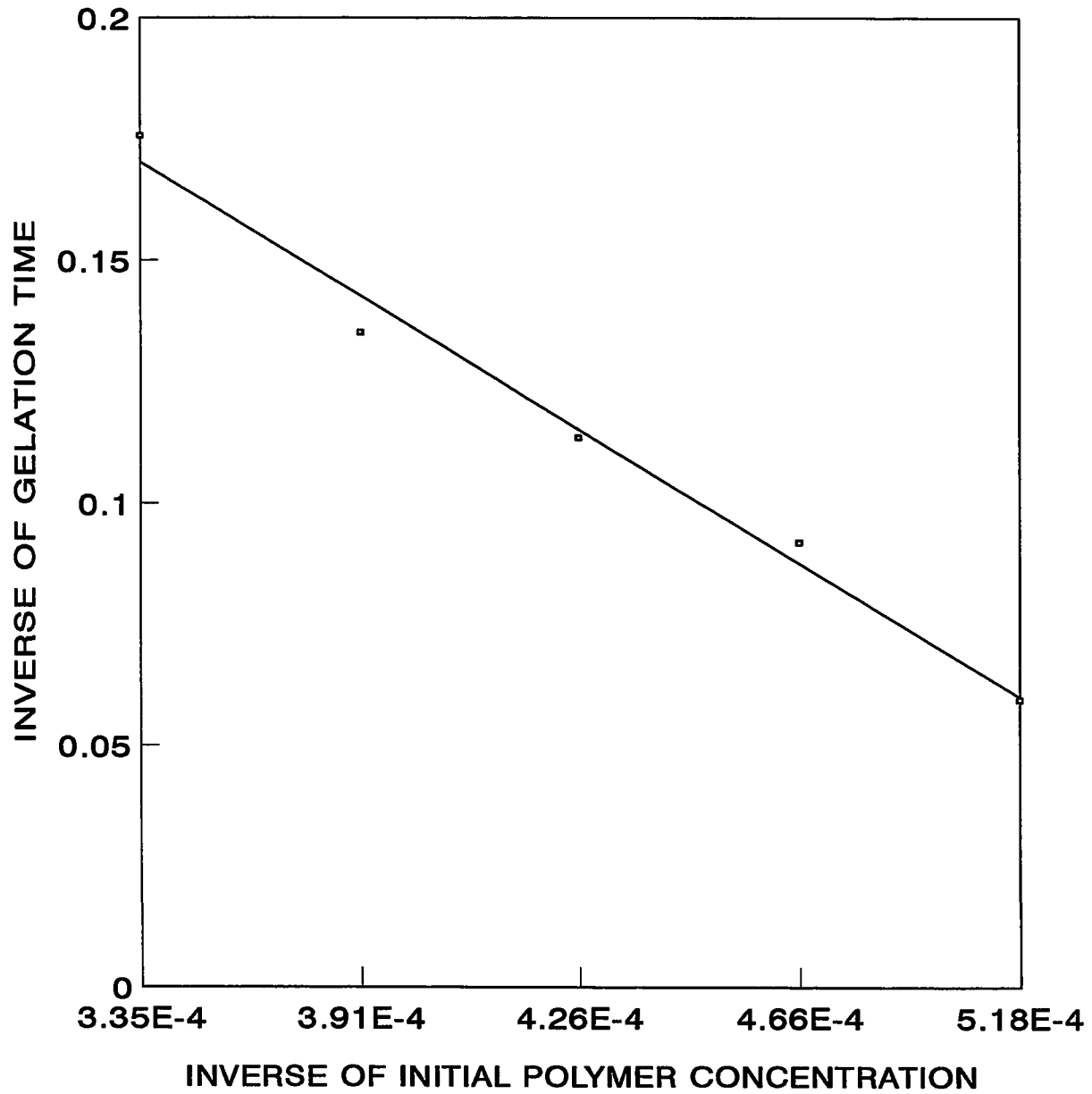


Figure 3.3 $1/\text{gelation time}$ versus $1/\text{initial polymer concentration}$ at constant redox concentration for polymer type "Calgon 800" (similar trend for the other polymer types), by Terry et al. 1981

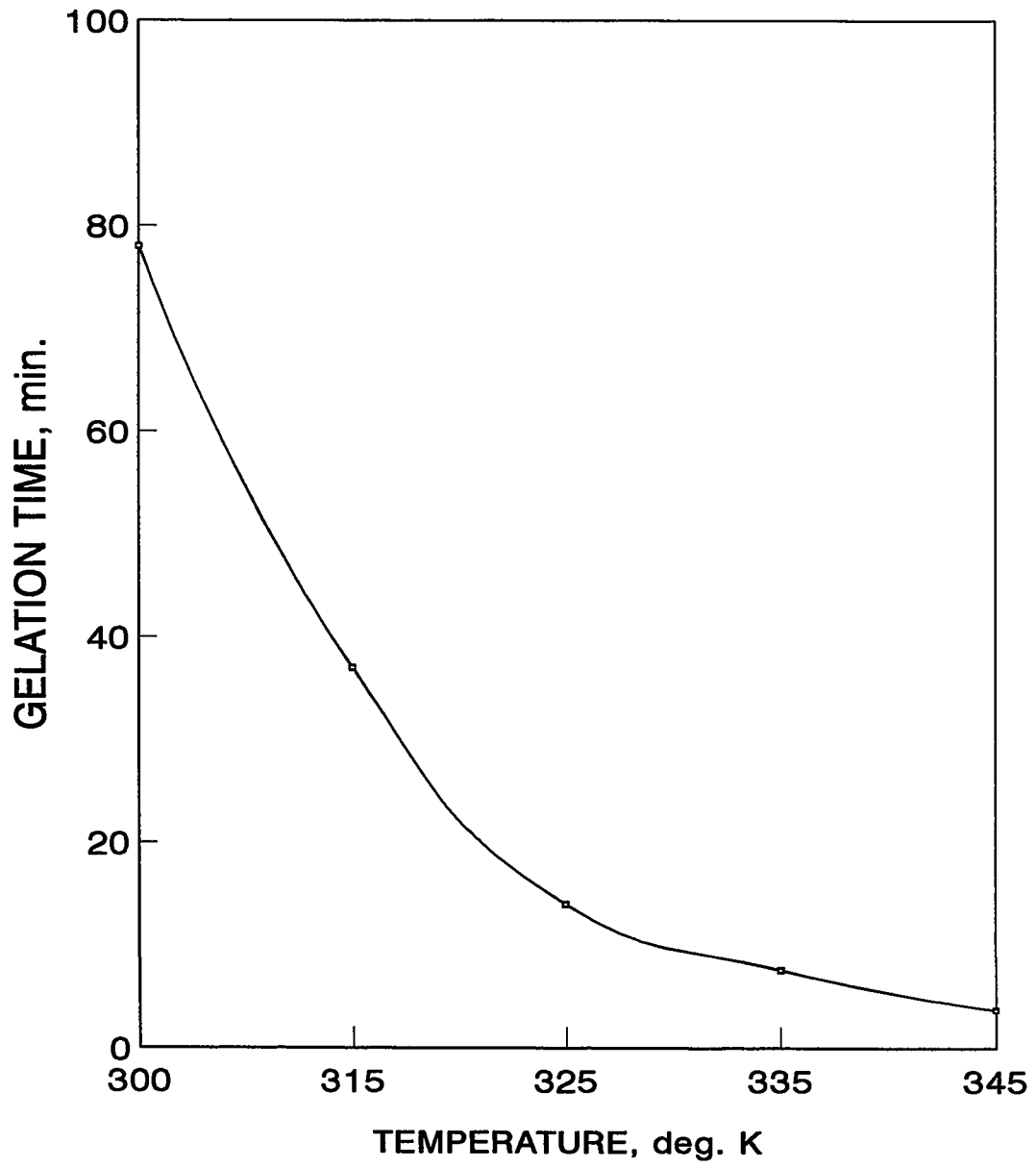


Figure 3.4 Gelation time versus temperature at Cl = 1724 ppm & CR = 1724 ppm for polymer type "Calgon 340" (similar trend for the other polymer types), by Jordan et al. 1981

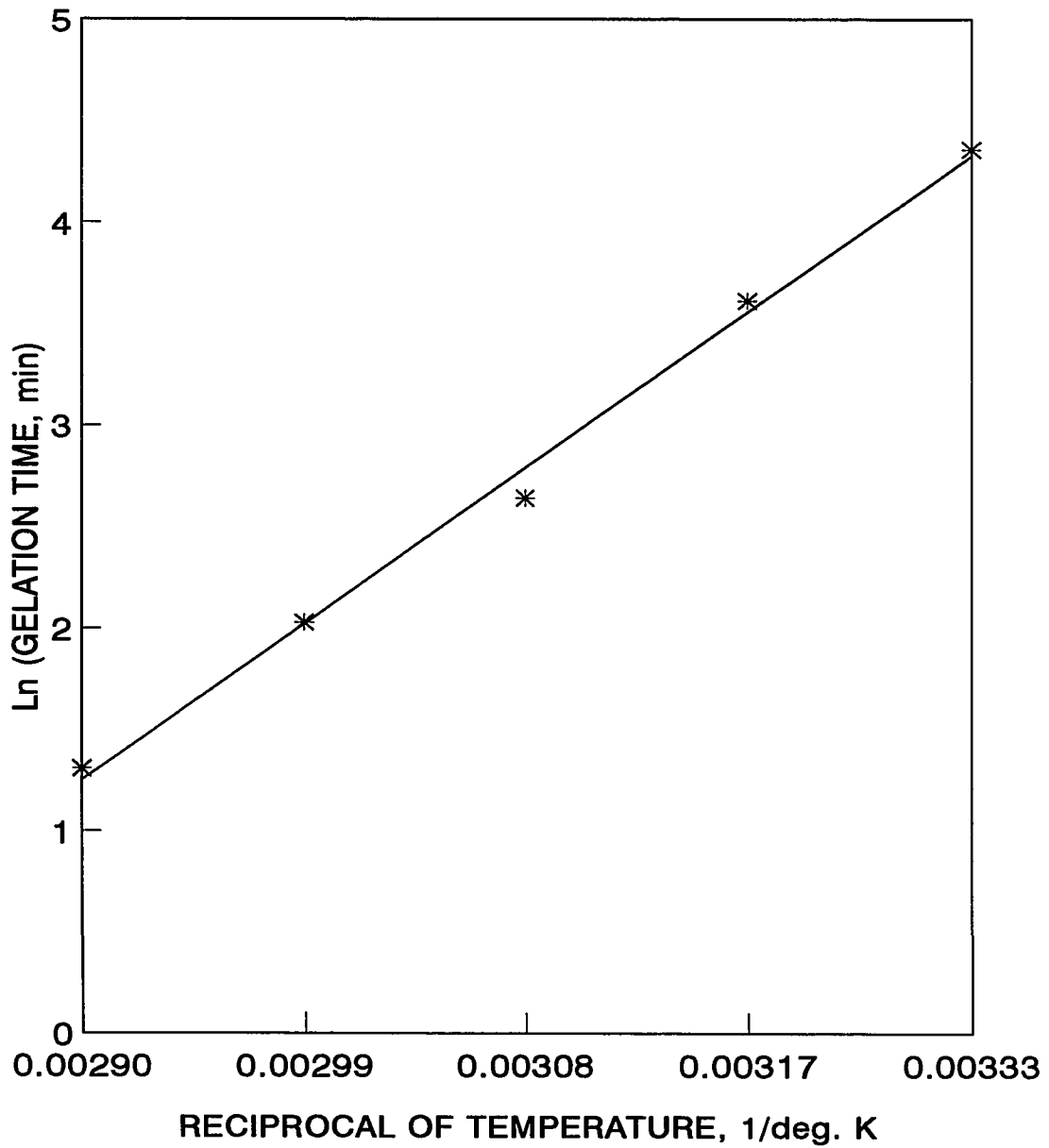


Figure 3.5 Natural log of gelation time versus 1/temperature at Cl = 1724 ppm & CR = 1724 ppm for polymer type "Calgon 340" (similar trend for the other polymer types), by Jordan et al. 1981

CHAPTER 4

CHAPTER 4

MATHEMATICAL MODELLING

Before presenting the mathematical modeling, I would like to discuss briefly the preparation of the polymer solution and the properties of the selected chemicals investigated in this study as well as the different gelling polymer systems and data employed. These data are extracted from the early works [3,13,69,70].

4.1 CHEMICALS USED FOR THIS STUDY

Polymer type	Average molecular weight	Characteristics
Calgon 800	3.0×10^6	nonionic linear polyacrylamide
Calgon 815	3.0×10^6	linear polyacrylamide with 15% degree of hydrolysis
Calgon 825	3.0×10^6	linear polyacrylamide with 25% degree of hydrolysis
Calgon 340	3.9×10^6	anionic polyacrylamide with zero degree of hydrolysis
Betz 1160	5.0×10^6	cationic polyacrylamide with 20% positive charge density

Table 4-1 Some properties of the polymers used in this study (by Terry et al. 1981)

Table 4.1 contains a list of the polymers investigated and some of their pertinent properties. Calgon 800, 815, and 825 are all linear polyacrylamide and have the same molecular weight, 3.0×10^6 , but vary in degree of hydrolysis. The degree of hydrolysis are 0, 15, and 25 percent for Calgon 800, 815, and 825, respectively. Calgon 340 is a non-hydrolyzed copolymer of acrylamide with a molecular weight of 3.9×10^6 . The other monomer unit is a 2-acrylamido-2-methyl propane sulfonate. Betz 1160 is a non-hydrolyzed cationic polymer with a 20 percent positive charge density.

The hexavalent chromium was introduced to the system as sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$). Although several reducing agents are capable of reducing the hexavalent chromium to trivalent chromium ions, only one reducing agent, sodium bisulfite (NaHSO_3), was selected for this study. These were reagent grade quality and used as obtained. Sodium dichromate and sodium bisulfite were always in a 1:1 weight ratio. The hexavalent chromium and reducing agent will be referred to as the redox system.

The gelled polymer process under consideration involves a polyacrylamide polymer, a reducing agent, and a metal ion.

The combination of chemical ingredients for the work involved in this study is shown in the next table 4.2.

System	Polymer	Gelling Agent	Reducing Agent
1	Calgon 800	sodium dichromate	sodium bisulfite
2	Calgon 815	sodium dichromate	sodium bisulfite
3	Calgon 825	sodium dichromate	sodium bisulfite
4	Calgon 340	sodium dichromate	sodium bisulfite
5	Betz 1160	sodium dichromate	sodium bisulfite

Table 4-2 The chemical system used for gelation tests (Jordan et al. & Terry et al. 1981)

4.1.1 PREPARATION OF THE POLYMER SOLUTION

The key point for properly preparing polyacrylamide solution is that the polymer particles must be thoroughly wetted during the initial dispersion of the sample. A satisfactory dispersion can be achieved with an ordinary laboratory , magnetically driven stirrer.

To prepare the polymer solution, mixing is the first step. The dry polymer must be sprinkled uniformly onto the shoulder of a well-developed vortex of 2% NaCl solution

within 60 seconds. As soon as all the polymer has been added, the stirrer is slowed down to a low speed in order to avoid shear degradation. The low speeds used in their studies were about 70 and 240 rpm for Calgon polymers and the Betz 1160, respectively.

After the fish-eye created by the polymer powder disappears, the stirrer is turned off. It usually takes one or two days for stirring process to be completed. Then, the polymer solution is stored in a dark place for one day or more before dilution.

The next step is that the polymer solution should be diluted. The polymer prepared in the first step is usually a concentrated one, such as 5000 ppm. It is diluted to the specified concentration. Before dilution, it is stirred at a low speed for 20 minutes. Then, a certain volume of polymer solution is introduced into a bottle which already contains a certain volume of a 2% NaCl solution. The bottle is gently agitated for about 2 minutes, and is stored in a dark place at least one day before the solution is used.

The last step is the viscometer reading. When the equipment has been set-up and the polymer solution has been prepared, the experiments can then be conducted. The

experimental procedure is basically separated into the following two parts. These are preparatory work and monitoring of the gelation reaction.

The former part is to make sure that the system is ready to measure the viscosity. First of all, temperature of water in the water bath should be checked. The cooling water valve is opened and maintained temperature of the cooling water is much lower than 25 °C. The thermal-jacketed beaker is connected to the constant-temperature water bath through the circulation system. The power of the water-bath system is turned on. The water circulates through the beaker and must be heated to set value. Lastly, the solution containing the specified concentration of sodium dichromate and reducing agent should be prepared.

The latter part is to conduct the gelation tests and obtain the results. When the water bath arrives at the desired temperature, the gelation process can be started.

The operational procedure is as follows:

The polymer solution stored in the bottle is totally introduced into the thermal-jacketed beaker. Then, 8 ml of dichromate solution is pipetted into the beaker. After that,

the mixed solution is gently agitated with a piece of metal until it becomes homogeneous and its temperature reaches the set one. A thermometer is used to check the solution temperature. A reducing agent solution which is at the desired temperature is then introduced very quickly into the beaker. The mixed solution is agitated very quickly to homogeneity. The reaction time is counted as soon as the reducing agent solution is injected . Continue to measure solution viscosity until the viscometer reading becomes very large.

4.1.2 DATA OF THE GELLING POLYMER SYSTEMS

As shown in table 4.2, System-1 consists of Calgon 800, sodium dichromate, and sodium bisulfite. Calgon 800 is a nonhydrolyzed polyacrylamide homopolymer. It contains only amide groups along the carbon backbone. The concentrations of Calgon 800 were originally prepared as 2990, 2560, 2350, 2150, and 1930 ppm. All the viscosity reading-time curves show the same tendency that the viscosity remains constant for a period of time, then increases very rapidly. The gelation time was determined for each experiment from the

viscosity reading-time curves. Table 4.3 lists the average gelation times as a function of chemical concentrations.

System-2 involves Calgon 815, sodium dichromate, and sodium bisulfite. Calgon 815 is a hydrolyzed polyacrylamide with 15 percent degree of hydrolysis and therefore contains carboxylate groups along the carbon backbone as well as amide groups. The acrylate group occupies 15% and the acrylamide group 85% of the monomeric units. It was found that the gelation times were less reproducible in the high polymer concentration region than in the lower region. This is thought to be caused by the difficulty in bringing the solution to homogeneity in a very short time, when the solutions were mixed together, due to the viscosity of the polymer solution. This agitation effect would not be serious if the gelation times are long enough. Table 4.4 gives the average gelation times.

System-3 deals with Calgon 825 polymer, sodium dichromate, and sodium bisulfite. Calgon 825 is a hydrolyzed polyacrylamide with 25 percent degree of hydrolysis. Similar to the system of Calgon 815, the gelation time data at high polymer concentrations are less reproducible because the solutions are viscous and gel in a short time. The average gelation times are given in table 4.5.

System-4 includes Calgon 340, sodium dichromate and sodium bisulfite. The previous systems were concerned with homopoly-acrylamide polymers with different degree of hydrolysis. Calgon 340 is an anionic polymer with zero degree of hydrolysis. The molecular structure consists of 2-acrylamido-2-methyl propane sulfonate besides acrylamide. The average gelation times are listed in Table 4.6.

Table 4.7 gives variation of gelation time with temperature and redox concentration for system-4. This table is used to develop a mathematical relation between gelation time and temperature-redox concentration.

System-5 includes Betz 1160, a cationic polyacrylamide copolymer, sodium dichromate, and sodium bisulfite. Betz 1160 is a cationic polymer composed of quaternized cationic monomers as well as acrylamide. The positive charge of this polymer is reported to be 20 percent. The average values for the gelation times are given in Table 4.8.

