

REPORT

DOE/ET/27146--T14

CHEMICAL DAMAGE DUE TO
DRILLING OPERATIONS

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PREPARED BY

DR. O. J. VETTER AND

DR. V. KANDARPA

VETTER RESEARCH

3189C AIRWAY AVE. - COSTA MESA - CALIFORNIA 92626

SUBMITTED TO

UNITED STATES DEPARTMENT OF ENERGY
DIVISION OF GEOTHERMAL ENERGY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISTRIBUTION LIST:

MR. A. ADDUCI, U.S. DEPARTMENT OF ENERGY	6 COPIES
DOE TECH INFORMATION CENTER	1 COPY
OFFICE OF CALIFORNIA PATENT COUNCIL	1 COPY
DR. O. J. VETTER, VR	1 COPY
DR. V. KANDARPA, VR	1 COPY
VR FILE	4 COPIES

DATE OF ISSUANCE: JULY 14, 1982

VR REPORT NO: 82-07-14

SIGNATURE(S):

Ollo Vetter
Uadu



TABLE OF CONTENTS

	<u>PAGE</u>
PREAMBLE.....	1
1.0 ABSTRACT.....	2
2.0 CONCLUSIONS.....	2
3.0 RECOMMENDATIONS.....	6
4.0 INTRODUCTION.....	8
5.0 VARIOUS TYPES OF DAMAGES EXPECTED DURING DRILLING OPERATIONS.....	9
5.1 PHYSICAL DAMAGE.....	11
5.2 CHEMICAL DAMAGE.....	11
5.2.1 THERMODYNAMIC INSTABILITY OF DRILLING FLUIDS.....	12
5.2.1.1 THERMODYNAMIC INSTABILITY OF MUD SOLIDS.....	12
5.2.1.2 THERMODYNAMIC INSTABILITY OF MUD FILTRATE.....	14
5.2.1.2.1 INSTABILITY OF DRILLING FLUID FILTRATE DUE TO TEMPERATURE AND PRESSURE CHANGES.....	15
5.2.1.2.2 MIXING OF INCOMPATIBLE WATERS AND RESULTING INSTABILITY PROBLEMS.....	16
5.2.2 DISAGGREGATION OF CLAY MINERALS.....	18
5.2.3 CHEMICAL ALTERATIONS OF SOME INVADED MUD SOLIDS.....	19
6.0 VARIOUS PRECAUTIONS TO BE TAKEN TO REDUCE CHEMICAL DAMAGE DURING DRILLING OPERATIONS.....	20
REFERENCES.....	21

PREAMBLE

The United States Department of Energy, Division of Geothermal Energy (DOE/DGE) awarded Vetter Research (VR) a contract to perform research related to injection and reinjection problems in geothermal operations. This contract No. DE-AC03-79ET-27146, is entitled: "Injection, Injectivity and Injectibility in Geothermal Operations". The present report is one of the deliverables under this contract. The present report discusses some of the possible chemical damages expected during drilling and completion of geothermal injection wells. The main objective of this report is to attract the attention of drilling operators to the commonly ignored chemically induced wellbore and reservoir damage created during drilling, completion and/or work-over of a geothermal well.

1.0 ABSTRACT

The drilling of geothermal wells can result in near wellbore damage of both the injection wells and production wells if proper precautions are not taken. Very little specific information on the chemical causes for drilling damage that can directly be applied to the drilling of a geothermal well in a given situation is available in the literature. As part of the present work, the sparse literature references related to the chemical aspects of drilling damage are reviewed.

The present report summarizes the various sources of chemically induced drilling damages that are related to drilling operations. The report also suggests various means of minimizing these chemical damages during and after the drilling of a geothermal well.

2.0 CONCLUSIONS

The following is a summary of our conclusions regarding the chemically induced damage mechanisms related to drilling of geothermal wells. These conclusions are based on (a) the information gathered from various sources of literature (b) our field experience and (c) some of our own laboratory work experiences under this present research contract (see Preamble):

1. There is very little published information on the chemical damage during and after drilling of a geothermal well, i.e., on the chemical damage that can be directly related to a geothermal drilling operation. Only some rather general and vague information is available in the open literature.
2. The susceptibility to chemically induced damage of geothermal wells which is directly attributable to drilling can be considerable. It has its cause in the various and sometimes extremely complex physical and chemical interactions between the constituents of the drilling mud and those of the reservoir. Most of these interactions are not known in sufficient detail.
3. Quite often, it is difficult, if not impossible, to distinguish between purely chemical and purely physical damages caused by drilling operations. Most chemical damages are initiated, followed, aggravated and/or accompanied by physical damages.
4. The majority of the physical damages caused during drilling operations arises from the introduction of solid particles into the wellbore. These particles can create damage by plugging critical portions of either the wellbore or the reservoir.

5. Theoretically, there are four different mechanisms by which particles can ruin the productivity or injectivity of a well:

- a) Fill-up of the wellbore with solids.
- b) Generating a mud cake on the "sand face" within either a wellbore or a fracture.
- c) Filling up of slots or perforation holes within a liner or casing installed within the well.
- d) Creating of damage collars within the reservoir by particles which invade the rock matrix and "settle" or are retained in some distance from the wellbore.

6. The chemically induced damage caused during drilling operations arises from numerous chemical reactions involving the invaded drilling mud particles, the drilling mud filtrate and/or the various constituents of the reservoir.

7. Seven major categories that can be related to the chemical damages are:

- a) The precipitation or formation of salts and other solids within the wellbore or within the reservoir due to the thermodynamic instability of the mud constituents at the high wellbore or reservoir temperature.
- b) The change in the properties of invaded mud particles can cause the subsequent formation of plugging with newly generated types of solids within the reservoir.
- c) The chemical interactions between the various components of the invading drilling fluids and the native reservoir materials can lead to an impairment of the injectivity (or productivity).
- d) The disaggregation and/or dislodging of clay or other cementing minerals that are native to the reservoir through the interactions between the dissolved species of the mud filtrate and the cement type materials can cause an injectivity (or productivity) impairment.

- e) The reservoir invasion of solid corrosion products, decay products of mud additives and/or other chemical reaction products can impair injectivity (or productivity).
These solid products are formed because of chemical reactions between the drilling fluid components and the materials used for the completion of a well during and/or after drilling operations.
 - f) The change of the surface energy of the reservoir solids due to the invasion of mud fluids containing organic liquids and surface active materials.
 - g) The utilization of improper fluids designed to remove the mud or completion fluids after drilling and/or completion of the well can lead to an impairment of the injectivity (or productivity) (e.g., formation of foam blocks due to the additives used in the cleaning fluids or formation of solids due to the use of chemically incompatible waters in the workover fluids).
8. The drilling mud filtrate that entered the reservoir can plug the pores of the rock matrix or fractures within the reservoir by the precipitation of salts which is caused by the thermodynamic instability and/or reactivity of both the invading fluids and the native reservoir materials. There are two ways in which these precipitations can be caused:
- a) The thermodynamic instability of the dissolved species in the mud filtrate created by the high temperature can lead to subsequent precipitations.
 - b) The thermodynamic instability of the solutions created by the mixing of the mud filtrate with the reservoir brine can generate various types of precipitation.
9. The thermodynamic instability of the mud filtrate itself, mainly due to temperature changes, can result in a near wellbore damage (skin), e.g., by CaSO_4 and/or BaSO_4 precipitations. The prevention of this type of damage would necessitate the proper removal of SO_4 --

ions from the mud or drilling fluid prior to using these fluids.

10. The thermodynamic instability caused by the mixing of mud filtrate with the formation fluid can create a potential for CaSO_4 , SrSO_4 and/or BaSO_4 type skins. This would necessitate either the removal of SO_4^{--} ions from the drilling fluids (if the reservoir fluid contains the ions of alkaline earth metals) or avoiding of alkaline earth metal compounds in the drilling fluids (if the reservoir fluid contains SO_4^{--} ions).
11. If the reservoir fluids contain high concentrations of divalent or trivalent cations, the normally high pH value and/or the high CO_3^{--} concentration of the drilling fluids can cause heavy precipitation of hydroxide and carbonate scales.
12. The chemical damage caused by the disaggregation or dislodging of clays and other cementing materials that are native to the formation due to the interaction between these solid materials and certain ionic species dissolved in the drilling fluids is caused by very complex chemical reactions. The chemistry of these reactions is not quite clear and will change from site to site or reservoir to reservoir.
13. The swelling of reservoir clays upon contact with drilling fluids can lead to reservoir damage. This type of damage can also be considered a chemically induced damage.
14. Certain clays used in drilling formulations can cause numerous problems. At least two types of reservoir damages can be expected due to improper clay additives:
 - a) Certain clays (e.g., montmorillonite) can form highly impermeable mud cakes which are difficult to remove and may lead to permanent injectivity problems.
 - b) Other clays (e.g., sepiolite and attapulgite) can convert to swellable clays (smectites) at the high temperatures, thus impairing the later injectivity (or productivity) of the well.
15. The damage caused by montmorillonite type clays in the high temperature environment of a geothermal well is not well understood. Most likely, it is created by the formation of Ca-montmorillonite, a reaction which should be further investigated.

16. The high-temperature behavior of many drilling fluid additives used in oilfield operations is uncertain at best and should be evaluated before these additives are used in geothermal operations.

3.0 RECOMMENDATIONS

The following general recommendations can be made to prevent the various types of chemically induced wellbore and/or reservoir damage during geothermal drilling operations:

1. Drilling operations should be aimed at maintaining a low differential pressure between the wellbore and the near wellbore region of the reservoir, thereby reducing the possibility of drilling mud invasion (particularly the filtrate).
2. Prior to the initiation of drilling operations, sufficient information on the nature of the formation solids and fluids should be obtained through chemical analysis or otherwise. This information should be used to make up proper drilling fluid compositions.
3. The mud composition, especially the make-up water must be carefully tailored to the very site specific conditions. There is no generally acceptable recipe for mud compositions.
4. Proper scale inhibitors, oxygen scavengers and clay stabilizers should be used in the drilling fluids.
5. If drill pipe corrosion is a major concern, adding of oxygen scavengers (e.g., hydrazine) and corrosion inhibitors should be attempted instead of the more conventional increasing of the pH value. This is of particular importance if the reservoir fluids contain large concentrations of divalent or trivalent ions.
6. Drilling fluids components should be checked for their high-temperature reactivity. These components should be evaluated for their high-temperature stability and their reactivity with other drilling fluid components and/or with the native reservoir materials.
7. Creating of near wellbore damage due to mixing of mud filtrate and formation water requires a scale or precipitation prediction modeling. The determination of the amount of filtrate and the mixing proportions between the mud filtrate and the formation water at various distances from the wellbore must be known for precise damage calculations.