4.2 FACTORIAL ANALYSIS

The present section gives insight the mathematical study of the affecting parameters and resulting gelation time. Statistical analysis is introduced as a first step. This provides understanding of most affecting parameters and their possible interactions. This also forms a base to develop an empirical relation between the most affecting parameters and resulting gelation time. As a second step, dimensional analysis is used to form dimensionless groups. Finally, a regression analysis is presented to develop an empirical relation between the groups and the gelation time.

With factors at three or more levels the main effect is represented by differences or comparisons between the means corresponding to different levels of the factors, and it can be expressed in several ways. For three levels with means y'_1 , y'_2 , y'_3 , possible differences are $y'_1 - y'_2$, $y'_2 - y'_3$, $y'_1 - y'_3$, $y'_1 - 0.5(y'_2 + y'_3)$, $y'_2 - 0.5(y'_1 + y'_3)$, and so on. Between three independent quantities there are two independent comparisons; the comparisons of interest will depend upon the nature of the factors, in particular whether they are qualitative (i.e., discontinuous) or quantitative.

For qualitative factors in which one level denotes a control with many y'_1 and the other two denote treatments, the comparisons of interest are either $y'_2 - y'_1$ and $y'_3 - y'_1$, or $y'_3 - y'_2$ and $y'_1 - 0.5(y'_2 + y'_3)$. The last comparison measures the extent to which the average of the two treatments differs from the control.

For quantitative factors where, by definition, the levels denote points on a numerical scale, e.g., the temperature scale, there may be a functional relation between the responses and the level of the factor, and the comparisons of interest will be those giving the most information on this relation, e.g., the slope and the curvature. It is usually desirable to determine whether or not this relation changes with the different conditions of the other factors.

There are four types of factorial design that cover most situations likely to be encountered in industrial research. These are as follows:

1. A multifactorial experiment with all factors qualitative.
2. A two-factor experiment with one factor qualitative and one quantitative.

3. A two-factor experiment with both factors quantitative.
4. Experiments with several factors, quantitative or qualitative, all at three levels.

The first stage in the analysis of a factorial design is the same, whether the factors are qualitative or quantitative.

4.2.1 FACTORIAL DESIGN AND F-TEST

Understanding the gelation parameters which affect the gelation time, relies on experimentation. The present study investigates the parametric effect of the relevant parameters on the gelation time by a statistical approach referred to as factorial design. The approach permits the relative importance of the factors to be assessed. The mathematical model representing the present analysis is:

$$GT_{ijk} = \mu + PT_i + CR_j + CI_k + (PT \times CR)_{ij} + (PT \times CI)_{ik} + (CR \times CI)_{jk} + \epsilon_{ijk} \quad (4.1)$$

Where GT represents the response (gelation time), μ is a common effect, PT is the polymer type, CR is the redox concentration, CI is the initial polymer concentration,

$(PT \times CR)_{i,j}$ is the first order interaction of polymer type and redox concentration, $(PT \times CI)_{i,k}$ is the first order interaction of polymer type and initial polymer concentration, $(CR \times CI)_{j,k}$ is the first order interaction of redox concentration and initial polymer concentration, and $\epsilon_{i,j,k}$ is the random error in the data while i , j , and k are the levels of the corresponding factors.

In the present study and based on the table produced, the values of i , j , and k are 5, 4, and 5, respectively. The properties of the five polymer types are given in table 4.9, and the range for the selected parameters are listed in table 4.10.

Since there are no repeat determinations and no independent estimates of the error variance, it is necessary to use the remainder (second order interaction) as an error variance. Hence, it is relegated to the error term by making the assumption that the interaction is equivalent to the remainder. Furthermore, the significance of each effect is tested by the initial hypothesis that the mean squares of the effects are from the same population as the error mean squares. Since the mathematical model for this analysis is a fixed and not random model. The expected mean squares for the main effects are all estimates of the error mean

variance. Hence, the mean squares for the main effects can be compared with the error mean square to test the respective hypothesis by means of an F-test.

The level of the significance depends on the particular problem being considered. In the present study 10, 5 and 1% are adopted to the given results which are significant, very significant, and highly significant, respectively. The definition of the variance ratio, $F_{p,q}$, is:

$$F_{p,q} = \frac{\text{mean sum of squares}}{\text{error mean sum of squares}} \dots\dots\dots (4.2)$$

where p and q are the degrees of freedom of the mean sum of the squares and the error mean sum of the squares, respectively.

4.3 MULTIPLE REGRESSION ANALYSIS

We now consider a powerful and comprehensive methodology for analyzing relationships between quantitative variables called regression analysis. Regression analysis is

concerned with the relation between a quantitative variable of interest, called the dependent variable or response variable, and one or more other variables called independent, explanatory, or predictor variables.

We begin with the concept of a relation between a dependent variable, to be denoted by Y , and one independent variable, to be denoted by X . It is useful to distinguish between a functional relation and a statistical relation.

A functional relation between a dependent variable Y and an independent variable X is an exact relation; the value of Y is uniquely determined when the value of X is specified. However, a statistical relation between a dependent variable Y and an independent variable X is an inexact relation; the value of Y is not uniquely determined when the value of X is specified.

In many situations, two or more independent variables are needed in a regression model to provide an adequate description of the process under study or to yield sufficiently precise inferences. Regression models containing two or more independent variables are called multiple regression models. A commonly used mathematical technique for analyzing data with more than two variables is

derived by applying the least-squares principle between one dependent variable and several independent variables.

The simple linear regression model can be extended directly to include two independent variables, X_1 and X_2 .

$$Y_i = \beta_0 + \beta_1.X_{i,1} + \beta_2.X_{i,2} + \varepsilon_i \quad i=1,2,\dots,n \quad \dots\dots (4.3)$$

Where Y_i is the response in the i th case, $X_{i,1}$ and $X_{i,2}$ are the values of the two independent variables in the i th case, assumed to be known constants, and β_0 , β_1 , and β_2 are parameters. As for the simple linear regression model, we are assuming here that the error terms ε_i are independent normal random variables, with mean zero and constant variance σ^2 .

For explanation purposes, consider two independent variables "CR" redox concentration, and "CI" initial polymer concentration, in relation to the yield "GT". The regression method will minimize the residual deviations, i.e. it will give the best fit for this particular set of data. For regression model (4.3), the estimated regression function is as follows:

$$GT_i = a + b.CR_i + c.CI_i \quad \dots\dots\dots (4.4)$$

Here, a , b , and c are the least square estimators of the parameters β_0 , β_1 , and β_2 . The method of least squares leads to a system of normal equations for obtaining a , b , and c , as follows:

$$\sum GT_i = n.a + b.\sum CR_i + c.\sum CI_i \quad \dots\dots\dots (4.4a)$$

$$\sum CR_i.GT_i = a.\sum CR_i + b.\sum CR_i^2 + c.\sum CR_i.CI_i \quad \dots\dots\dots (4.4b)$$

$$\sum CI_i.GT_i = a.\sum CI_i + b.\sum CR_i.CI_i + c.\sum CI_i^2 \quad \dots\dots\dots (4.4c)$$

The least squares estimates are obtained by solving this system of equations simultaneously. Statistical regression package used in this study called STATGRAPH, gives these estimates as part of its output. However, the coefficients b and c can be calculated from the correlation coefficients ($r_{GT \cdot CR}$, $r_{GT \cdot CI}$, $r_{CR \cdot CI}$), and the standard deviations (S_{GT} , S_{CR} , S_{CI}) of the variables. Therefore, the coefficient b , here is called the partial regression of GT and CR , is given by:

$$b = \frac{r_{GT \cdot CR} - r_{GT \cdot CI} \times r_{CR \cdot CI}}{1 - r_{CR \cdot CI}^2} \times \frac{s_{GT}}{s_{CR}}$$

If CR and CI are not correlated, the coefficients "b" and "c" simplify to the ordinary regression coefficients of GT on CR and GT on CI. The intercept-coefficient "a" is determined by forcing the equation to go through the overall mean values of all three variables.

4.3.1 COEFFICIENTS OF MULTIPLE DETERMINATION

The fit of a multiple regression equation is expressed in a different manner, namely in terms of the multiple correlation coefficient R^2 . The square root of R^2 is another descriptive measure of the degree of linear statistical relation between CR, CI, and GT. It could also be defined as the correlation between the measured values of GT and the estimated values using the developed equation. The R^2 can range from 0 to 1. It can be interpreted like the ordinary product-moment correlation coefficient given by:

$$R^2 = 1 - \frac{\text{residual variance}}{\text{variance of GT}} \dots\dots\dots (4.5)$$

If the correlation is satisfactory, the R^2 value is expected to be close to one.

The resulted empirical equation using multiple regression analysis may be introduced as follows: In the first step, an attempt is made to develop a polynomial relation between the gelation time and process variables. After considering so many combinations of the variables in the equation, the regression analysis leads to the following equations giving the minimum errors. Therefore, this results:

$$GT = a_0 + a_1 x (1/CI) + a_2 x (1/(CRxCI)) + a_3 x (1/CR) \dots \quad (4.6)$$

In the above equation combination of $(1/CRxCI)$ is introduced as a third term.

In order to develop the relation employing exponential function, the following relation is produced.

$$GT = b_0 + b_1 x (\exp(CI/CR)) + b_2 x (CI/CR) + b_3 x (CI/CR)^3 \dots \quad (4.7)$$

Where the $[\exp(CI/CR)]$ is employed as a second term.

On the other hand, with the data available (table 4.7) an empirical equation employing temperature is developed, i.e.:

$$GT = c_0 + c_1 \times CR + c_2 \times (1/T)^2 + c_3 \times \exp(1/T) + c_4 \times (CR/T) \dots (4.8)$$

To achieve the multiple regression analysis a software called STATAGRAPH was used. This provided the coefficients and power of the dimensionless groups in the resulting equations. It is a powerful software package which enables us to obtain a correlation coefficient as well as the relative error resulted for the equations.

The statagraphics which stands for the Statistical Graphics System is a unique PC software package integrating a wide variety of statistical functions with high-resolution color graphics. Statgraphics provides access to graphics from within most of the statistical procedures, making it easy for the scientist to explore the data more fully from both numerical and graphical perspectives. The statagraphics is intended for use in a broad range of industrial, service, and educational applications by data analysts familiar with the concepts underlying the procedures. Industrial engineers, quality control engineers, statisticians, market

analysts, business analysts, operations researchers, educators, students, and others can benefit from the comprehensive data analysis capabilities statgraphics offers.

In the present study, the statgraphics software is used to carry out regression analysis. This provides an empirical equation developed between the response (gelation time) and the source variables (redox concentration, initial polymer concentration, and temperature)

4.4 *DIMENSIONAL ANALYSIS TECHNIQUES*

All variables used in Science or Engineering are expressed in terms of a limited number of basic dimensions. For most engineering problems the basic dimensions are either mass, length, time, and temperature. In 1915, Buckingham [34] showed that the number of independent dimensionless groups of variables (dimensionless parameters) needed to correlate the variables in a given process is equal to $q-u$, where q is the number of variables involved and u is the number of basic dimensions included in the variables. Dimensional homogeneity requires that each term

in a given equation have the same units. Then, the ratio of each one term in the equation to another term is dimensionless. Knowing the physical meaning of each term in the equation, we are then able to give a physical interpretation to each of the dimensionless parameters or numbers formed.

The method of obtaining the important dimensionless numbers from the basic differential equations is generally the preferred method. In many cases, however, we are not able to formulate a differential equation which can be clearly applied. A more general procedure known as the Buckingham method is required. In this method the listing of the important variables in the particular physical problem is done first. Then we determine the number of dimensionless parameters into which the variables combined by using the Buckingham theorem. Therefore, the dimensional analysis is often used to group the variables in a given physical situation into dimensionless parameters or numbers which can be useful in experimentation and correlating data.

The Buckingham theorem states that the functional relationship among q quantities or variables whose units may be given in terms of u fundamental units or dimensions may be written as $q-u$ independent dimensionless groups, often

called π 's. This type of analysis is useful in empirical correlation of data. However, it does not tell us the importance of each dimensionless group, which must be determined by experimentation, nor does it select the variables to be used.

4.4.1 METHODS OF DEVELOPING DIMENSIONLESS GROUPS

There are two methods to develop dimensionless groups, namely: the step-by-step method and the exponent method.

4.4.1.1 THE STEP-BY-STEP METHOD

This method is very clearly presented by Ipsen [36]. The basic objective in this method is to reduce the number of separate variables involved in a problem to a smaller number of independent dimensionless groups of variables. The rationale for this is that all rational equations can be nondimensionlized and that all rational equations have a certain number of independent terms in them. Thus, by the procedure of dimensional analysis, one can simply arrange variables into a dimensionless equation. In the process of combining the variables to form dimensionless groups or

terms, the number of independent variables obtained is less than the number of original variables.

4.4.1.2 THE EXPONENT METHOD

Once the significant variables have been identified, dimensionless parameters may be formed. A set of algebraic simultaneous equations have been solved in which derive from the requirement of dimensional homogeneity for equations describing physical systems. This will be referred to as the exponent method.

4.5 *PROCESS OF DIMENSIONAL ANALYSIS*

The procedure of dimensional analysis may be outlined as follows:

- 1] Identify all significant variables associated with the problem and include them in the functional equation, such as:

$$GT = f(u, v, w, x, y) \quad \dots\dots\dots \quad (4.9)$$

where u, v, w, x, and y are the affecting parameters.

2] Combine one variable that includes a given dimension with other variables having that same dimension in such a way as to eliminate that dimension.

3] choose another variable to combine with other variables and groups of variables to eliminate a second dimension.

4] Repeat the process until the entire equation consists of dimensionless groups as parameters.

If the exponent method is used, a set of algebraic equations for exponents of the physical variables that satisfy dimensionless homogeneity is developed. Three exponents (for systems with three dimensions) are related and solved for in terms of the remaining exponents. Substituting the three exponents back into the combination of physical variables yields the dimensionless parameters.

5. The final form will appear something like the following.

$$\Pi_1 = f(\Pi_2, \Pi_3, \dots \Pi_{q-u}) \quad \dots\dots\dots \quad (4.10)$$

where $\Pi_1, \Pi_2, \Pi_3, \Pi_{n-m}$ represent the dimensionless parameters obtained, q is the number of variables, and u is the numbers of dimensions included in the list of variables.

In our case, use of the step-by-step method provides simplicity in mathematical arrangements, since the factors involved have the same units. Consequently, exponential method described previously has not been considered here.

In applying the step-by-step method in the present case, the function for the gelation time and the factors can be written as:

$$GT = f_1 (CR, CI) \quad \dots\dots\dots \quad (4.11)$$

It is evident from the above function that, the factors can be made non-dimensional form by dividing one factor to other.

Since both factors have the same dimensional units, i.e.,: [CR/CI] and/or [CI/CR]

However, once this is carried out, it becomes difficult to arrange table 4.11 such that it can possibly be used in developing power relations between the gelation time and the factors. Therefore, simplification in arrangement of table

4.11 can become possible when the following arrangement is made:

$$CRN = CR/CR_0$$

and

$$CIN = CI/CI_0$$

where "CRN" and "CIN" are the non-dimensional form of redox and initial polymer concentrations respectively. CR_0 and CI_0 are the first values of redox and initial polymer concentrations respectively. Hence, the functional form for the gelation time and the non-dimensionalized factors becomes:

$$GT = f_2(CRN, CIN) \dots\dots\dots (4.12)$$

Consequently, Table 4.12 is produced to give sets of data for the gelation time and CRN and CIN. The dimensional analysis presented in the present work provides dimensionless group in terms of concentration ratios. This is due to the number of affecting variables, which are only four. Therefore, the resulting dimensionless group includes: $CIN = CI/CI_0$ and $CRN = CR/CR_0$.

4.6 POWER RELATIONS

Petroleum engineering is more heartily involved with empirical work than other engineering disciplines because the analytical tools presently available are not capable of yielding exact solutions to many of the problems in Petroleum Engineering. It is true that exact analytical solutions may be available for well established topics in Petroleum Engineering. However, due to the experimental studies, empirical approach becomes fruitful to employ to develop an empirical relation. Consequently, power relations become an alternative empirical method to correlate the existing data.

To develop an empirical relation between the dimensionless group and the resulting gelation time, two attempts were made.

In the first attempt, power relation is introduced. The power relation may result in the following equation:

$$GT = K \times [(CI/CI_0)^m] \times [(CR/CR_0)^n] \quad \dots\dots\dots (4.13)$$

Due to the scattering nature of the data and the corresponding gelation time, the error related to this approach becomes higher and reaches to unacceptable values. Therefore, this approach is disregarded.

In the second attempt, a power relation in the polynomial form is introduced. A polynomial form between the gelation time and the dimensionless group is considered for each polymer type. The initial polymer concentration is divided by the first value of the initial polymer concentration for a given redox concentration. This process is then repeated for the other redox concentrations. This provides dimensionless groups formed in terms of initial polymer concentration. This results in a gelation time in the form of:

$$GT = C + K_1 [CI/CI_0] + k_2 [CI/CI_0]^2 \quad \dots\dots\dots (4.14)$$

To develop a single equation governing the given polymer type and including the dimensionless groups, a polynomial equations governing the coefficients were introduced. In this case, a polynomial equation between the coefficients and the redox concentration is introduced, i.e., the parameter CR/CR_0 is introduced. Consequently,

three polynomial equations for the coefficients are developed for each constants in Equation 4.13. A computer program is developed to determine the coefficients of equation 4.14 (appendix-B) and table 4-12 is used to feed the computer program. Therefore, the final and general form of the polynomial equation is:

$$GT = X + Y + Z \quad \dots\dots\dots (4.15)$$

where:

$$X = [C_1 + K_{1.1} \times (CR/CR_0) + K_{1.2} \times (CR/CR_0)^2]$$

$$Y = [C_2 + K_{2.1} \times (CR/CR_0) + K_{2.2} \times (CR/CR_0)^2] \times (CI/CI_0)$$

$$Z = [C_3 + K_{3.1} \times (CR/CR_0) + K_{3.2} \times (CR/CR_0)^2] \times (CI/CI_0)^2$$

or

$$\begin{aligned} GT = & \{C_1 + k_{1.1} [CR/CR_0] + k_{1.2} [CR/CR_0]^2\} \\ & + \{C_2 + k_{2.1} [CR/CR_0] + k_{2.2} [CR/CR_0]^2\} \times [CI/CI_0] \\ & + \{C_3 + k_{3.1} [CR/CR_0] + k_{3.2} [CR/CR_0]^2\} \times [CI/CI_0]^2 \\ & \dots\dots\dots (4.16) \end{aligned}$$

The appearance of X, Y, and Z is due to the fact that $[CR/CR_0]$ varies with varying redox concentrations.

Therefore, the equation has variable coefficients, i.e., the coefficients of the equation vary with the redox concentration. It should be noted that CI , CI_0 , CR , and CR_0 are the initial polymer concentration, first value of the initial polymer concentration, redox concentration, and the first value of the redox concentration respectively.

To obtain the values of CI/CI_0 and CR/CR_0 used for the extreme values of gelation time, a classical optimization technique can be utilized, since the equation governing the gelation time (equation 4.15) has already been developed. Consequently, the derivative of gelation time with respect to CI/CI_0 results:

$$\frac{dGT}{d(CI/CI_0)} = \frac{dGT}{dy} = 0 \quad \dots\dots\dots (4.17)$$

Since:

$$GT = [a + a_1 x + a_2 x^2] + [b + b_1 x + b_2 x^2] y + [c + c_1 x + c_2 x^2] y^2 \quad \dots\dots\dots (4.18)$$

Hence:

$$\frac{dGT}{dy} = [b + b_1 x + b_2 x^2] + 2y [c + c_1 x + c_2 x^2] = 0 \quad \dots\dots\dots (4.19)$$

$$y = -\frac{1}{2} \left[\frac{(b + b_1 x + b_2 x^2)}{(c + c_1 x + c_2 x^2)} \right] \quad \dots\dots\dots (4.20)$$

Where:

$$x = \frac{CR}{CR_0}$$

and

$$y = \frac{CI}{CI_0}$$

$$\begin{aligned} [GT]_{\text{extreme}} &= (a + a_1 x + a_2 x^2) \\ &+ [b + b_1 x + b_2 x^2] \left[-\frac{1}{2} \left\{ \frac{(b + b_1 x + b_2 x^2)}{(c + c_1 x + c_2 x^2)} \right\} \right] \\ &+ [c + c_1 x + c_2 x^2] \left[-\frac{1}{2} \left\{ \frac{(b + b_1 x + b_2 x^2)}{(c + c_1 x + c_2 x^2)} \right\} \right] \\ &\dots\dots\dots (4.21) \end{aligned}$$

or

$$\begin{aligned}
 \text{[GT] extreme} &= (a + a_1 x + a_2 x^2) - \frac{1}{2} \left[\frac{(b + b_1 x + b_2 x^2)^2}{(c + c_1 x + c_2 x^2)} \right] \\
 &+ \frac{1}{4} \left[\frac{(b + b_1 x + b_2 x^2)^2}{(c + c_1 x + c_2 x^2)} \right] \\
 &\dots\dots\dots
 \end{aligned} \tag{4.22}$$

or

$$\begin{aligned}
 \text{[GT] extreme} &= (a + a_1 x + a_2 x^2) - \frac{1}{4} \left[\frac{(b + b_1 x + b_2 x^2)^2}{(c + c_1 x + c_2 x^2)} \right] \\
 &\dots\dots\dots
 \end{aligned} \tag{4.23}$$

However, differentiating GT with respect to CR/CR₀ will give:

$$\begin{aligned}
 \frac{d\text{GT}}{dx} &= [a_1 + 2 a_2 x] + [b_1 + 2 b_2 x] y + [c_1 + 2 c_2 x] y^2 = 0 \\
 &\dots\dots\dots
 \end{aligned} \tag{4.24}$$

or

$$A = a_1 + 2 a_2 X$$

$$B = b_1 + 2 b_2 X$$

$$C = c_1 + 2 c_2 X$$

or

$$A + By + Cy^2 = 0 \quad \dots\dots\dots 4.25)$$

The solution of the above equation yields:

$$y_{1,2} = \frac{-B \pm \sqrt{B^2 - 4AC}}{2A} \quad \dots\dots\dots (4.26)$$

Hence:

$$y_{1,2} = \frac{-(b_1 + 2b_2x) \pm \sqrt{(b_1 + 2b_2x)^2 - 4(a_1 + 2a_2x)(c_1 + 2c_2x)}}{2(a_1 + 2a_2x)} \quad \dots\dots\dots (4.27)$$

Redox Concentration (ppm)	Initial Polymer Concentration (ppm)				
	2985	2558	2347	2146	1931
3103	9.55	9.86	10.28	10.65	11.39
2414	10.96	11.83	12.33	12.87	13.70
1724	14.79	16.0	16.18	18.45	19.08
1034	23.70	25.71	28.17	29.59	34.84

Table 4-3 Average gelation time (min.) for system-1 (by Terry et al. 1981)

Redox Concentration (ppm)	Initial Polymer Concentration (ppm)				
	2985	2558	2347	2146	1931
3103	7.07	8.33	9.33	11.11	14.58
2414	7.58	9.34	10.9	12.97	17.95
1724	9.61	11.96	15.56	18.52	29.16
1034	12.41	17.27	22.22	29.16	58.48

Table 4-4 Average gelation time (min.) for system-2 (by Terry et al. 1981)

Redox Concentration (ppm)	Initial Polymer Concentration (ppm)				
	2985	2558	2347	2146	1931
3103	5.69	7.40	8.81	10.88	16.82
2414	7.12	9.74	11.01	14.8	26.43
1724	9.74	13.22	16.82	25.0	74.0
1034	14.23	21.77	30.83	61.67	76.10

Table 4-5 Average gelation time (min.) for system-3 (by Terry et al. 1981)

Redox Concentration (ppm)	Initial Polymer Concentration (ppm)				
	2985	2558	2347	2146	1931
3103	38.91	42.43	44.86	47.62	50.74
2414	48.61	54.03	56.92	60.75	65.53
1724	68.63	77.76	83.33	93.37	101.4
1034	145.8	166.7	182.15	212.13	233.1

Table 4-6 Average gelation time (min.) for system-4 (by Terry et al. 1981)

Calgon 340		
Temperature, °K	CR = 3103 ppm	CR = 1724 ppm
344.83	0.98	3.70
333.33	2.80	7.60
322.58	5.70	14.0
312.50	15.0	37.0
303.03	38.0	78.0

Table 4-7 Temperature effects on gelation time (min.) at initial polymer concentration of 1724 ppm for system-4 (by Jordan et al. 1981)

Redox Concentration (ppm)	Initial Polymer Concentration (ppm)				
	2985	2558	2347	2146	1931
3103	9.86	10.15	10.54	10.94	11.48
2414	11.86	12.28	12.96	13.46	14.0
1724	11.75	11.48	11.86	18.92	20.59
1034	31.82	35.0	38.04	38.9	43.75

Table 4-8 Average gelation time (min.) for system-5 (by Terry et al. 1981)

LEVEL	POLYMER PROPERTIES		
	Polymer Type	Average molecular weight	Characteristics
1	CALGON 800	3.0×10^6	nonionic linear polyacrylamide with 0% hydrolysis
2	CALGON 815	3.0×10^6	linear polyacrylamide with 15% hydrolysis
3	CALGON 825	3.0×10^6	linear polyacrylamide with 25% hydrolysis
4	CALGON 340	3.9×10^6	anionic polyacrylamide copolymer with 0% hydrolysis; anionic group is 2-acrylamido-2-methyl propyl sulfonate
5	BETZ 1160	5.0×10^6	cationic polyacrylamide copolymer with 20% positive charge density; cationic group is unknown

Table 4-9 Polymer properties and their level (by Terry et al. & Jordan et al. 1981)

NO.	PARAMETERS	RANGE
1	Initial polymer concentration, ppm	1931 - 2985
2	Redox concentration, ppm	1034 - 3103
3	Temperature, °C	30 - 70

Table 4-10 Factors examined

Polymer Type	Redox Cont. ppm	Initial Polymer Concentration ppm				
		2985	2558	2347	2146	1931
Calgon 800	3103	9.55	9.86	10.28	10.65	11.39
	2414	10.96	11.83	12.33	12.87	13.70
	1724	14.79	16.0	16.18	18.45	19.08
	1034	23.70	25.71	28.17	29.59	34.84
Calgon 815	3103	7.07	8.33	9.333	11.11	14.58
	2414	7.58	9.34	10.90	12.97	17.95
	1724	9.61	11.96	15.56	18.52	29.16
	1034	12.41	17.27	22.22	29.16	58.48
Calgon 825	3103	5.69	7.40	8.81	10.88	16.82
	2414	7.12	9.74	11.01	14.8	26.43
	1724	9.74	13.22	16.82	25.0	74.0
	1034	14.23	21.77	30.83	61.67	0.10
Calgon 340	3103	38.91	42.43	44.86	47.62	50.74
	2414	48.61	54.03	56.92	60.75	65.53
	1724	68.63	77.76	83.33	93.37	101.4
	1034	145.8	166.7	182.15	212.13	233.1
Betz 1160	3103	9.86	10.15	10.54	10.94	11.48
	2414	11.86	12.28	12.96	13.46	14.0
	1724	11.75	11.48	11.86	18.92	20.59
	1034	31.82	35.0	38.04	38.9	43.75

Table 4-11 Average gelation time (min.) for systems 1-5 at different initial polymer and redox concentrations (by Terry et al. 1981)

Polymer Type	CRN = CR/CRO	CIN = CI/CI0				
		1	0.8570	0.7863	0.7189	0.6469
Calgon 800	1	9.55	9.86	10.28	10.65	11.39
	0.7780	10.96	11.83	12.33	12.87	13.70
	0.5556	14.79	16.0	16.18	18.45	19.08
	0.3332	23.70	25.71	28.17	29.59	34.84
Calgon 815	1	7.07	8.33	9.333	11.11	14.58
	0.7780	7.58	9.34	10.90	12.97	17.95
	0.5556	9.61	11.96	15.56	18.52	29.16
	0.3332	12.41	17.27	22.22	29.16	58.48
Calgon 825	1	5.69	7.40	8.81	10.88	16.82
	0.7780	7.12	9.74	11.01	14.8	26.43
	0.5556	9.74	13.22	16.82	25.0	74.0
	0.3332	14.23	21.77	30.83	61.67	0.10
Calgon 340	1	38.91	42.43	44.86	47.62	50.74
	0.7780	48.61	54.03	56.92	60.75	65.53
	0.5556	68.63	77.76	83.33	93.37	101.4
	0.3332	145.8	166.7	182.15	212.13	233.1
Betz 1160	1	9.86	10.15	10.54	10.94	11.48
	0.7780	11.86	12.28	12.96	13.46	14.0
	0.5556	11.75	11.48	11.86	18.92	20.59
	0.3332	31.82	35.0	38.04	38.9	43.75

Table 4-12 Average gelation time (min.) for systems 1-5 at different non-dimensional of initial polymer and redox concentrations

CHAPTER 5

CHAPTER 5

RESULTS AND DISCUSSIONS

The gelation of polyacrylamide-Cr(+6) system has been studied experimentally by many investigators [3,12-14,20]. They have studied the effects of concentration and type of reactants on the gelation time. It has been shown that the gelation time decreases with increasing initial polymer concentration or increasing redox concentration. However, the mathematical formula they developed was in the linear form, resulting in considerable error for high values of redox concentration. Their findings show that the slope of this linear relation varies with the degree of hydrolysis, the anionic or cationic character of the polymer, and the type of reducing agent. All of these findings were for a constant temperature and fixed brine concentration. Consequently, the following discussion covers the statistical approach to the problem and the mathematical formulation allowing multi degree of polynomial equations, which in turn provides more general form.

Statistical analysis results for gelation time and affecting parameters are given in table 5.1. The effect of initial polymer concentration, redox concentration, and polymer type were found to be very significant. It is also evident from the table that first order interactions of these parameters have very significant effect on the gelation time. This indicates that gelation time is very sensitive to these parameters and a small change in level of these parameters may lead to significant changes in the gelation time. Consequently, when an empirical formulation is introduced, the effect of the parameters should be considered equally weighted.

The effects of the initial polymer and redox concentrations were very important for the gelation process. Figure 5.1 shows the variation of estimated values of gelation time, obtained by using equation (5.1), with the measured data, obtained at 25 °C.

$$GT = a_0 + a_1 \times (1/CI) + a_2 \times (1/(CR \times CI)) + a_3 \times (1/CR)^2$$

..... (5.1)

The values for the coefficients of equation (5.1) are listed in table 5.2. The estimated values show an extremely good fit with the data used in the analysis. Small

scattering in the estimated values occurred with the data points. This appeared when the data corresponding to each polymer type was changed. Since the resulting equation does not include the properties of the polymer as parameters, this scattering may be explained in terms of the polymer properties, which was found to have significant effect on the resulting data (factorial analysis results). The error related to this formulation was considerably small (figure 5.2). However, sudden increase in error occurred with the data points. This again is due to change in the polymer type. The effect of the polymer type may be explained in terms of the polymer properties such as high molecular weight and high degree of hydrolysis resulting in shorter gelation time.

The variation of the estimated values of gelation time with the measured data is shown in figure 5.3 while table 5.3 gives the values of coefficients. The estimated values were obtained using equation (5.2) which resulted from the second trial.

$$GT = b_0 + b_1 \times (\exp(CI/CR)) + b_2 \times (CI/CR) + b_3 \times (CI/CR)^3$$

..... (5.2)

Considerably large scattering of the estimated values occurred with the number of data points. This may be due to the equation developed for the gelation time. In this case, exponential function is employed in the equation. This clearly indicated that the exponential relation failed to represent the measured data. Consequently, the variation of the gelation time with the redox and initial polymer concentrations was in polynomial rather than exponential form.

Figure 5.4 shows the relative error with the number of data points. It is evident that the relative error oscillated with the number of data points. The effect of the polymer type was also evident from the sudden increase in the relative error. When comparing figures 5.1 and 5.3, it is evident that equation (5.1) gives close results to the measured data. The relation between the gelation time with redox and initial polymer concentrations should be in the polynomial form rather than in the exponential form.

The effect of temperature on the gelation time was very significant. However, this appeared as an inverse relationship form with temperature. Consequently, the temperature is employed in the inverse form in equation (5.3). Figure 5.5 shows the variation of the estimated values for gelation

time and the measured data. The experimental data were obtained at initial polymer concentration of 1724 ppm. Generally, the estimated values fit well with the measured data and little scattering occurs. This may be caused by the error developed while extracting the data. As can be seen from Figure 5.6, the variation of the relative error was considerably small and less oscillation occurs. This small oscillation may be due to the polymer type effect.

With the data available in the literature, the equation developed is:

$$GT = c_0 + c_1 \times CR + c_2 \times (1/T)^2 + c_3 \times \exp(1/T) + c_4 \times (CR/T) \dots\dots\dots (5.3)$$

Table 5.4 gives the values for the coefficients. This shows that the gelation time varies exponentially with the temperature providing that the reciprocal of the temperature appears in the exponential form. The redox concentration appears in the polynomial form in the equation. This agrees well with the form of the equation developed previously for these two properties.

The dimensional analysis used in the present work provides dimensionless group in terms of concentration ratios. Therefore, the resulting dimensionless group includes:

$$CIN = CI/CI_0 \quad \text{and} \quad CRN = CR/CR_0$$

An empirical relation between the dimensionless group and the resulting gelation time was developed. The polynomial form due to second the attempt was expressed in equation (4.13):

$$GT = C + K_1 [CI/CI_0] + K_2 [CI/CI_0]^2 \quad \dots\dots\dots \quad (4.13)$$

The coefficients (C, K₁, and K₂) are given in table 5.5 for each polymer type. It can be seen that for each polymer type, the coefficients of equation 4.13 are function of the initial polymer concentrations which is also evident from figures 5.7 through 5.9.

A single equation governing the given polymer type and including the dimensionless group was also developed. In this case, polynomial equations between the coefficients and the redox concentrations are introduced, i.e., the ratio/the

parameter is CR/CR_0 introduced. Therefore, equation (4.15) is the final form of polynomial relation.

$$\begin{aligned}
 GT = & [C_1 + K_{1.1} (CR/CR_0) + K_{1.2} (CR/CR_0)] \\
 & + [C_2 + K_{2.1} (CR/CR_0) + K_{2.2} (CR/CR_0)] (CI/CI_0) \\
 & + [C_3 + K_{3.1} (CR/CR_0) + K_{3.2} (CR/CR_0)] (CI/CI_0)^2
 \end{aligned}$$

Equation (4.15) is the general form representing the gelation time in terms of the affecting parameters. The coefficients for equation 4.15 is given in table 5.6. The equations resulted for each polymer type are:

$$\begin{aligned}
 GT = & [316 - 738.33739x(CR/CR_0) + 449.485072x(CR/CR_0)^2] \\
 & + [-616.43944 + 1574.337386x(CR/CR_0) - 966.87063x(CR/CR_0)^2]x(CI/CI_0) \\
 & + [347.000619 - 920.676472x(CR/CR_0) + 595.189561x(CR/CR_0)^2]x(CI/CI_0)^2 \\
 & \dots\dots\dots (5.4)
 \end{aligned}$$

Equation 5.4 gives the gelation time and redox, initial polymer concentrations for system-1.

$$\begin{aligned}
GT = & [1174.489226 - 2523.2338x(CR/CR_0) + 1428.431x(CR/CR_0)^2] \\
& + [-2626.70 + 5731.865x(CR/CR_0) - 3262.2919x(CR/CR_0)^2]x(CI/CI_0) \\
& + [1665.847 - 3919.59x(CR/CR_0) + 2325.031x(CR/CR_0)^2]x(CI/CI_0)^2 \\
& \dots\dots\dots (5.5)
\end{aligned}$$

Equation 5.5 gives the gelation time and redox, initial polymer concentrations for system-2.

$$\begin{aligned}
GT = & [4466.17546 - 9395.278872x(CR/CR_0) + 5037.501642x(CR/CR_0)^2] \\
& + [-10420.27 + 22025.802792x(CR/CR_0) - 11829.49x(CR/CR_0)^2]x(CI/CI_0) \\
& + [7384.647261 - 16559.25x(CR/CR_0) + 9296.638242x(CR/CR_0)^2]x(CI/CI_0)^2 \\
& \dots\dots\dots (5.6)
\end{aligned}$$

Equation 5.6 gives the gelation time and redox, initial polymer concentrations for system-3.

$$\begin{aligned}
GT = & [1717.6390 - 3754.747437x(CR/CR_0) + 2148.250742x(CR/CR_0)^2] \\
& + [-2769.57007 + 6253.00523x(CR/CR_0) - 3607.9753x(CR/CR_0)^2]x(CI/CI_0) \\
& + [1355.00114 - 3097.30954(CR/CR_0) + 1796.23549x(CR/CR_0)^2]x(CI/CI_0)^2 \\
& \dots\dots\dots (5.7)
\end{aligned}$$

Equation 5.7 gives the gelation time and redox, initial polymer concentrations for system-4.

$$\begin{aligned} GT = & [107.4812 + 51.120501x(CR/CR_0) - 147.813715x(CR/CR_0)^2] \\ & + [-8.641144 - 640.576428x(CR/CR_0) + 654.076342x(CR/CR_0)^2]x(CI/CI_0) \\ & + [-28.930576 + 440.768835x(CR/CR_0) - 416.567977xCR/CR_0^2]x(CI/CI_0)^2 \\ & \dots\dots\dots\dots\dots\dots\dots\dots (5.8) \end{aligned}$$

Equation 5.8 gives the gelation time and redox, initial polymer concentrations for system-5.

The variation of constants and coefficients with number of polymer systems are shown in figure 5.7 through 5.9. It is evident that coefficients of the equation 5.5 is varied with varying polymer systems as well as redox and initial polymer concentrations. This variation is not linear. This suggests that the equation needed to be developed for the coefficients should be at least in parabolic form. Consequently, this indicates that equation 4.15 generalizes this relation for a given polymer system.

Figures 5.10 - 5.14 show the variation of relative error, resulted from the dimensional analysis and polynomial equation, with the initial polymer concentration. The relative error developed is of the order of 10% , which is considerably small and being considered as acceptable.

The effort made to develop this relation is considerable and the resulting equation (equation 4.15) may be used to obtain a redox and an initial polymer concentrations which optimize the gelation time.

Figure 5.15 shows the variation of the optimum (critical) value of the polymer concentration with the number of systems (resulted from equation 4.15) corresponding to the extreme (maxima or minima) value of the gelation time. It is evident that for given sets of redox concentrations (table 4.11), the first two redox concentrations result extreme value of the gelation time. With the other two redox concentrations (1724 and 1034 ppm), there is no extreme value of the gelation time that occurs. When comparing the optimum values (corresponding to the extreme points), that are shown in figure 5.15, with the values tabulated in table 4.11, it is evident that the values resulted for the extreme value of the gelation time are less than that corresponding to the values in table 4.11. This indicates that optimum values of initial polymer concentration existing for a given redox concentration, in table 4.11, is beyond the value given in this table. Table 5.8 gives the optimum values of initial polymer concentration at redox concentration of 3103 and 2414 ppm for systems 1-5.