8. The water used for drilling mud formulation should contain a very low SO_4^{--} ion concentration and should have a fairly low pH value if the reservoir brine contains appreciable concentrations of divalent ions (particularly, Ca^{++} , Sr^{++} and Ba^{++} ions) as usually found in the geothermal reservoirs within the United States.
9. The make-up water for drilling fluids should be carefully chosen. If the available water is a water which is chemically incompatible with the reservoir fluids, special water preparations could include a proper mixing of source water with reservoir water or the precipitating of undesired water compounds by adding of chemicals and removing of the undesired reaction products prior to using the mixtures as a make-up water for drilling fluids.
10. The volume ratio of source water to produced reservoir water for drilling fluid preparations should be carefully calculated based upon the chemical compositions of the various types of water and the reservoir temperature.
11. The formulations for drilling muds should be selected such that their various constituents do not adversely affect the clays and other cementing materials that are contained in the formation. There is no generally acceptable recipe. Each formulation should be tailored to the very site specific conditions.
12. The solid components of drilling mud should be selected so that the high temperatures of the geothermal formation do not adversely affect the nature of these solid mud components. A typical example is the conversion of sepiolite or attapulgite to smectites (e.g., to stevensite).
13. The clays used in some high temperature drilling fluids (e.g., sepiolite and attapulgite) should be checked for their quality. Often, these clays are heavily contaminated with other clays (e.g., sepiolite contaminated with montmorillonite).
14. Injection wells should always be back-flowed after each drilling, completion or work-over operation. All materials which invaded a well or reservoir should be removed through back-flowing before any other well operation is started. Displacing of the invaded fluids with the injection brine prior to back-flowing may generate severe and irreparable damage far away from the wellbore.

15. Disposal of waste fluids (including drilling fluids) into the injection wells should be avoided or carefully evaluated for the potential of generating reservoir damage prior to starting of any of these disposal operations. These disposal operations of drilling fluids may solve an environmental problem but may create a damage problem.
16. Disposal of drilling fluids into a injection well during or after drilling operations is often adviseable if these fluids are chemically treated in a proper way prior to their disposal into a well.

4.0 INTRODUCTION

Basically, the conventional oilfield technology of rotary drilling is used for drilling of geothermal wells. Some minor improvements are made to the drilling fluid components used in oilfield operations so that they become suitable for the high temperature environment of geothermal reservoirs [1,2]. Some extensive R&D efforts are being made by Sandia National Laboratories under the auspices of the U. S. Department of Energy not only in improving the various components used for conventional rotary drilling operations, but also in developing of an advanced technology for geothermal drilling [3,4]. Water based drilling muds using sepiolite and/or attapulgite or simply clear brines are suggested (a) to transport the cuttings to the surface, (b) to cool the bit and (c) to prevent the formation fluids from entering the wellbore [5,6]. The technology of geothermal drilling is constantly improving through some research programs funded by DOE/DGE as well as through industry sponsored R&D programs.

No matter what types of drilling practice are utilized, these operations can result in an injectivity impairment due to chemically induced damages if proper precautions are not taken. In addition, the disposal of various fluids during and/or after these drilling operations into the injection wells is still common practice. Such disposal can also result in serious injectivity problems due to chemically induced damages.

Very little specific information is available on the chemically induced damages of injection wells due to drilling and completion operations which are presently prevailing in the geothermal industry. Only some rather general and vague information is available.

Despite the potential danger, some geothermal reinjection operations seem to be rather successful. These "successes" do not change the facts that (a) immense reinjection problems are caused in several foreign [7] and domestic operations despite frequent claims to the contrary and, (b) some of these

"successful" operations may use damaged injection wells even without the recognition or knowledge of the operator. Many of these damage problems can be related to chemical damages created during well drilling and completion operations.

The purpose of the present report is (a) to review the literature on the damages that are anticipated during the drilling and completion of geothermal injection wells, (b) to evaluate our own laboratory studies under this present contract as far as they relate to drilling operations, and (c) to offer some possible solutions to prevent or repair such damages based on our field experience. Even though the report mentions the physical damages as well as chemical damages, the emphasis is placed here on the various damages of chemical origin.

5.0 VARIOUS TYPES OF DAMAGES EXPECTED DURING DRILLING OPERATIONS

The damages to injection wells (or production wells) of oil field and geothermal operations have their origin in the various physical and chemical interactions between the components of the drilling muds and the components of the geothermal formations. Glenn and Slusser [9,10] and Nicholson [11] have summarized some of the various factors contributing to the damage to geothermal wells during and/or after the well drilling and completion operations. However, none of the literature references seems to contain sufficient detail of the chemically induced damages.

Two types of damages can be expected during geothermal drilling operations:

1. Physical damage: the damage caused by the invasion of suspended particles of the drilling fluid into the porous formation.
2. Chemical damage: the damage caused by the chemical reactions involving the invaded particles, drilling mud filtrate and the formation components.

It should be noted, however, that it is often very difficult, if not impossible, to distinguish between purely chemical and purely physical causes for a wellbore and/or reservoir damage created during and after drilling operations. Considering the specifics of geothermal formations, the major factors contributing to drilling damages are as follows:

1. The reservoir rock is porous and, normally highly permeable and/or contains pronounced fractures, thus allowing drilling fluids to enter the reservoir.