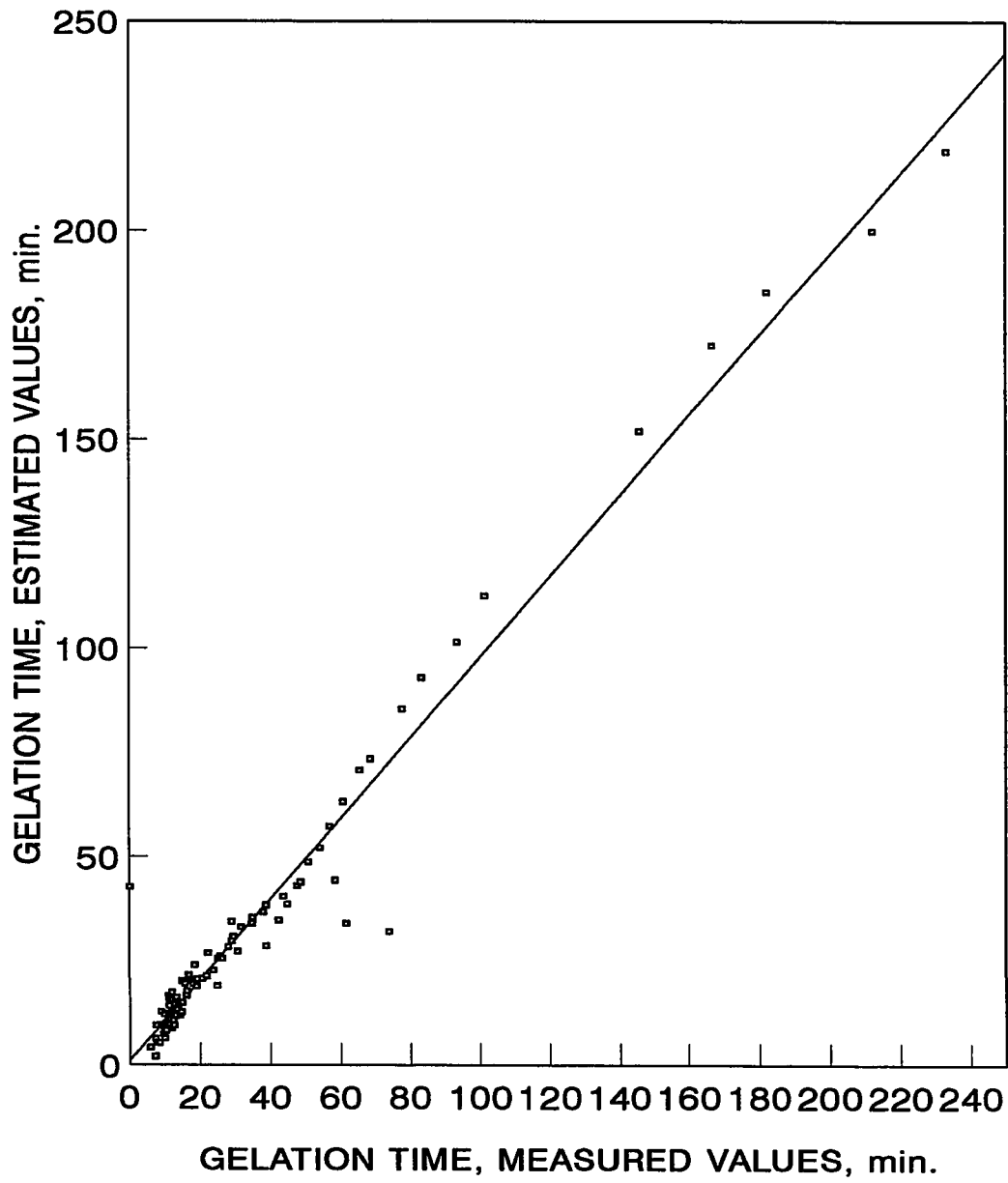


Figure 5.1 Variation of estimated and measured values of gelation time using Equation (1)

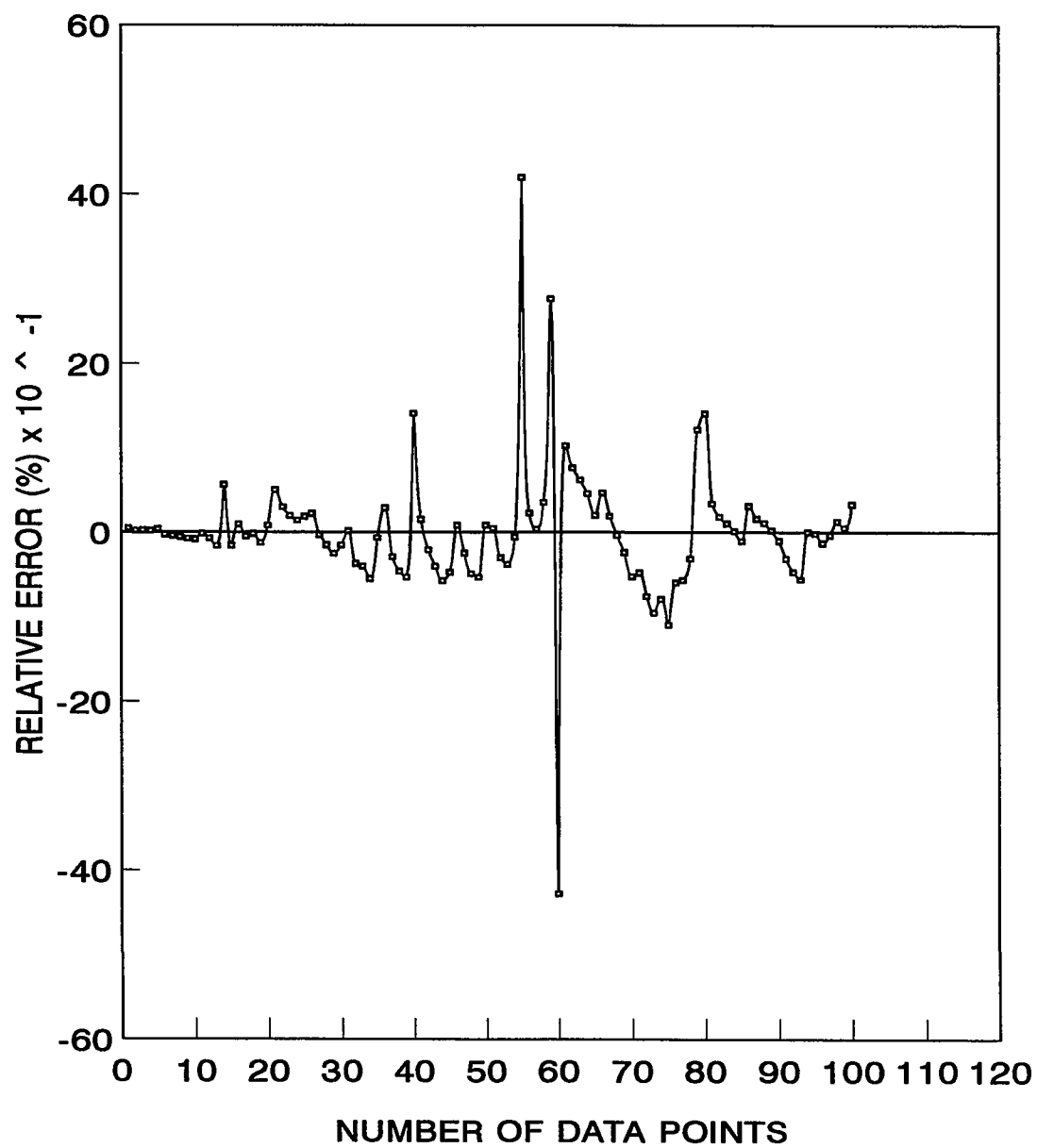


Figure 5.2 Variation of relative error with the number of data points using Equation (1)

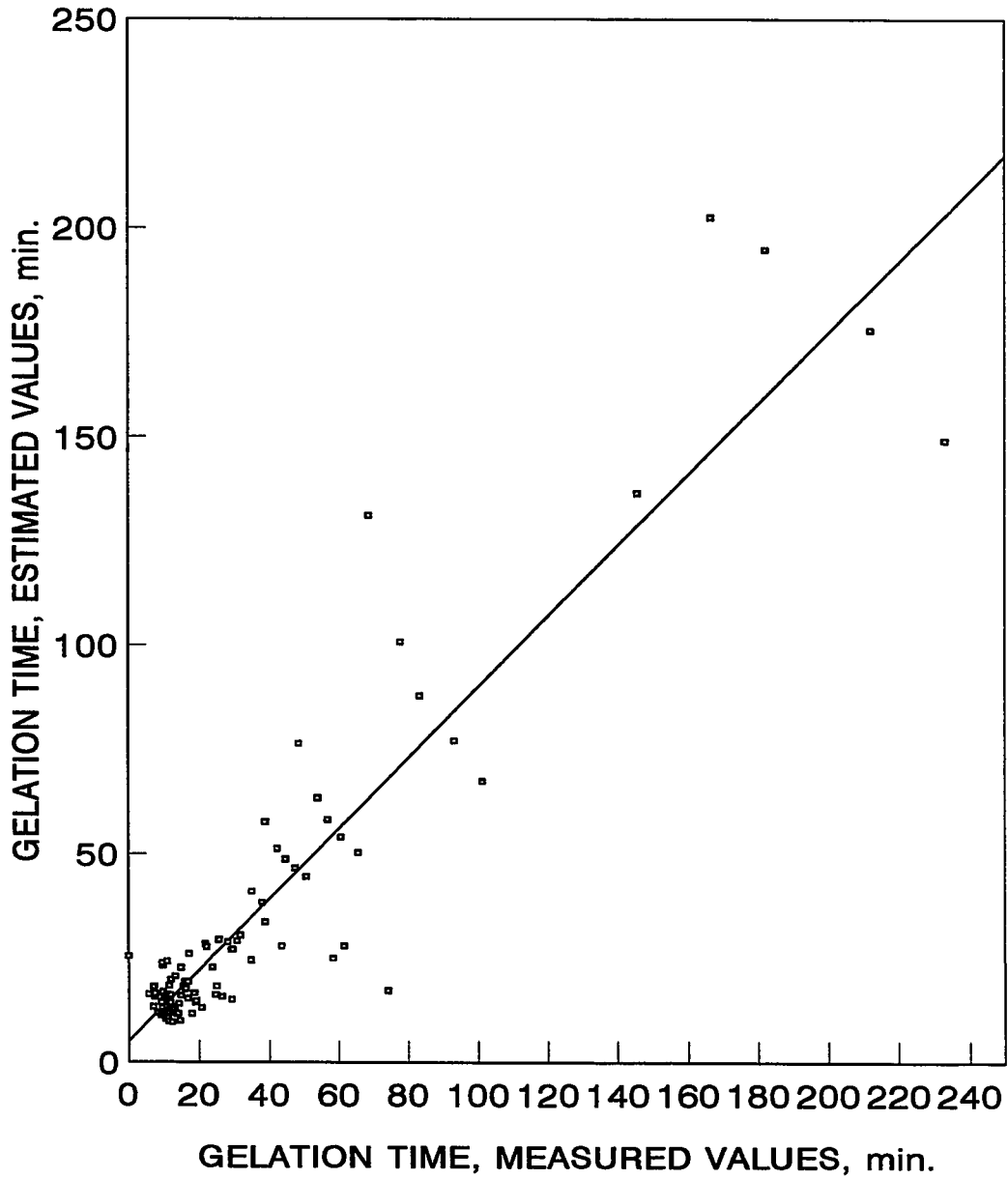


Figure 5.3 Variation of estimated and measured values of gelation time using Equation (2)

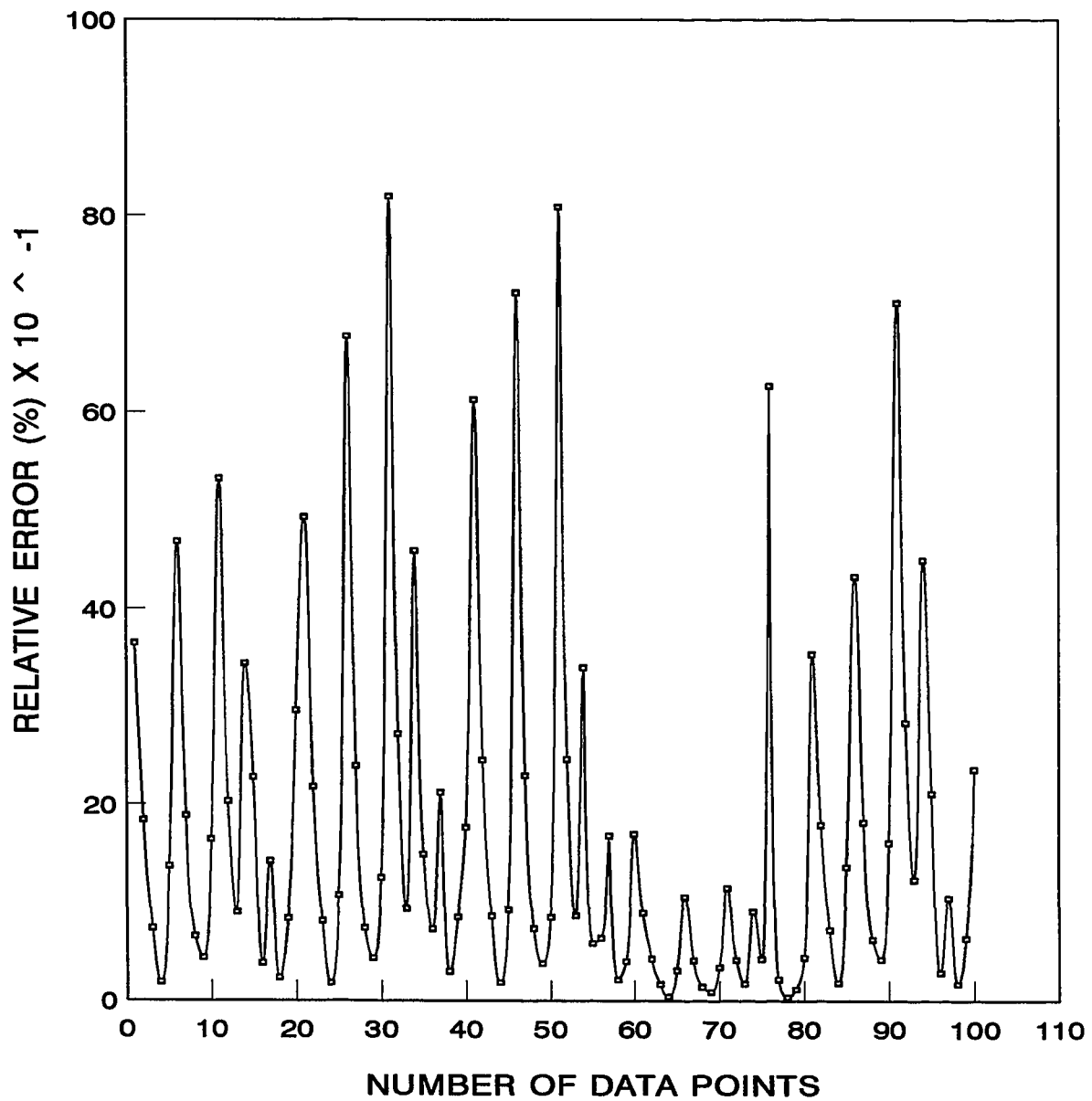


Figure 5.4 Variation of relative error with the number of data points using Equation (2)

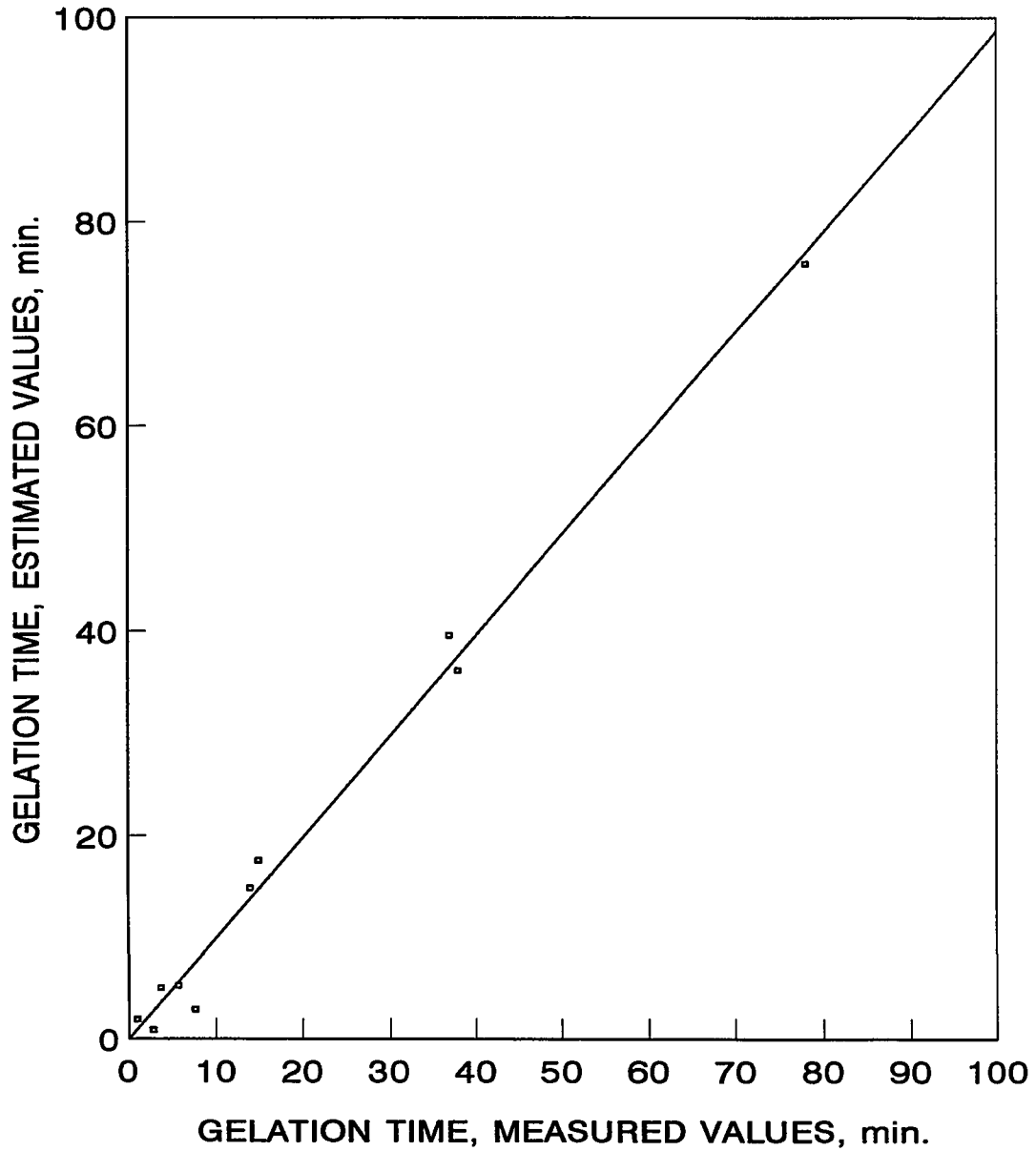


Figure 5.5 Variation of estimated and measured values of gelation time using Equation (3)

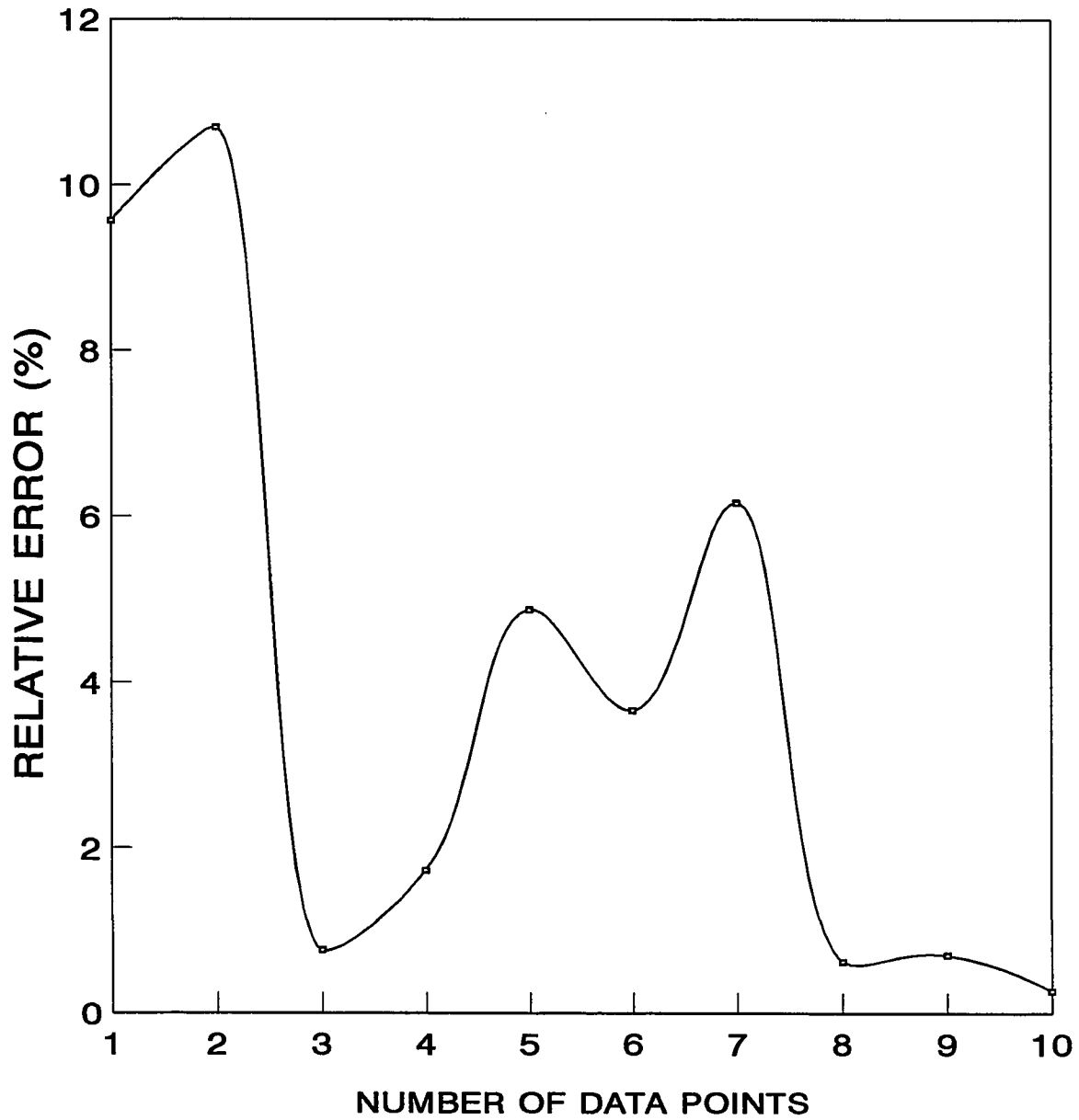


Figure 5.6 Variation of relative error with the number of data points using Equation (3)

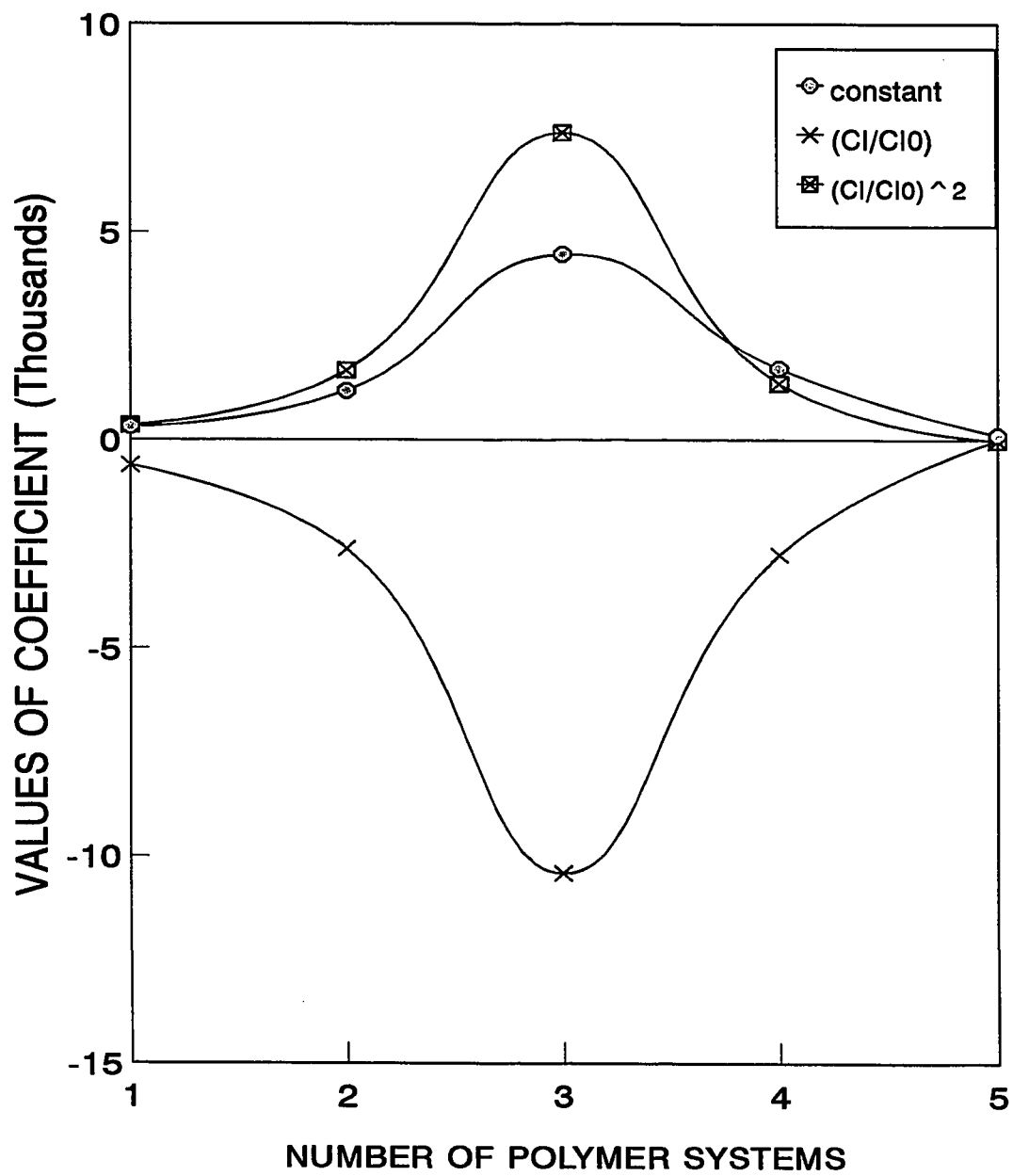


Figure 5.7 Variation of constants in equations corresponding to different type of polymers

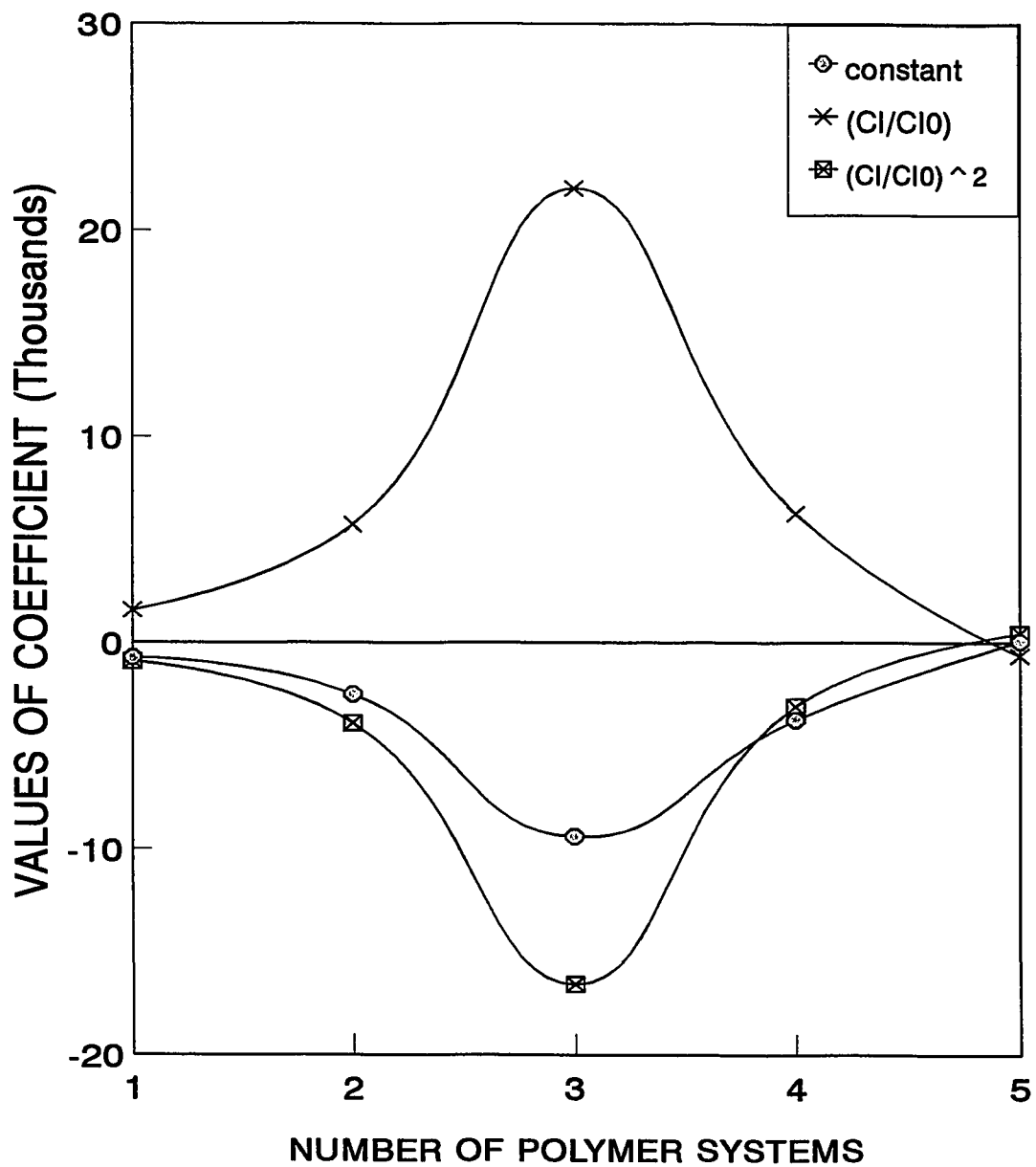


Figure 5.8 Variation of coefficients of (Cl/Cl_0) with number of equations corresponding to corresponding to different type of polymers

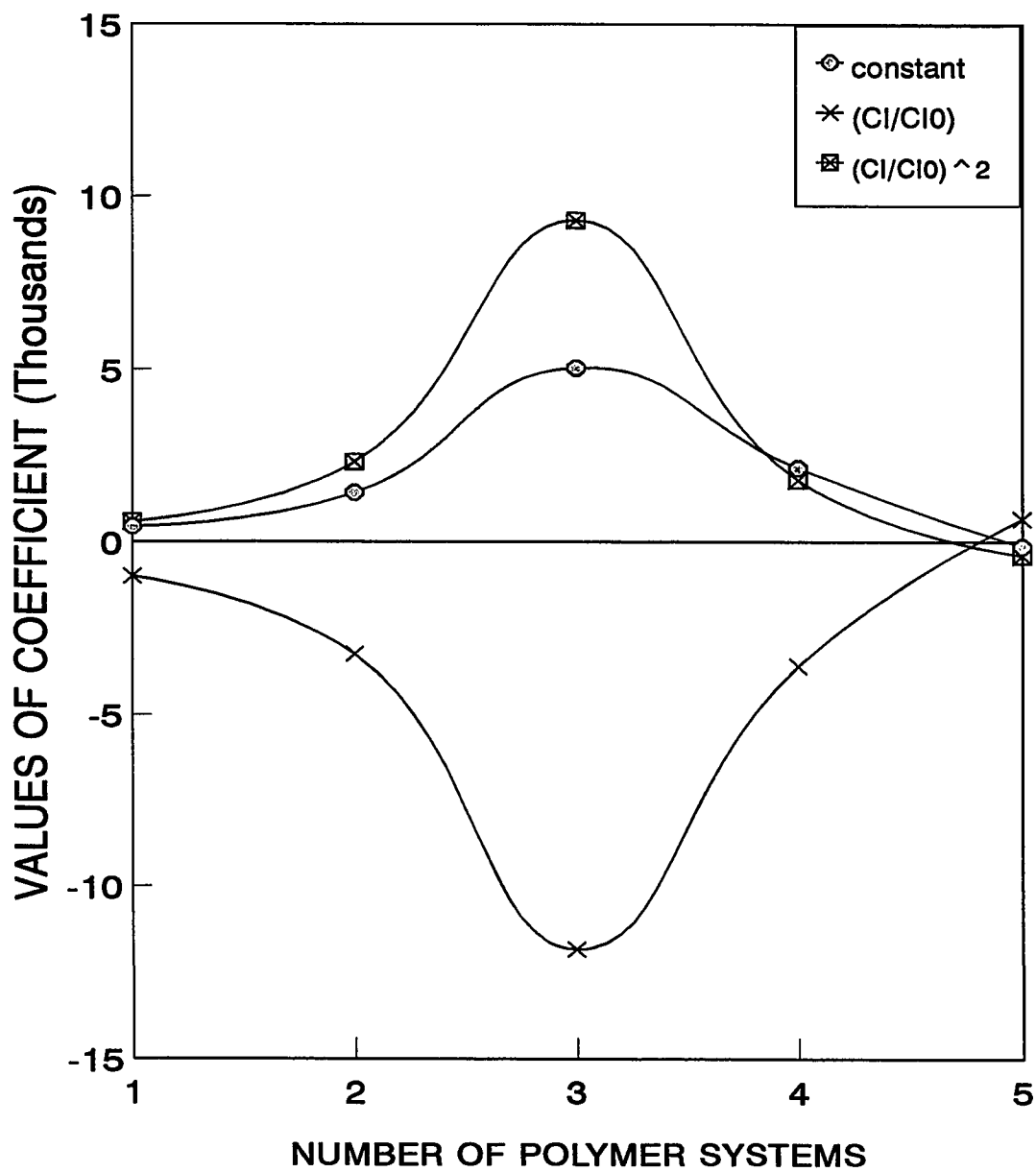


Figure 5.9 Variation of coefficients of $(Cl/ClO)^2$ with number of equations corresponding to different type of polymes

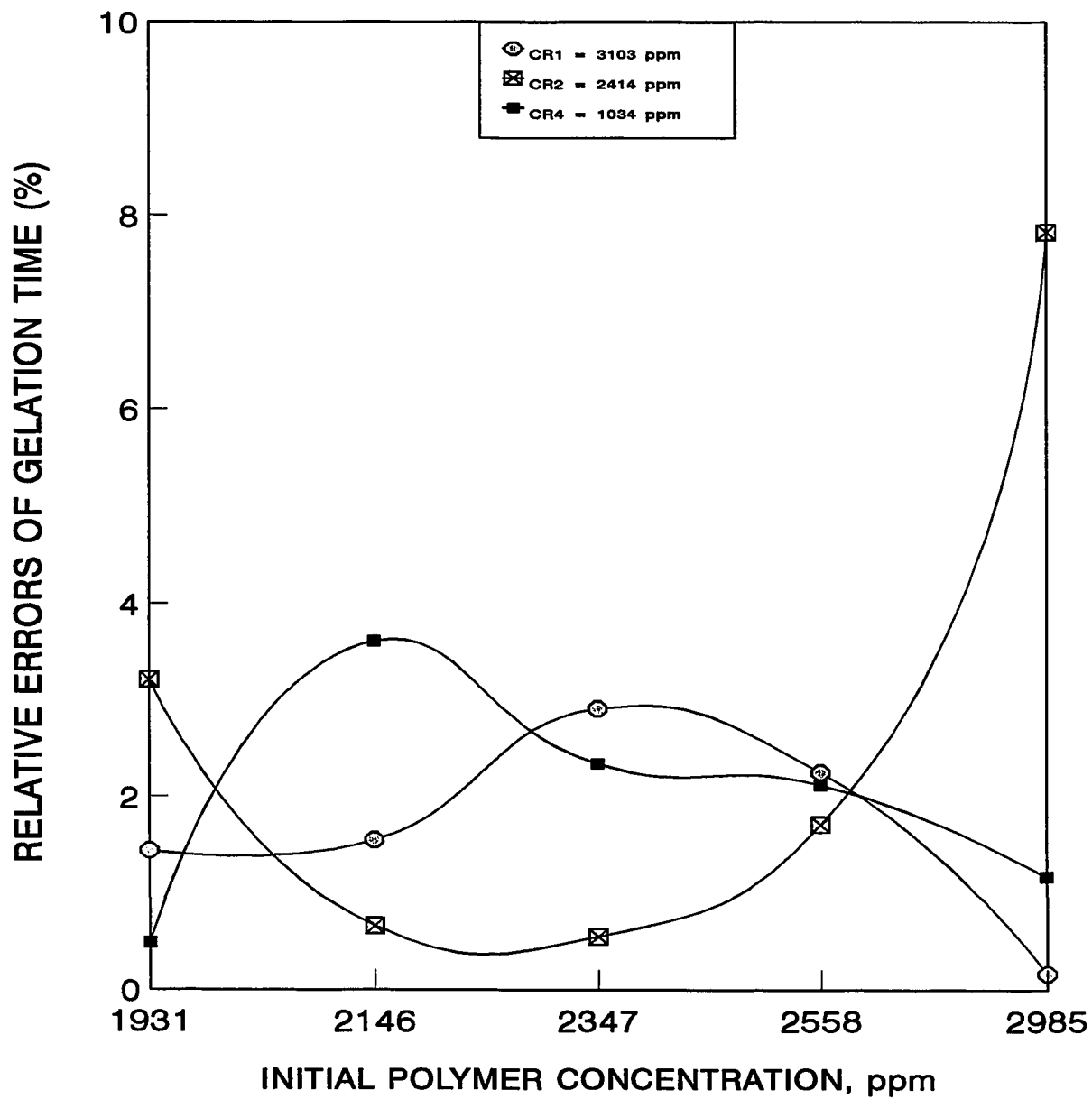


Figure 5.10 Relative error in gelation time with initial polymer concentration at constant redox concentration for system-1