2. The reservoir is under relatively low pressure and the drilling fluids are often applied at external pressures higher than the reservoir pressure during drilling, thus forcing the drilling fluids into the reservoir.
3. The drilling fluids entering the reservoir contain suspended particles. Both the entering suspended solids and liquids will generate a host of undesired reactions either through their own thermodynamical instability or through chemical interactions between the various components of the invading drilling fluids and the materials that are native to the reservoir.
 - a) The drilling and/or completion fluids entering the reservoir may be thermodynamically unstable under these high temperatures and may form chemical reaction products leading to subsequent reservoir damage.
 - b) The temperature of the geothermal formations are high (in excess of 260°F and sometimes as high as 800°F), thereby creating a favorable environment for many undesired chemical reactions.
 - c) The formation fluids often contain fairly high concentrations of dissolved species which are chemically incompatible with the entering drilling fluids thereby also creating the basis for many undesired high temperature chemical reactions. These reactions include (but are not limited to) the precipitation of many scale forming and plugging solids.

Some of the components normally contained in drilling fluids may lead to formation damage through physical and chemical interactions. The major factors that contribute to this chemically induced formation damage are as follows:

1. The drilling fluids may contain various dissolved species (especially, the SO₄-- and CO₃-- ions), and can have an artificially high pH value thereby creating an environment in the porous formation which is favorable for sulfate, carbonate and hydroxide scale formation.
2. The drilling fluids may contain newly generated and very fine suspended particles (reaction products) which can invade and plug the porous formation.

3. The drilling fluids contain clay minerals (e.g., montmorillonite, attapulgite or sepiolite) which can enter the high temperature environment of the formation and can chemically react to create a massive damage to the formation.
4. The drilling fluids may contain thermodynamically unstable additives or chemicals which can chemically react with each other or with the reservoir materials, thus causing various types of wellbore and reservoir damage.

Summarizing we can state that the drilling fluids may contain additives which chemically react (a) by themselves (b) with other additives (c) with any material native to the formation, thus causing a host of different types of chemically induced damage. This means, the major sources for a chemical wellbore and reservoir damage during drilling and completion operations must be seen in the chemical reactivity of various components of the geothermal formation and the drilling fluid system.

5.1 PHYSICAL DAMAGE

Fine particles of clay solids are added (a) to increase the viscosity of the drilling fluid, (b) to improve the hole stability and (c) to aid in the suspending of the drilling cuttings. These clay particles can form filter cakes within the wellbore or on the faces of a fracture. At high differential pressures, some of these clay particles can also enter the porous formation. A comprehensive research work was conducted at Vetter Research as part of the present DOE/DGE contract to study the characteristics of the flow of particle suspensions through porous media. The results of this work are being described in a separate DOE report [12]. A portion of this work was already published before [14].

5.2 CHEMICAL DAMAGE

This type of damage to the geothermal formation has its origin in the chemical reactions occurring during the drilling operations. The various types of chemically induced damages within the wellbore or reservoir have their origin in various sources as follows:

1. The changes in the properties of invaded mud particles and other mud components in the drilling fluid within the environment of the geothermal formation due to the thermodynamic instability of the drilling fluid components.
2. The precipitation of salts or other solids due to the

chemical reactions between the mud filtrate and the reservoir brine.

3. The disaggregation of clay minerals that are native to the formation caused by certain ionic species contained in the mud filtrate.
4. The conventional operating methods aimed at overcoming corrosion of drilling equipment at high temperature in the presence of highly saline geothermal brines.

5.2.1 THERMODYNAMIC INSTABILITY OF DRILLING FLUIDS

The thermodynamic instability of a drilling fluid and its implications are rather difficult to measure or even to comprehend. This instability is not only a function of the precise mud composition and the various temperatures encountered in the wellbore, but also the relationship between the nature of the suspended mud solids and their concentration within the mud. To complicate things further, the nature of the solids suspended in the mud and their concentration may change constantly in an actual drilling operation as a function of temperature, time, drilling conditions, etc. An additional and complicating factor is given by the change of the mud composition as mixing with reservoir materials (liquids and solids) may occur during the drilling operations.

In the following paragraphs, we will outline some of the damage problems created by the thermodynamic instability of the drilling fluids. These problems are twofold, namely, the problems caused by the solid particles suspended in the mud and those caused by the liquid phase ("mud filtrate").

5.2.1.1 THERMODYNAMIC INSTABILITY OF MUD SOLIDS

The mud solids are normally difficult to define. When mud is freshly prepared and stored in the mud tanks, the solid composition, concentrations and particle size parameters can be fairly well defined and measured. All these parameters become drastically changing variables as soon as the mud is pumped into the wellbore and becomes exposed to the high temperatures of a geothermal well even without the mud coming in contact with reservoir material. New solids may form due to precipitation of salts created in the liquid phase of the mud caused by the temperature effects as outlined later in this report. The "old" or original particles contained in the freshly prepared mud may (a) dissolve or (b) change their nature based on various physicochemical reactions. Thus, the chemical composition, concentration and physical particle characteristics of the suspended mud solid may already drastically change as a function of temperature and time even without any further complicating factors.