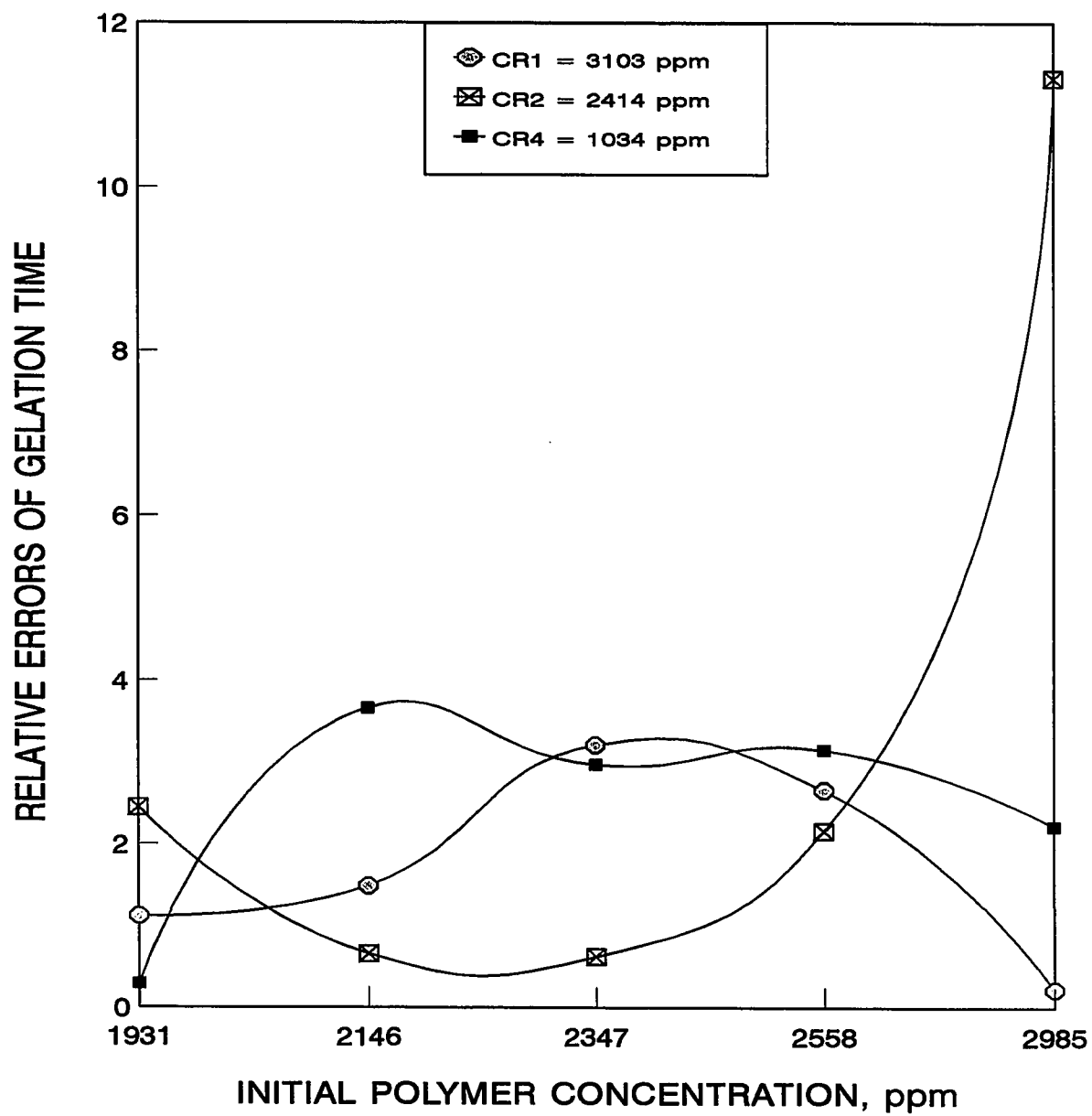


Figure 5.11 Relative error in gelation time with initial polymer concentration at constant redox concentration for system-2

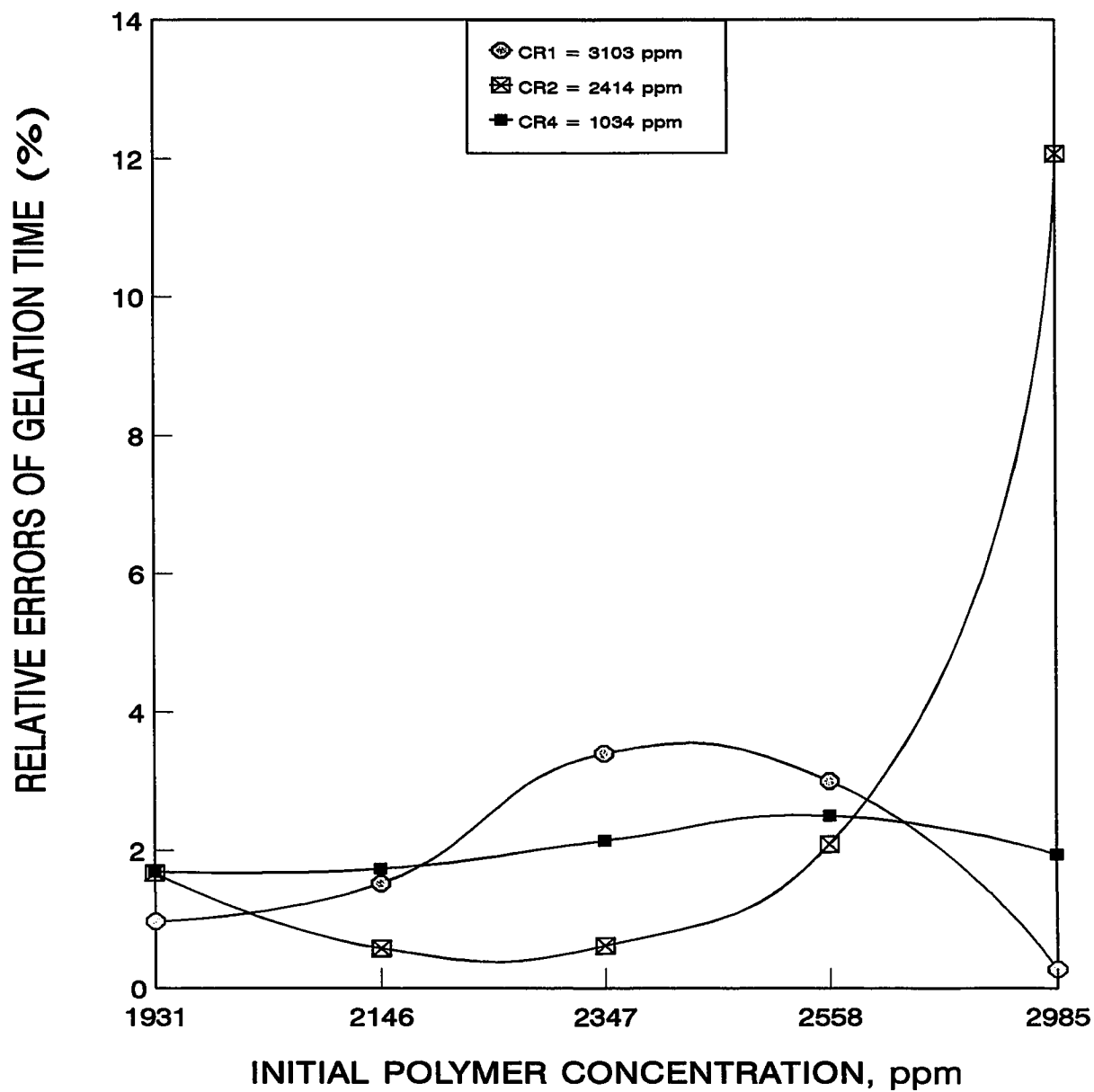


Figure 5.12 Relative error in gelation time with initial polymer concentration at constant redox concentration for system-3

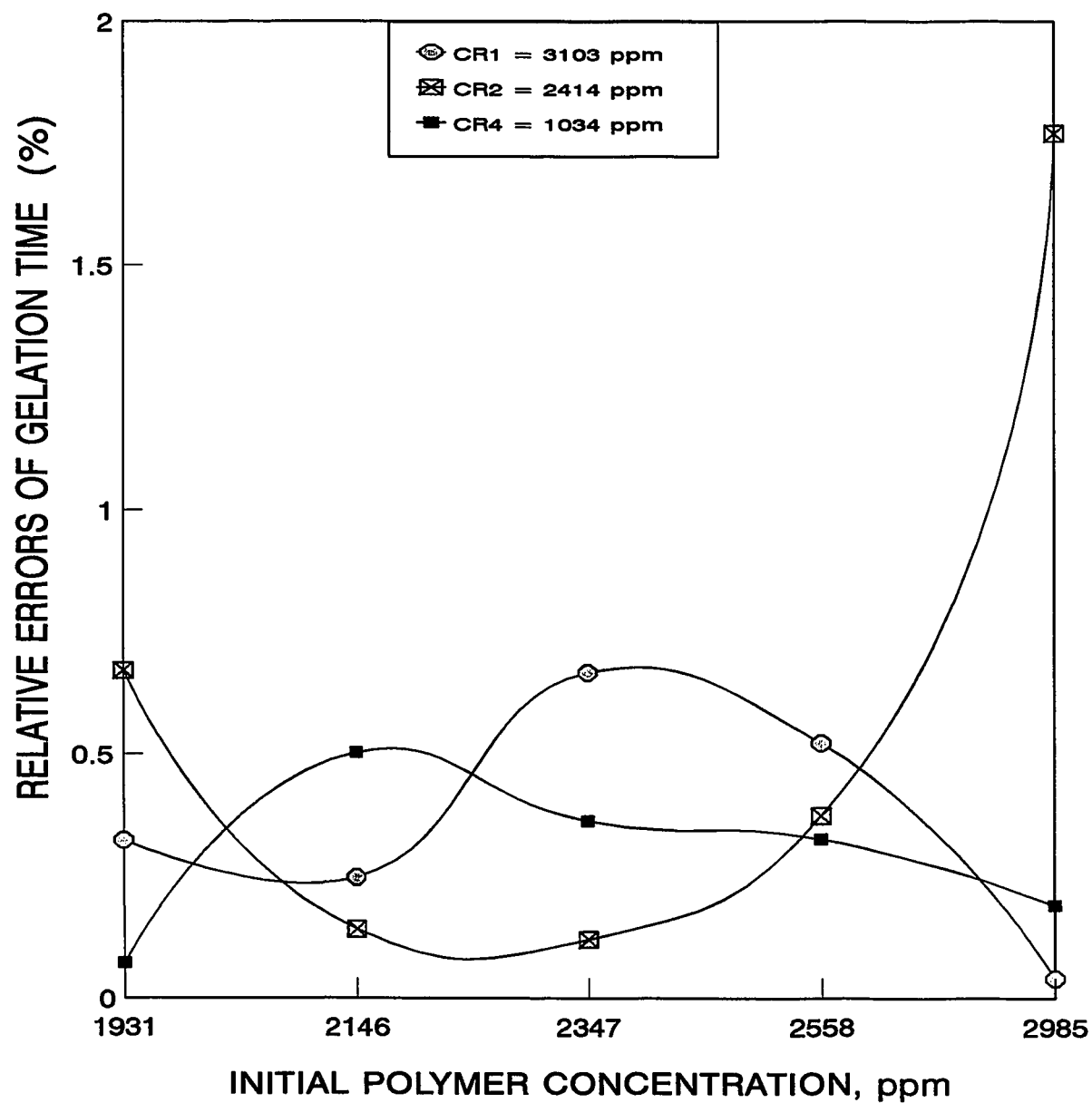


Figure 5.13 Relative error in gelation time with initial polymer concentration at constant redox concentration for system-4

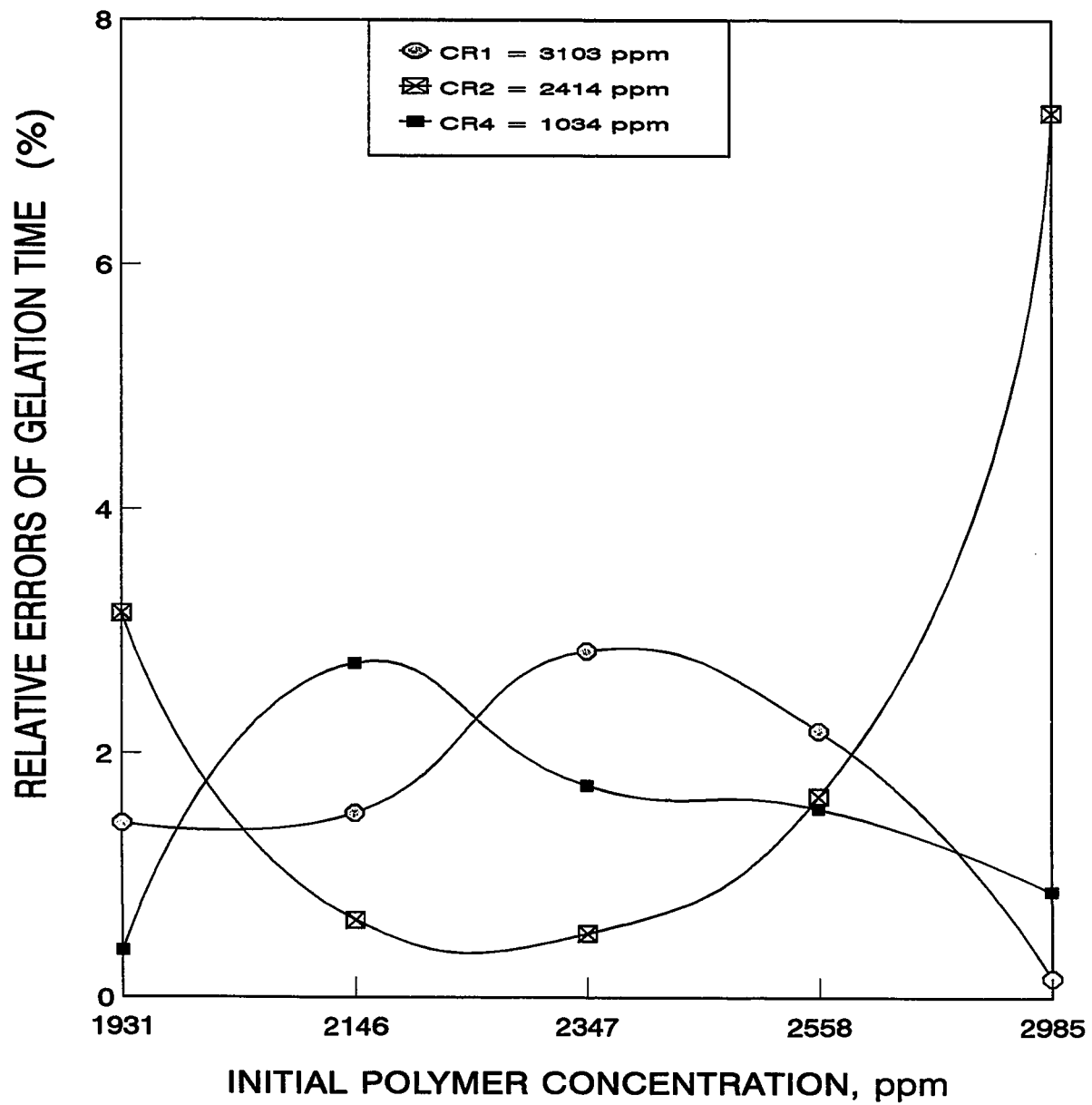


Figure 5.14 Relative error in gelation time with initial polymer concentration at constant redox concentration for system-5

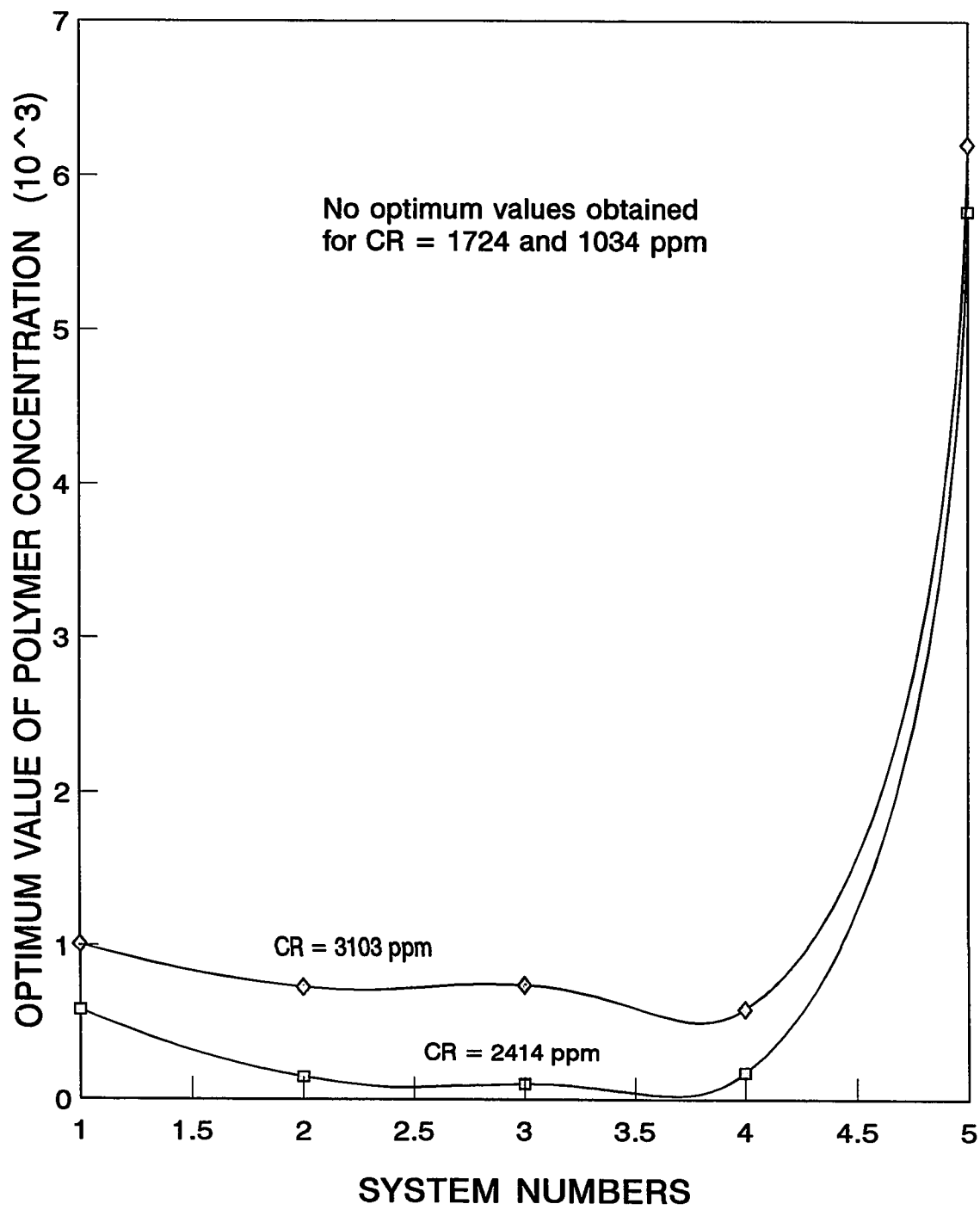


Figure 5.15 Optimum value of initial polymer concentration versus system numbers.