As the mud comes in contact with the reservoir materials under drilling conditions, additional and, possibly, more drastic changes of the solid properties may occur. Liquid from the original mud may invade the reservoir, thus leaving the solid behind, or liquids from the reservoir may enter the mud, thus also causing drastic changes of the solids properties of the suspended solids in the drilling fluids. In addition, the grinding action of the drill bit and friction and/or impact forces within the mud phase can also have large effects on the critical solid properties within these drilling fluids.

These mechanical and thermodynamic instability problems related to the drilling fluids within the wellbore can be carried back into the surface facilities. Solids may be continuously taken out through the shakers, desanders, desilters, centrifuges or any other type of solid removal equipment, thus constantly changing the pertinent solid characteristics and composition of the drilling fluids pumped back into the hole.

However, this already complex situation regarding the pertinent characteristics of the solids in the drilling fluids is further compounded by the facts that (a) some solids may form a mud cake on the sandface (within the wellbore or within a fracture) and (b) other solids may be small enough to invade the pore of the reservoir rock.

To complicate things even further, the operator may change deliberately his mud composition, particularly, the solid content at any time during a given drilling operation. He may see a need to add or delete a weighing agent (e.g., barite), an oxygen scavenger (e.g., hydrazine), and H₂S scavenger (e.g., ZnCO₃), a fluid loss agent (e.g., saw dust), a viscosifier (e.g., clay or an organic polymer) and/or many other additives depending upon the condition and/or problems encountered and/or suspected in the wellbore.

The chemically induced damages caused by changing, adding or deleting of any of these and other mud additives can be very complex. These solid additives mixed into the drilling fluid for various reasons and purposes can chemically react and can, conceivably, cause numerous types and degrees of damages to the wellbore and reservoir. Because of this high temperature reactivity and/or thermodynamic instability, these additives can react:

1. By themselves, i.e., they can chemically degrade under the conditions of a wellbore during and/or after drilling.
2. With other components or additives in the drilling fluids.
3. With reservoir fluids or solids after being exposed to

these reservoir materials either during or after drilling operations.

The numerous additives used during drilling operations in a geothermal field and the large variety of different reservoirs or wellbore conditions generates a host of complex chemical reactions which can lead to an infinite number of different chemical damages. It is impossible to name all the possibilities for these chemical reactions and the subsequently induced damages to geothermal wellbores and reservoirs.

There does not seem to be any alternative to the old-fashioned testing of any of these materials (mud additives) prior to applying these mud additives in a given situation. Some of these additive candidates have been checked in our laboratories [49,50,51]. The conclusions of this test work are not quite definite about the damage mechanisms. However, the experimental results given in these references [49 through 51] indicate that chemically induced damages must be expected due to the application of these materials during drilling of a geothermal well.

Thus, one of the most complex problems in drilling operations is caused by these solids partially forming a mud cake and partially invading the porous matrix of a reservoir rock. The particles that entered the porous matrix of the reservoir can begin to plug the pores. The plugging of the pores (or the reduction in the local, microscopic permeability) is physical in nature. All the information related to the mechanical or physical plugging by particles is described in a separate report [12]. However, as described above, some of the invaded solids may alter their critical properties as a function of (a) the mud temperature and composition and (b) the mixing of mud components with reservoir fluids at the reservoir temperature. Some specifics of these changes of the critical mud solid properties due to chemical reactions is described in some detail later in this report (see Section 5.2.3).

5.2.1.2 THERMODYNAMIC INSTABILITY OF MUD FILTRATE

During the initial stages of drilling into a geothermal formation, the solid particles as well as the liquid components of the drilling fluid enter the pores of the reservoir. The depth and the rate at which the filtrate enters the porous matrix of the reservoir are determined by many factors. Some of these factors include, (1) the local (microscopic) permeabilities of the reservoir, (2) the viscosity of the fluid at the temperature and pressure near the invaded region, (3) the pressure difference between the wellbore and the near wellbore region of the reservoir (differential pressure). Similarly, the depth and the concentration of the particles entering the reservoir are also determined by many factors. Some of these factors are:

1. The differential pressure between wellbore and reservoir.
2. The pore size distribution near the entrance into the reservoir.
3. The size and shape distribution of the particles.
4. The forces between the particles and the surface within the porous matrix of the reservoir.

In addition to this type of pore plugging, the suspended particles can also form a filter cake which reduces the rate at which the drilling mud enters the formation. Some evaluations regarding the plugging of the porous media and the subsequent clean up by acidizing or high pH fluids has also been done as part of the present DOE/DGE contract. This work will be described in a separate report [14].

The filtrate that entered the formation can cause the plugging of the pores through the precipitation of salts which occurs because of the thermodynamic instability of the entering fluids and the reactions between mud filtrate and reservoir brine. Thus, damaging precipitations are caused by two different thermodynamic instabilities:

1. The thermodynamic instability of the dissolved species in the filtrate mainly due to temperature changes.
2. The thermodynamic instability of the dissolved species through mixing of incompatible waters.

Some of the causes for a chemically induced wellbore or reservoir damage during and after geothermal drilling are described in the following paragraphs.

5.2.1.2.1 INSTABILITY OF DRILLING FLUID FILTRATE DUE TO TEMPERATURE AND PRESSURE CHANGES

The filtrate of the drilling mud contains various dissolved species in thermodynamic equilibrium at the temperature and pressure under surface conditions. During and after drilling, the formation near the wellbore contains some filtrate. The filtrate is now subjected to the higher temperatures and pressures of the geothermal reservoir. Various thermodynamic instability problems related to this filtrate fluid invasion are described in this paragraph.

The invading mud filtrate can form scale deposits even without mixing with the chemically incompatible reservoir fluids (see Section 5.2.1.2.2). As the CaSO_4 solubility decreases with increasing in temperature, the filtrate in the pores is now

supersaturated in respect to CaSO_4 . Of course, the degree of supersaturation is usually low. In spite of the low supersaturation of CaSO_4 and frequently used arguments, it can precipitate due to the heterogeneous environment of the porous structure (heterogeneous nucleation). Some laboratory injection experiments conducted as part of the present contract clearly indicated that CaSO_4 can precipitate easily within the porous media even at low degrees of supersaturation. The results of these experiments are described in another report [15].

Another typical damage caused by the thermodynamic instability of the mud filtrate is caused by the organic compounds used as mud additives in drilling fluids. For example, water soluble polymers still find their geothermal use in the drilling fluids and can rapidly deteriorate under the conditions of a geothermal well [50,51] after invading the pores of the reservoir. The degradation products can cause chemically induced reservoir damage.

Numerous other soluble mud additives are highly suspect to create similar chemical problems. Only the previously suggested testing of these drilling fluids and the suggested additives under simulated or real field conditions can determine the full potential of these chemicals as far as chemically induced reservoir damage is concerned.

5.2.1.2.2 MIXING OF INCOMPATIBLE WATERS AND RESULTING INSTABILITY PROBLEMS

The filtrate of the drilling mud generally contains small concentration of SO_4^{--} ions and the formation brine of frequently encountered geothermal fluids can contain substantial concentrations of Ba^{++} , Sr^{++} and Ca^{++} ions. Mixing of the mud filtrate and the formation fluid creates a potential for BaSO_4 , SrSO_4 and CaSO_4 precipitations within the reservoir. Thus, BaSO_4 , SrSO_4 , and/or CaSO_4 skins can form near the wellbores and can cause a reduction in the critical permeability. In other words, the drilling mud filtrate is incompatible with the reservoir brine and mixing with reservoir brines containing appreciable concentrations of Ba^{++} , Sr^{++} and Ca^{++} ions can form SrSO_4 and CaSO_4 scale through mixing near the wellbore [16 through 18].

Some geothermal reservoir brines contain high concentrations of sulfate ions. In this case, the potential chemical problems caused by brine incompatibilities are similar. What is changed is only the origin of the chemically incompatible ions. This means, the drilling fluids, in this case, may not contain appreciable concentrations of divalent ions.

Not only sulfate scale problems must be expected upon mixing of chemically incompatible reservoir fluids and invading drilling fluid filtrate, but also carbonate and hydroxide precipitation

can occur and will subsequently lead to very similar problems. Quite often, water soluble carbonates, bicarbonates or hydroxides are added to the drilling fluids. The resulting high CO_3^{--} , HCO_3^{--} and/or OH^{--} content of these drilling fluids renders the drilling fluid filtrate invading the reservoir extremely incompatible with many geothermal reservoir fluids. For example, a pH value of 10 or even 11 in the drilling mud will definitely cause a chemically induced damage in a reservoir such as the Mercer, Currier or various Niland leases in the Imperial Valley, California. These reservoir fluids contain large concentrations of various divalent and trivalent ions which will eagerly react with these filtrates to form numerous and heavy carbonate and hydroxide scales in the reservoir near the wellbore upon using these drilling fluids.

The damage due to the incompatible water mixing during drilling has been recognized for many years, but has been discussed in the literature only in a very qualitative manner [9,11,19]. A quantitative discussion of the chemical problems (sulfate scale) due to mixing of incompatible waters has been discussed previously as part of the present contract [16 through 18]. Some experimental work related to the various aspects of drilling filtrate is being done by the investigators of Sandia Laboratories [3]. However, the results of their studies are not fully published at the present time.

Besides the prediction of scale formation, two other factors are extremely important in determining the near wellbore damage due to the mixing of the drilling mud filtrate and the reservoir fluids. These two factors are, (1) the determination of the amount of filtrate that invaded the formation water, and (2) the mixing proportions of the two waters. Millar and Buckles [20] have used radioactive techniques using tritiated water to determine the drilling mud filtrate which has invaded the formation water. Using this technique, the radial extent of the invasion was determined. In a similar way, the invasion of the core samples can be determined by comparing the pore water with the drilling fluid [21,22].

A calculation of the mixing proportions of the drilling mud filtrate and the formation water at various locations is needed to determine the amount of scale formed during and after a drilling operation. This is generally done through models based on the dispersion equation. Some of the concepts that are pertinent to the drilling mud filtrate and the formation can be found in the literature on the mixing of fluids in porous media [23 through 27]. However, to our knowledge, none of these techniques have been used for actual investigations of drilling damages in the field.

5.2.2 DISAGGREGATION OF CLAY MINERALS

Certain clay minerals that are native to the formation may be extremely sensitive to the various ionic species (including pH) of the drilling mud filtrate. These clay minerals may disaggregate upon coming in contact with these ionic species. This, in turn, can cause damage to the porous media of the reservoir by a chemical alteration of the reservoir clays. Specific information related to this type of chemical damage has not been found in the literature which is directly applicable to geothermal drilling operations. There is a considerable amount of literature related to the clay minerals and the damage caused by these clay minerals in oilfield operations. This information, however, cannot be directly transferred to the discussion of clays in geothermal operations. The clays found in geothermal formations are substantially different from those found in oilfield formations. Also, the high temperature reactions leading to various reservoir damages may be quite different from the low temperature reactions in oil and gas fields.