POLYMER TYPE	CORRECTED MEAN VALUES	VARIANCE RATIO	DEGREE OF FREEDOM	SIGNIFICANCE LEVELS
"PT"	22935.4	417.0889	4	less than 1%*
INITIAL POLYMER CONCENTRATION "CI"	9939.706	180.7586	4	less than 1%*
REDOX CONCENTRATION "CR"	1033.556	18.79575	3	less than 1%*
PT x CI	12431.57	226.0755	16	less than 1%*
CI x CR	9318.36	127.31	12	less than 1%*
CR x PT	7000.75	169.46	16	less than 1%*

Table 5-1 Factorial design analysis results

* indicates most significant

COEFF.	POLYMER TYPE				
	CALGON 800	CALGON 815	CALGON 825	CALGON 340	BETZ 1160
a0	5.94809	-12.85696	-25.6077	-12.8184	-7.7200
a1	-14950.3	-7829.581	58509.562	-18734.7	29864.7
a2	79447250	205087500	113579700	399345600	10505080
a3	-4210575	- 44312690	-20134030	44383100	29337170

Table 5-2 Values of coefficients for Equation (5.1)

COEFF.	POLYMER TYPE				
	CALGON 800	CALGON 815	CALGON 825	CALGON 340	BETZ 1160
b0	16.61043	23.54727	35.93704	177.9413	46.53466
b1	-12.8154	-20.3730	-22.4409	-154.115	-33.2808
b2	24.82376	35.13469	29.28918	213.2055	36.35423
b3	6.832457	10.39348	12.30685	87.59463	19.7833

Table 5-3 Values of coefficients for Equation (5.2)

COEFFICIENTS	CALGON 340
c0	2801330.0
c1	0.194842
c2	499794400.0
c3	- 2797410.0
c4	- 66.490273

Table 5-4 Values of the coefficients for Equation (5.3)

Polymer Type	CR/CR ₀	c	k ₁	k ₂
Calgon 800	1	23.795005	-29.437151	15.210971
	0.7780	24.504337	-23.549891	9.85819
	0.5556	34.085572	-20.924621	0.333213
	0.3332	123.629332	-212.0273	112.58597
Calgon 815	1	72.803823	-140.94913	75.587784
	0.7780	96.654359	-190.4273	10.844
	0.5556	192.926	-400.695	218.723
	0.3332	499.1619	-1095.0809	613.620
Calgon 825	1	108.39823	-223.95260	122.034697
	0.7780	205.83491	-444.54875	128.74698
	0.5556	801.224791	-1834.4689	1054.17361
	0.3332	-507.18266	-1392.6320	-889.50065
Calgon 340	1	99.084982	-105.17888	44.293242
	0.7780	132.893804	-146.62311	61.406631
	0.5556	258.557241	-351.1990	159.782203
	0.3332	717.031889	-1105.8538	531.963393
Betz 1160	1	21.782839	-24.111316	12.17156
	0.7780	24.846685	-24.318632	11.211995
	0.5556	123.176745	-249.38083	137.975741
	0.3332	97.131751	-120.56234	54.824955

Table 5-5 Variation of the coefficients with CR/CR₀ and polymer type for system 1-5

Polymer Type		c	k1	k2
Calgon 800	constant	316	-738.33739	449.485072
	k _{1.1}	-616.43944	1574.33739	-996.87063
	k _{2.1}	347.000619	-920.67647	595.189561
Calgon 815	constant	1174.48923	-2523.2338	1428.431
	k _{1.1}	-2626.70	5731.865	-3262.2919
	k _{2.1}	1665.847	-3919.59	2325.031
Calgon 825	constant	4466.17546	-9395.2789	5037.50164
	k _{1.1}	-10420.27	22025.8028	-11829.49
	k _{2.1}	7384.64726	-16559.25	9296.63824
Calgon 340	constant	1717.6390	-3754.7474	2148.25074
	k _{1.1}	-2769.5701	6253.00523	-3607.9753
	k _{2.1}	1355.00114	-3097.3095	1796.23549
Betz 1160	constant	107.481199	51.120501	-147.81372
	k _{1.1}	-8.641144	-640.57643	654.076342
	k _{2.1}	-28.930576	440.768835	-416.56798

Table 5-6 Variation of the coefficients with CR/CR₀ and polymer type after obtaining final polynomial equations (5.4-5.8) for systems 1-5

Polymer Type	Redox Cont.	Initial Polymer Concentration				
		2985	2558	2347	2146	1931
Calgon 800	3103	1.64E-3	2.25E-2	2.91E-2	1.55E-2	1.44E-2
	2414	7.83E-2	1.71E-2	5.52E-3	6.64E-3	3.21E-2
	1724	4.72E-3	5.04E-2	0.11902	0.20985	0.11024
	1034	1.17E-2	2.12E-2	2.34E-2	3.61E-2	4.87E-3
Calgon 815	3103	2.22E-3	2.66E-2	3.21E-2	1.49E-2	1.12E-2
	2414	0.11325	2.16E-2	6.24E-3	6.59E-3	2.45E-2
	1724	7.27E-3	6.74E-2	0.12380	0.27976	7.22E-2
	1034	2.22E-2	3.15E-2	2.97E-2	3.66E-2	2.90E-3
Calgon 825	3103	2.75E-3	3.0E-2	0.03395	1.52E-2	9.73E-3
	2414	0.12065	2.08E-2	6.18E-3	5.78E-3	1.67E-2
	1724	7.17E-3	0.06102	0.11451	0.20725	2.84E-2
	1034	1.94E-2	2.50E-2	2.14E-2	1.73E-2	1.70E-2
Calgon 340	3103	4.03E-4	5.23E-3	6.67E-3	3.47E-3	3.23E-3
	2414	1.77E-2	3.74E-3	1.20E-3	1.41E-3	6.72E-3
	1724	1.02E-3	1.04E-2	2.31E-2	5.55E-2	2.07E-2
	1034	1.90E-3	3.26E-3	3.63E-3	5.03E-3	7.27E-4
Betz 1160	3103	1.59E-3	0.02186	2.84E-2	0.01512	1.43E-2
	2414	7.24E-2	1.65E-2	5.25E-3	6.35E-3	3.15E-2
	1724	6.31E-3	7.03E-2	0.16238	0.27385	0.10218
	1034	8.69E-3	1.55E-2	1.74E-2	2.74E-2	3.88E-3

Table 5-7 Relative errors of the gelation time (min.) for systems 1-5 at different initial polymer and redox concentrations

System	(CI ₁) _{optimum}	(CI ₂) _{optimum}
1	1008.983	584.2439
2	731.6227	147.0171
3	743.7534	100.9601
4	587.5404	174.0615
5	6203.098	5770.464

Table 5-8 Optimum values of initial polymer concentration at redox concentrations of 3103 and 2414 ppm

CHAPTER 6

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 CONCLUSIONS

The following conclusions can be derived from the analysis of the factors affecting the in-situ gelation process:-

(1) Statistical analysis results indicate that redox concentration, initial polymer concentration and polymer type have significant effects on the gelation time. These effects may be expressed in the coupling form, since the first order interaction of these parameters are found to be very significant.

(2) For a given polymer type, a polynomial form exists between the gelation time, initial polymer concentration and redox concentration. The coefficients of this relation vary with polymer type.

(3) The effect of temperature on the gelation time appears as an inverse exponential relationship.

(4) The variation of the coefficients in equation 4.15 is not linear. Therefore, second order polynomial equations are introduced. This provides the relative errors within the acceptable limits (10%). The relation developed helped determine the extreme value of the gelation time with respect to initial polymer and redox concentrations.

(5) An opportunity exists to determine the optimum values of the parameters effecting gel formation by the use of the equations developed in this study. Consequently, the limits of the applicability of the empirical equation is determined and it is found that the optimum value of the initial polymer concentration corresponding to the extreme value of the gelation time is beyond the values given in table 4.11.

6.2 RECOMMENDATIONS

The recommendations made due to the present study are as follows:-

1. After completing empirical formulations using the existing data, it may be suggested that:

a. To complete the comprehensive empirical formulation, more data, covering other variables (pH, salinity, temperature, and initial polymer and redox concentrations), is needed. This requires awaiting of more data available in the open literature.

b. Empirical equations developed are based on the individual polymer system. Mathematically, it is rather difficult to relate these individually developed empirical equations with the polymer systems. This is due to the fact that the data related to number of systems is not sufficient to generalize the empirical equations, i.e., only five systems are utilized in the present study. In addition, it is rather difficult to decide which is the most affecting polymer system parameters to use in this general empirical equation.

In the light of the above discussions, it may be recommended that experimentations for the gelation time needs to be extended in such away so that more polymer systems as well as more variables should be considered. Consequently, there may be more data produced in the literature. This makes able to develop better and general form of empirical equation between the gelation time and the process variables.

2. After obtaining the results from the extreme analysis of the gelation time, it may be recommended that experimentations for the gelation time may be extended to include small values (smaller than the values given in table 4.11) of the initial polymer concentration.

3. It may also be recommended that the present investigation can be applied to other gelling systems.

NOMENCLATURE

NOMENCLATURE

Arabic Characters:

- a = Partial regression.
- CI = Initial polymer concentration, ppm.
- CI₀ = First value of initial polymer concentration.
- CIN = Non-dimensional form of initial polymer concentration.
- CR = Redox concentration, ppm.
- CR₀ = First value of redox concentration.
- CRN = Non-dimensional form of redox concentration.
- F = Variance ratio.
- GT = Gelation time, min.
- i = Levels of polymer type.
- j = ~ ~ redox concentration.
- K = ~ ~ initial polymer concentration.
- p = Degree of freedom of the mean sum of squares.
- q = ~ ~ ~ ~ error mean sum of squares.
= Number of variables.
- PT = Polymer type.
- r = Correlation coefficient.
- R² = Multiple correlation coefficient.
- S = Standard deviation.

T = Temperature, °C

u = Number of dimensions.

Greek Characters:

β = Parameter used in linear regression model.

ε = Random error.

Π = Dimensionless parameter.

μ = Common effect.

σ^2 = Variance.

REFERENCES

REFERENCES

- [1] Willhite, G.P. (1986). Water Flooding, SPE Textbook Series Vol. 3, 1st ed.
- [2] Graig, F.F. (1980). The Reservoir Engineering Aspects of Water Flooding, Monograph of the H.L. Doherty Series, 3rd ed., Vol. 3.
- [3] Terry, R.E., Huang, C.G., Green, D.W., Michnick, M.J., and Willhite, G.P. (1981). Correlation of Gelation Times for Polymer Solutions Used as Sweep Improvement Agents, SPEJ, pp. 229-235.
- [4] Sydansk, R.D. (1990). Acrylamide-Polymer / Chromium(III) Carboxylate Gels for Near Wellbore Matrix Treatments, SPE paper 20214.
- [5] Navratil, M., Mitchell, M., and Slovak, M. (1982). Blocking and Diverting Agents for Enhanced Oil Recovery, CIM paper 82-23-54, Calgary.
- [6] Purkuple, J.D. and Summers, L.E. (1988). Evaluation of Commercial Crosslinked Polyacrylamide Gel Systems for Injection Profile Modification, SPE/DOE paper 17331.
- [7] Seright, R.S. (April 1993). Reduction of Gas and Water Permeabilities Using Gels, SPE# 25855, SPE Rocky Mountain Regional/Low Permeability Reservoirs Symposium, Denver, USA.
- [8] Liang, J.T., Lee, R.L., and Seright, R.S. (April 1990). Placement of Gels in Production Wells, SPE 20211 presented at the 7th Symposium on Enhanced Oil Recovery, Tulsa.
- [9] Nagra, S.S., Batycky, J.P. and Nieman, R.E. (1986). Stability of Waterflood Diverting Agents at Elevated Temperatures in Reservoir Brines, SPE paper 15548.
- [10] Sloat, B.F., Fitch, J.P., and Taylor, J.T. (Nov. 1972). How to Produce More Oil and More Profit With Polymer Treatment, SPE paper 4185, presented at the 43rd Annual California Regional Meeting of the SPE, Bakersfield.
- [11] Hessert, J.E., and Fleming, P.D. (April 1979). Gelled Polymer Technology for Control of Water in Injection and Production Wells, presented at the 3rd Tertiary Oil Recovery Conference, Wichita, Kansas.

- [12] McCool, C.S., Green, D.W., Willhite, G.P. (1988). Permeability Reduction Mechanisms Involved in In-Situ Gelation of Polyacrylamide/Chromium(VI)/Thiourea System, SPE/DOE paper 17333.
- [13] Jordan, D.S., Green, D.W., Terry, R.E., and Willhite, G.P. (1981). The Effect of Temperature on Gelation Time for Polyacrylamide-Chromium (III) Systems, SPE paper 10059.
- [14] Southard, M.Z., Green, D.W., and Willhite, G.P. (1984). Kinetics of the Chromium(VI)/Thiourea Reaction in the Presence of Polyacrylamide, SPE paper 12715.
- [15] Davies, O.L., (1978). Factorial Experiments With Factors at More Than two Levels, The Design and Analysis of Industrial Experiments, 2nd. ed., pp 290-296.
- [16] Buchingham, E. (1915). Model Experiments and the Forms of Empirical Equations, Trans. ASME, 35, pp. 263.
- [17] Vollmert, B. (1973). Polymer Chemistry, Springer-Verlag, Inc., New York.
- [18] Flory, P.J. (1953). Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York.
- [19] Glass, J.E. (1989). Polymers in Aqueous Media, Performance Through Association, advances in chemistry series 223, ACS.
- [20] Huang, C.G. (1983). An Experimental Study of the In-Situ Gelation of Chromium(III)-Polyacrylamide Polymer Systems in Porous Media, Ph.D. Dissertation, printed in 1993, University Microfilms International U.M.I., A Bell & Howell Company.
- [21] Ryles, R.G. (1988). Chemical Stability Limits of Water-Soluble Polymers Used in Oil Recovery Processes, SPE Res. Eng. 3, pp. 23-34.
- [22] Kulicke, W.M., Kniewske, R., and Klein, J. (1982). Preparation, Characterization, Solution Properties and Rheological Behavior of Polyacrylamide, Progress in Polymer Science 8, pp. 373.
- [23] Holzwarth, G. and J. Ogletree, J. (1979). Pyruvate-free Xanthan, Carbohydr. Res. 76, pp. 277-280.

- [24] Jeanes, A., Pittsley, J.E. and Senti, F.R. (1961). Polysaccharide B-1459: A New Hydrocolloid Polyelectrolyte Produced from Glucose by Bacterial Fermentation, *J. Appl. Poly. Sci.* 5 (17), pp. 519-526.
- [25] Schamp, N. and Huylebroeck, J. (1973). Phase Transition in Polymer Solution, *Nature, Physical Science*, 242, pp. 143.
- [26] Sorbie, K.S. (1991). *Polymer-Improved Oil Recovery*, 1st ed., Thomson Ltho Ltd., UK.
- [27] Chatterji, J. and Borchardt, J.K. (1980). Applications of Water-Soluble Polymers in the Oilfield, Presented at the 55th Annual Conference of the SPE, Held in Dallas, Texas.
- [28] Smith, F.W. (1970). The Behavior of Partially Hydrolyzed Polyacrylamide Solutions in Porous Media, *Journal of Petroleum Technology*, 22, pp. 148.
- [29] Maerker, J.M. (Oct. 1974). Shear Degradation of Polyacrylamide Solutions, SPE 5101, Presented at the 49th annual Fall Meeting of the SPE, Held in Houston, Texas.
- [30] Knight, B.L. (1973). Reservoir Stabilization of Polymer Solutions, *Journal of Petroleum Technology*, 25, pp. 618.
- [31] Shupe, R.D. (1981). Chemical Stability of Polyacrylamide Polymers, SPE paper 9299, presented at the 55th Annual Fall Conference of the SPE, Dallas, Texas.
- [32] Chauveteau, G. and Kohler, N. (April 1974). Polymer Flooding: The Essential Elements for Laboratory Evaluation, SPE paper 4745, Symposium on Improved Oil Recovery, Tulsa.
- [33] Mungan, N. (1972). Rheology and Adsorption of Aqueous Polymer Solutions, *Journal of Canadian Petroleum Technology* 8(2), pp. 45.
- [34] Shyluk, W.P. and Stow, F.S. (1969). Aging and Loss of Flocculation Activity of Aqueous Polyacrylamide Solutions, *Journal of Applied Polymer Science*, 13, pp. 1023.
- [35] Sparlin, D.D. (1976). An Evaluation of Polyacrylamide for Reducing Water Production, *Journal of Petroleum Technology*, 28, pp. 906.
- [36] Montgomery, W.H. (1962). *Polyacrylamide in Water-Soluble Resins*, 2nd ed., Reinhold Publ. Co., New York.

- [37] Martin, F.D. and Sherwood, N.S. (April 1975). The Effect of Hydrolysis of Polyacrylamide on Solution Viscosity, Polymer Retention, and Flow Resistance Properties, SPE paper 5339, Presented at the Rocky Mountain Regional Meeting of the SPE, Denver, Colorado.
- [38] Nouri, H.H. and Root, P.J. (Oct. 1971). A Study of Polymer Solution Rheology, Flow Behavior and Oil Displacement Processes, SPE paper 3523, Presented at the 46th Annual Fall Meeting of the SPE, New Orleans, Louisiana.
- [39] Hirasaki, G.H. and Pope, G.A. (1974). Analysis of Factors Influencing the Mobility and Adsorption in Flow of Polymer Solutions Through Porous Media, Society of Petroleum Engineering Journal, 14, pp. 337.
- [40] Gogarty, W.B. (1967). Rheological Properties of Pseudoplastic Fluids in Porous Media, Society of Petroleum Engineering Journal, 7, pp. 149.
- [41] Flory, P.J. (1942). Constitution of Three-Dimensional Polymers and the Theory of Gelation, Journal of Physical Chemistry, 46, pp. 132.
- [42] Prakash, S. (1931). Theory of Gelly Formation, Journal of the Society of Chemical Industry, 50, pp. 887.
- [43] Burkholder, L. (1985). Xanthan Gel System Effective for Profile Modification, Oil & Gas Journal.
- [44] Avery, M.R., Wells, T.A., Chang, P.W., Millican, J.D. (1988). Field Evaluation of a New Gelant for Water Control in Production Wells, SPE paper 18201.
- [45] Sparlin, D.D. and Hagen, R.W. (July 1984). Controlling Water in Producing Operations, World Oil, pp. 137-142.
- [46] Moradi-Arghi, A., Bjornson, G., and Doe, P.H. (Feb. 1989). Thermally Stable Gels for Near-Wellbore Permeability Contrast Corrections, SPE 18500 presented at the Oilfield Chemistry Symposium, Houston.
- [47] Islam, M.R. and Farouq Ali, S.M. (1993). Use of Silica Gel for Improving Waterflooding Performance of Bottom-Water Reservoirs, Journal of Petroleum Science and Engineering, 8, pp. 303-313.

- [48] Sydansk, R.D. and Smith, T.B. (April 1988). Field Testing of A New Conformance Improvement Treatment Chromium(III) Gel Technology, SPE paper 17383.
- [49] Krumrine, P.H. and Boyce, S.D. (April 1985). Profile Modification and Water Control with Silica Gel-Based Systems, SPE paper 13578.
- [50] Jurinak, J.J. and Summers, L.E. (Feb. 1989). Oilfield Application of Colloidal Silica Gel, SPE 18505.
- [51] Hurd, C.B. and Letteron, H.A. (1932). Studies on Silici Acid Gels, (I) Measurements on Surface Tension During Setting and the Effect of Temperature on the Time of Set, Journal of Physical Chemistry, 36, pp. 604.
- [52] Billheimer, J.S. and Parrette, R. (1956). Apparatus for Automatic Determination of Gelation Time, Analytical Chemistry, 28, pp. 272.
- [53] Nijenhuis, K. (1981). Investigation into the Aging Process in Gels of Gelatin/Water System by the Measurement of Their Dynamic Moduli, Colloid and Polymer Science, 259, pp. 522.
- [54] Masterton, W.L. and Hurley, C.N. (1989). Chemistry: Principles & Reactions, Inter. ed., Saunders College Publishing.
- [55] Thorstensen, T.C. (1958). The Chemistry of the Chromium Salts, Chapter 21, The Chemistry and Technology of Leather, Vol. II, Reinhold Publishing Corporation, New York.
- [56] Nichols, D. (1975). Chromium, From Complexes and First-Row Transition Elements, Chapter 13, American Elsevier Publishing Co., Inc., pp. 159.
- [57] Mumallah, N.A. (Feb. 1987). Chromium (III) Propionate: A Crosslinking Agent for Water-Soluble Polymers in Real Oilfield Waters", SPE paper 15906.
- [58] Shu, P. (Jan. 1989). Gelation Mechanism of Chromium (III), Oil-Field Chemistry - Chapter-6, Mobil Research and Development Corporation, pp. 136-44.
- [59] Gentile, A.J. (1963). Water Insolubilization of Acrylamide Polymers With a Salt of Trivalent Chromium, U.S. Patent 3,114,651.