Montmorillonite clays are commonly found in shallow oil and gas fields. In geothermal fields, on the other hand, montmorillonite, montmorillonite mixtures, and montmorillonite mixed-layers are comparatively rare. Especially under the high temperature conditions of a geothermal reservoir they may have been completely converted to non-expanding phases such as illite and chlorite. These converted clays and clay-type compounds (illites and chlorites) show considerable ion exchange capacities which have serious implications in causing a chemically induced drilling mud filtrate damage.

The types of clay structures found in geothermal formations are given in the literature [28 through 31]. For example, Fan [29] noted that the first zone of alteration in Hawaiian basalt is characterized by an alteration of the montmorillonite at a temperature range between 290 and 325°C. A second zone of clay alteration is characterized by a chlorite zone at higher temperatures.

Kristmansdottir [30] reported three zones of clays depending upon temperature in Icelandic geothermal areas. The first zone is characterized by smectites (below 200°C), the second zone by the swelling chlorites (between 200 and 230°C and the third zone by chlorites (above 231°C). Hoagland and Elders [30] on the other hand, reported a different type of distribution at depths of sandstone reservoirs. They report a transition from the "diagenetic" to the "illite-chlorite" stage around 150° at the Cerro Prieto geothermal field. The diagenetic zone is defined by the presence of kaolinite and montmorillonite.

Based upon this information, the effect of the following clays on the damage during drilling operations should be considered: Montmorillonite, chlorites, smectites, illite and kaolinite.

However, it should be mentioned that chlorites (non-expandable) are the more common clays for most high temperature geothermal formations.

The non-expandable clays such as chlorites and illites can absorb enough water in their characteristic platelet-type structure and consequently, thus making the platelets easily slip and cleave the original clay particles into smaller particles. Illite and chlorite, normally bonded by K⁺ ions, can degrade and lose the ions by leaching when exposed to slightly acidic fresh water. After the removal of potassium ions, illite will expand to 24 Å (normally 9.5 Å) [31]. Even if the individual particles of these clays do not disintegrate, all clays are subject to deflocculation, a condition wherein agglomerated masses of clays (flocs) are broken up and dispersed, thus leading to moveable fines within the reservoir. The presence of salt water in the rock pores make the clays to exist in flocculated condition. Neesham [33] has shown with SEM micrographs the physical appearance of some of these clay flocs. He found that kaolinite exists in discrete, plate-like particles scattered throughout the pore system. Illite, chlorite and montmorillonite, on the other hand, are attached to pore walls to form a relatively continuous and thin (less than 12 microns) coating ("pore-lining") or extend far into or completely across a pore or pore throat to create a bridging effect. This microporous structure is comparatively easily broken down. When fresh water (such as drilling mud filtrate) enters the rock, the clays will be in a deflocculated condition. The individual particles will then be entrained by the fluid, transported, and deposited as microscopic filter cakes plugging narrow pore openings. Such interal filter cakes can reduce the permeability of the rock considerably [33].

One of the most damaging clay substance is montmorillonite. This type of clay is found to be present in high temperature geothermal reservoirs only in greatly reduced amounts, or to be completely altered due to the high temperatures found in the geothermal formation. However, it should be pointed out that if montmorillonite is present even in small amounts, this could become significant from the point of drilling damage because of the proximity of the expected damage to the wellbore or productive portions of fracture faces.

5.2.3 CHEMICAL ALTERATIONS OF SOME INVADED MUD SOLIDS

Drilling muds that are utilized in geothermal well drilling are normally formulated from an aqueous liquid phase with various solid phases to provide the proper viscosity and fluid loss control. Also, various chemicals are added to the drilling muds. The chemicals generally added to the mud are fluid loss agents, scale inhibitors, corrosion inhibitors, friction reducers, clay stabilizers, etc. During drilling operations all the components of the drilling mud may enter the reservoir and will be exposed to the high temperatures of the geothermal formation. This generates numerous possibilities for some unwanted chemical

reactions and subsequent chemical alterations of these additives.

One of the most damaging additive used in geothermal drilling mud is montmorillonite. In oilfield drilling, montmorillonite type clay has been in use for some time. The high temperature geothermal environment not only would create a gelation tendency to this type of clay [34], but, long exposures of this type of clay to high temperatures can actually form low grade cement (calcium montmorillonite) inside the pores of the formation near the wellbore. Field experiences in the Imperial Valley clearly demonstrated the severity of the damage caused by chemical changes of the invaded clays [11].

Montmorillonite type clays are not generally used in the United States for high-temperature geothermal applications. Instead, sepiolite and attapulgite clays are used in drilling of geothermal wells. Very little information on the chemical damaging effects due to sepiolite and attapulgite clay particles seems to be available. On the otherhand, recent literature contains information on the hydrothermal transformation of sepiolite and attapulgite to smectite type clays i.e., the normally non-swelling clays (e.g., sepiolite) because now swellable clays (e.g., smectites, e.g. stevensite). Such transformation is favorable for drilling operations because of the resulting alteration of the rheological properties of the drilling fluids [8]. However, there is considerable disagreement among the various studies on the hydrothermal transformation of sepiolite [35,43]. Of notable importance of this transformation is the existence of a new species of clay, namely the stevensite, and its relation to montmorillonite [39 through 42]. Guven and Carney [42] reported the effect of pressure, temperature and the presence of various alkaline metals on the hydrothermal transformation of sepiolite to stevensite. Carney et al [43] utilized the information of these transformation studies in formulating some fluid loss control agents for geothermal drilling applications. However, the impact of such transformation reactions on the damage to the formation is not known and needs further study.