[60] Clampitt, R.L. and Hessert, J.E. (1974). Method for Controlling Formation Permeability, U.S. Patent 3,785,437.

[61] Routson, W.G. (1972). Method for Controlling Flow of Aqueous Fluids in Subterranean Formations, U.S. Patent 3,687,200.

[62] Sydansk, R.D. and Moore, P.E. (Jan. 1992). Gel Conformance Treatments Increase Oil Production in Wyoming, Oil & Gas Journal, pp40-45.

[63] Kohler, N., Rahbari, R., and Zaitoun, A. (March 1993). Week Gel Formulations for Selective Control of Water Production in High-Permeability and High-Temperature Production Wells, SPE paper# 25225, pp709-722.

[64] Thompson, K.E. and Fogler, H.S. (March 1993). A Study of Diversion Mechanisms by Reactive Water-Diverting Agents, SPE paper# 25222, pp681-694.

[65] Seright, R.S. (April 1988). Placement of Gels to Modify Injection Profiles, SPE paper# 17332, pp137-148.

[66] Sorbie, K.S. and Seright, R.S. (April 1992). Gel Placement in Heterogeneous System with Crossflow, SPE paper# 24192, pp369-385.

[67] Hwan, R-N. R. (April 1993). Numerical Simulation Study of Water Shut-Off Treatment, SPE paper#25854, pp129-135.

[68] Todd, B.J., Willhite, G.P., and Green, D.W. (1990). A Mathematical Model of In-Situ Gelation of Polyacrylamide by Redox Process, SPE paper# 20215, pp409-419.

[69] Seright, R.S. (Feb. 1989). Effect of Rheology on Gel Placement, SPE paper# 18502, pp389-402.

[70] Rocha, C.A., Green, D.W., Willhite, G.P., and Michnick, M.J. (Feb. 1989). An Experimental Study of the Interactions of Aluminum Citrate Solutions and Silica Sand, SPE paper# 18503, pp403-414.

APPENDICES

APPENDIX- A

In the appendix-A, this Q-Basic program "Factorial Design Test" was used to determine the influence of each process parameter individually and the combination between the two affecting parameters in gelation time.

```

DIM X(5,4,5)
OPEN "I", #1, "GEL.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
INPUT #1, X(K,J,I)
NEXT I
NEXT J
NEXT K
REM CALCULATE MAIN EFFECTS FOR K (POLYMER TYPE)
SSUMK = 0
CSUM = 0
FOR K = 1 TO 5
SUMK = 0
FOR J = 1 TO 4
FOR I = 1 TO 5
SUMK = SUMK + X(K,J,I)
NEXT I
NEXT J
CSUM = SUMK + CSUM
SSUMK = (SUMK) ^ 2 + SSUMK
NEXT K
CSAK = SSUMK / 20 - (CSUM) ^ 2 / 100
REM CALCULATE MAIN EFFECTS FOR J (REDOX CONCENTRATION)
SSUMJ = 0
CSUM = 0
FOR J = 1 TO 4
SUMJ = 0
FOR K = 1 TO 5
FOR I = 1 TO 5
SUMJ = SUMJ + X(K,J,I)
NEXT I
NEXT K
CSUM = SUMJ + CSUM
SSUMJ = (SUMJ) ^ 2 + SSUMJ

```

```
NEXT J
CSAJ = SSUMJ / 25 - (CSUM) ^ 2 / 100
REM CALCULATE MAIN EFFECTS FOR I (INITIAL POLYMER CONCENTRATION)
SSUMI = 0
CSUM = 0
FOR I = 1 TO 5
SUMI = 0
FOR K = 1 TO 5
FOR J = 1 TO 4
SUMI = SUMI + X(K,J,I)
NEXT J
NEXT K
CSUM = CSUM + SUMI
SSUMI = (SUMI) ^ 2 + SSUMI
NEXT I
CSAI = SSUMI / 20 - (CSUMI) ^ 2 / 100
REM CALCULATE INTERACTIONS BETWEEN K AND J
SSUJ = 0
TCSSI = 0
FOR K = 1 TO 5
FOR J = 1 TO 4
SSI = 0
FOR I = 1 TO 5
SSUJ = SSUJ + X(K,J,I)
SSI = SSI + X(K,J,I)
NEXT I
TCSSI = (SSI) ^ 2 + TCSSI
NEXT J
NEXT K
TCSSI = TCSSI / 5
REM CALCULATE INTERACTIONS BETWEEN K AND I
TCSSJ = 0
FOR K = 1 TO 5
FOR I = 1 TO 5
SSJ = 0
FOR J = 1 TO 4
SSJ = SSJ + X(K,J,I)
NEXT J
TCSSJ = (SSJ) ^ 2 + TCSSJ
NEXT I
NEXT K
TCSSJ = TCSSJ / 4
REM CALCULATE INTERACTIONS BETWEEN J AND I
TCSSK = 0
FOR J = 1 TO 4
FOR I = 1 TO 5
SSK = 0
FOR K = 1 TO 5
SSK = SSK + X(K,J,I)
NEXT K
```

```

TCSSK = (SSK) ^ 2 + TCSSK
NEXT I
NEXT J
TCSSK = TCSSK / 5
REM CALCULATE CRUDE SQUARE SUM
CCSS = 0
CSS = 0
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
CSS = X(K,J,I) + CSS
CCSS = CCSS + X(K,J,I) ^ 2
NEXT I
NEXT J
NEXT K
MCSS = CSS / 100
MCCSS = CCSS / 100
SSAB = TCSSI - CSAJ - CSAK - MCSS
SSAC = TCSSJ - CSAI - CSAK - MCSS
SSBC = TCSSK - CSAI - CSAJ - MCSS
CMCCSS = MCCSS - CSUM / 100
SSAB = SSAB / 12
SSAC = SSAC / 16
SSBC = SSBC / 12
SSAK = CSAK / 4
SSAJ = CSAJ / 3
SSAI = CSAI / 4
PRINT SSAK; SSAJ; SSAI; SSAB; SSAC; SSBC
ER = CMCCSS / 51
VARA = SSAK / ER
VARB = SSAJ / ER
VARC = SSAI / ER
VARAB = SSAB / ER
VARAC = SSAC / ER
VARBC = SSBC / ER
REM CLS
PRINT "VA"; VARA; "VB"; VARB; "VC"; VARC; "VAB"; VARAB;
PRINT "VAC"; VARAC; "VBC"; VARBC

```


APPENDIX- B

In the appendix-B, three Q-Basic programs have been made to compute the relative errors in the polynomial equation 5.1 - 5.3 due to the regression analysis for initial polymer concentration, redox concentration, and temperature in gelation time.

THE FIRST PROGRAM:

```

DIM CI(5), CR(5), X(5,4,5), G(5), RES(5,4,5), DRES(5,4,5)
DIM MER(5), C(5), A0(5), A1(5), A2(5), A3(5), A4(5)
OPEN "I", #1, "C.DAT"
FOR I = 1 TO 5
INPUT #1, CI(I)
PRINT CI(I)
NEXT I
FOR J = 1 TO 4
INPUT #1, CR(J)
PRINT CR(J)
NEXT J
CLOSE #1
FOR I = 1 TO 5
G(I) = (CI(I) / CR(1))
NEXT I
OPEN "I", #1, "GEL.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
INPUT #1, X(I,J,K)
NEXT I
NEXT J
NEXT K
CLOSE #1
CLS
OPEN "I", #1, "COEF4.DAT"
FOR K = 1 TO 5
INPUT #1, C(K), A0(K), A1(K), A2(K)

```

```

NEXT K
CLOSE #1
FOR K = 1 TO 5
PRINT C(K), A0(K), A1(K), A2(K)
NEXT K
FOR K = 1 TO 5
SDRES = 0
FOR J = 1 TO 4
FOR I = 1 TO 5
AA = C(K) + A0(K)*(1/CI(I)) + A1(K)*1/(CI(I)*CR(J))
BB = A2(K)*(1/CR(J)) ^ 2
RES(I,J,K) = AA + BB
DRES(I,J,K) = X(I,J,K) - RES(I,J,K)
SDRES = SDRES + DRES(I,J,K) ^ 2
PRINT X(I,J,K), RES(I,J,K), DRES(I,J,K)
NEXT I
NEXT J
MER(K) = (SDRES/400) ^ 0.5
PRINT "MEAN ERROR", SDRES; MER(K)
NEXT K
N = 1
OPEN "O", #1, "PRE4.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
PRINT #1, N, X(I,J,K), RES(I,J,K), DRES(I,J,K)
N = N + 1
NEXT I
NEXT J
NEXT K
CLOSE #1
OPEN "O", #1, "ERROR4.DAT"
FOR K = 1 TO 5
PRINT #1, k, MER(K)
NEXT K
CLOSE #1
OPEN "O", #1, "NAK.DAT"
FOR I = 1 TO 5
PRINT #1, G(I)
NEXT I
CLOSE #1

```

THE SECOND PROGRAM:

```

DIM CI(5), CR(5), X(5,4,5), G(5), RES(5,4,5), DRES(5,4,5)
DIM MER(5), C(5), A0(5), A1(5), A2(5), A3(5), A4(5), A5(5)
DIM OSIL(5,4,5), DRMS(5,4,5)
OPEN "I", #1, "C.DAT"

```

```

FOR I = 1 TO 5
INPUT #1, CI(I)
PRINT CI(I)
NEXT I
FOR J = 1 TO 4
INPUT #1, CR(J)
PRINT CR(J)
NEXT J
CLOSE #1
FOR I = 1 TO 5
G(I) = (CI(I) / CR(1))
NEXT I
OPEN "I", #1, "GEL.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
INPUT #1, X(I,J,K)
NEXT I
NEXT J
NEXT K
CLOSE #1
CLS
OPEN "I", #1, "COEF2.DAT"
FOR K = 1 TO 5
INPUT #1, C(K), A0(K), A1(K), A2(K)
NEXT K
CLOSE #1
FOR K = 1 TO 5
PRINT C(K), A0(K), A1(K), A2(K)
NEXT K
FOR K = 1 TO 5
SDRES = 0
N = 1
RRMS = 0
FOR J = 1 TO 4
FOR I = 1 TO 5
AA = C(K) + A0(K)*EXP(CI(I)/CR(J)) + A1(K)*(CI(I)/CR(J))
BB = A2(K)*(CI(I) / CR(J)) ^ 3
RES(I,J,K) = AA + BB
DRES(I,J,K) = X(I,J,1) - RES(I,J,1)
SDRES = SDRES + DRES(I,J,K) ^ 2
OSIL(I,J,K) = ABS(DRES(I,J,K)) / X(I,J,K)
RRMS = DRES(I,J,K) + RRMS
PRINT X(I,J,K); RES(I,J,K); DRES(I,J,K); OSIL(I,J,K)
N = N + 1
NEXT I
NEXT J
MER(K) = (SDRES/400) ^ 0.5
PRINT "MEAN ERROR", SDRES; MER(K)
NEXT K

```

```

N = 1
OPEN "O", #1, "PRE3.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
PRINT #1, N, X(I,J,K), RES(I,J,K), OSIL(I,J,K)
N = N + 1
NEXT I
NEXT J
NEXT K
CLOSE #1
OPEN "O", #1, "ERROR3.DAT"
FOR K = 1 TO 5
PRINT #1, k, MER(K)
NEXT K
CLOSE #1
OPEN "O", #1, "NAK.DAT"
FOR I = 1 TO 5
PRINT #1, G(I)
NEXT I
CLOSE #1

```

THE THIRD PROGRAM:

```

DIM T(5), X(5,2,2), RES(5,2,2), DRES(5,2,2), CR(2)
DIM A0(2), A1(5), A2(5), A3(5), OSIL(5,4,5), A4(5)
OPEN "I", #1, "T.DAT"
FOR I = 1 TO 5
INPUT #1, T(I)
PRINT T(I)
NEXT I
FOR J = 1 TO 2
INPUT #1, CR(J)
PRINT CR(J)
NEXT J
CLOSE #1
OPEN "I", #1, "TEMP.DAT"
FOR J = 1 TO 2
FOR I = 1 TO 5
INPUT #1, X(I,J,1)
PRINT X(I,J,1);
NEXT I
NEXT J
CLOSE #1
OPEN "I", #1, "COEF5.DAT"

```

```
INPUT #1, CC(1), A0(1), A1(1), A2(1), A3(1)
CLOSE #1
PRINT CC(1), A0(1), A1(1), A2(1), A3(1)
CLS
SDRES = 0
FOR J =1 TO 2
FOR I =1 TO 5
AA = CC(1) + A0(1) * (CR(J)) + A1(1) * (1/T(I)) ^ 2
BB = A2(1) * EXP(1/T(I)) + A3(1) * CR(J)/T(I)
RES(I,J,1) = AA + BB
DRES(I,J,1) = X(I,J,1) - RES(I,J,1)
SDRES = SDRES + DRES(I,J,1) ^ 2
OSIL(I,J,1) = ABS(DRES(I,J,1))/X(I,J,1)
PRINT X(I,J,1), RES(I,J,1), DRES(I,J,1), OSIL(I,J,1)
NEXT I
NEXT J
MER = (SDRES/400)^(1/2)
PRINT "MEAN ERROR", SDRES; MER
N = 1
OPEN "O", #1, "PRE5.DAT"
FOR J = 1 TO 2
FOR I = 1 TO 5
PRINT #1, N, X(I,J,1), RES(I,J,1), OSIL(I,J,1)
N = N + 1
NEXT I
NEXT J
CLOSE #1
```

APPENDIX- c

In this appendix, we have two Q-Basic programs. The first one is used to compute the relative errors in the power relation analysis equation 5.5. The second program is used to compute the optimum value of the initial polymer concentration.

THE FIRST PROGRAM:

```

DIM CI(5), CR(5), X(5,4,5), G(5), RES(5,4,5), DRES(5,4,5)
DIM MER(5), AC1(5), AC2(5), AC3(5), AK11(5), AK12(5)
DIM AK21(5), AK22(5), AK31(5), AK32(5)
OPEN "I", #1, "C.DAT"
FOR I = 1 TO 5
INPUT #1, CI(I)
PRINT CI(I)
NEXT I
FOR J = 1 TO 4
INPUT #1, CR(J)
PRINT CR(J)
NEXT J
CLOSE #1
FOR I = 1 TO 5
G(I) = (CI(I) / CI(1))
NEXT I
OPEN "I", #1, "GEL.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
INPUT #1, X(I,J,K)
NEXT I
NEXT J
NEXT K
CLOSE #1
CLS
OPEN "I", #1, "COEF.DAT"
FOR K = 1 TO 5

```

```

INPUT #1, AC1(K), AK11(K), AK12(K), AC2(K), AK21(K), AK22(K)
INPUT #1, AC3(K), AK31(K), AK32(K)
NEXT K
CLOSE #1
FOR K = 1 TO 5
PRINT AC1(K), AK11(K), AK12(K), AC2(K), AK21(K), AK22(K)
PRINT AC3(K), AK31(K), AK32(K)
NEXT K
FOR K = 1 TO 5
SDRES = 0
FOR J = 1 TO 4
FOR I = 1 TO 5
C(K) = AC1(K) + AK11(K) * (CR(J) / CR(1)) + AK12(K) * (CR(J) / CR(1)) ^ 2
K1(K) = AC2(K) + AK21(K) * (CR(J) / CR(1)) + AK22(K) * (CR(J) / CR(1)) ^ 2
K2(K) = AC3(K) + AK31(K) * (CR(J) / CR(1)) + AK32(K) * (CR(J) / CR(1)) ^ 2
RES(I, J, K) = C(K) + K1(K) * (CI(I) / CI(1)) + K2(K) * (CI(I) / CI(1)) ^ 2
DRES(I, J, K) = X(I, J, 1) - RES(I, J, 1)
SDRES = SDRES + DRES(I, J, K) ^ 2
PRINT X(I, J, K), RES(I, J, K), DRES(I, J, K)
NEXT I
NEXT J
MER(K) = (SDRES / 400) ^ 0.5
PRINT "MEAN ERROR", SDRES; MER(K)
NEXT K
N = 1
OPEN "O", #1, "PRE1.DAT"
FOR K = 1 TO 5
FOR J = 1 TO 4
FOR I = 1 TO 5
PRINT #1, N, X(I, J, K), RES(I, J, K), DRES(I, J, K)
N = N + 1
NEXT I
NEXT J
NEXT K
CLOSE #1
OPEN "O", #1, "ERROR1.DAT"
FOR K = 1 TO 5
PRINT #1, k, MER(K)
NEXT K
CLOSE #1
OPEN "O", #1, "NAK.DAT"
FOR I = 1 TO 5
PRINT #1, G(I)
NEXT I
CLOSE #1

```

THE SECOND PROGRAM:

The values of A's, B's, and C's can be obtained from table 5.6 to use in the following program. For system-1 as an example:

```

DIM X(10), Y1(10), Y2(10), AA(10), BB(10), CC(10), CRR(10)
DIM CR(10), CI(10), CICAL(10), CIR(10), CICAL1(10), CICAL2(10)
A1 = 316:          A2 = -738.33739#:  A3 = 449.485072#
B1 = -616.43944#: B2 = 1574.337386#: B3 = -966.87063#
C1 = 347.000619#: C2 = -920.676472#: C3 = 595.189561#
OPEN "I", #1, "C.DAT"
FOR I = 1 TO 5
INPUT #1, CI(I)
NEXT I
FOR J = 1 TO 4
INPUT #1, CR(J)
NEXT J
CLOSE #1
FOR J = 1 TO 4
CRR(J) = CR(J) / CR(1)
NEXT J
CLS
FOR I = 1 TO 4
BB(I) = B1 + B1 * 2 * CRR(I)
AA(I) = A1 + 2 * A2 * CRR(I)
CC(I) = C1 + C2 * 2 * CRR(I)
DELTA = 4 * AA(I) * CC(I)
IF (DELTA < 0) THEN PRINT "NEGATIVE ROOT", I: GOTO 100
Y1(I) = (-BB(I) + DELTA ^ 0.5) / (2 * AA(I))
Y2(I) = (-BB(I) - DELTA ^ 0.5) / (2 * AA(I))
IF (Y1(I) < 0) THEN Y1(I) = 0: IF (Y2(I) < 0) THEN Y2(I) = 0
CICAL2(I)=Y2(I):CICAL1(I)=Y1(I)
PRINT "VALUES OF CI", Y1(I), Y2(I), I
100 NEXT I
PRINT "CI RATIO AND CI OPTIMUM RATIO"
FOR I = 1 TO 5
CIR(I) = CI(I) / CI(1)
CICAL1(I) = CICAL1(I) * CI(1)
CICAL2(I) = CICAL2(I) * CI(1)
PRINT CIR(I), CICAL1(I), CICAL2(I)
NEXT I
CLOSE #1

```