6.0 VARIOUS PRECAUTIONS TO BE TAKEN TO REDUCE CHEMICAL DAMAGE DURING DRILLING OPERATIONS

The prevention of the near wellbore damage during drilling of the injection of wells should address the various damaging mechanisms described in Section 5.0. One obvious way of preventing drilling damage is by reducing the differential pressure so that there will be a minimum of drilling mud invasion. This requires some development work on drilling techniques. Another way of preventing drilling damages is by back-flowing sufficient quantities of reservoir fluid immediately upon drilling and completion of a well to remove any invaded material. In addition to these, several other precautionary methods can be utilized to

minimize the drilling damage. They are as follows:

1. Select the liquid components of the drilling mud formulation so that they are chemically compatible with the reservoir materials. If no such source water is available, use chemically incompatible waters only after a proper treatment prior to injecting these fluids into the wellbore.
2. Select the solid additives so that they do not form adverse reaction products at high temperatures.
3. In cases such as exploratory drilling, where the nature of the reservoir materials is not known, use chemical inhibitors [44] to prevent a potential scale formation.
4. The selected chemical inhibitors should not form adverse by-products at high temperatures (pseudo scales [47,48]).
5. Select suitable clay stabilizers so that the formation clays do not disaggregate [44 through 46].
6. Avoid using of high pH drilling fluids wherever possible.
7. Avoid using excessive amounts of carbonates and bicarbonates in geothermal drilling muds.
8. In case the high temperature behavior of a geothermal drilling fluid is not known, avoid utilizing these fluids prior to the proper testing of these fluids.

REFERENCES

1. Alsteimer, J.H., "Geothermal Well Technology and Potential Applications of Subterranean Devices - A Status Review", Geothermal Resources Council, Transactions, Vol. 1, pp.1453-1470, 1977.
2. Maurer, W.C., "Geothermal Drilling Technology", Geothermal Resources Council, Transactions, Vol. 1, pp.1509-1521, 1977.
3. Vernado, S.G., Ed., "Geothermal Drilling and Completion Technology Development Program Quarterly Progress Report", SAND 80-0703, Report Issued by Sandia National Corporation, April 1980.
4. Finger, J.T., "Investigations of Percussion Drills for

- Geothermal Applications", SPE 10238, paper presented at the 56th Annual Fall Technical Conference of SPE of AIME, San Antonio, Texas, October 5-7, 1981.
5. Bannerman, J. K. ,and Davis, N., "Sepiolite Muds Used for Hot Wells, Deep Drilling", Oil and Gas J., February 27, 1978.
 6. Jonsson, I., "The Use of Water in Geothermal Drilling", Geothermal Resources Council, Transactions Vol. 1, pp.1501-1502, 1977.
 7. Horne, R. N. , "Geothermal Reinjection Experiences in Japan", Journal of Petroleum Technology, pp. 495-503, 1982.
 8. Carney, L.L. ,and Meyer, R.L., "A New Approach to High Temperature Drilling Fluids", SPE 6025, paper presented at 51st Annual Technical Conference SPE of AIME, New Orleans, October 3-6, 1976.
 9. Glenn, E.E. ,and Slusser, M.L., "Factors Affecting Well Productivity, I. Drilling Fluid Filtration", Petroleum Transactions, AIME, Vol. 210, pp. 126-131, 1957.
 10. Glenn, E.E. ,and Slusser, M.L., "Factors Affecting Well Productivity,, II. Drilling Fluid Particle Invasion into Porous Media", Petroleum Transactions, AIME, Vol. 210, pp. 132-139, 1957.
 11. Nicholson, R.W., "Drilling Fluid Formation Damage in Geothermal Wells", Geothermal Resources Council, Transactions, Vol. 2, pp. 503-505, 1978.
 12. Vetter, O.J., Kandarpa, V. ,and Harouaka, A., "Flow of Particle Suspensions through Porous Media", DOE/DGE Report being submitted 1982.
 13. Kandarpa, V. ,and Sparrow, J.T., "A Useful Technique to Study Particle Invasion in Porous Media by Backscattered Electron Imaging", SPE 10134, paper presented at the 56th Annual Fall Technical Conference of SPE of AIME, San Antonio, Texas, October 5-7, 1981.
 14. Vetter, O.J. ,and Kandarpa, V. , "Acidizing and Acidizing Design", Report being prepared under DOE/DGE Contract, 1982.
 15. Vetter, O.J. ,and Kandarpa V. ., "Scale Prediction at Various Locations", Report being prepared under this DOE/DGE Contract, No. DE-AC03-79ET-27146 to be issued in 1982.

16. Vetter, O.J., Kandarpa, V., and Harouaka, A., "The Prediction of Scale Problems Due to Injection of Incompatible Waters", Journal of Petroleum Technology, pp. 273-284, February 1982.
17. Vetter, O.J., and Kandarpa, V., "Foreign Water Injection into Geothermal Reservoirs (Chemical Compatibility Problems)", DOE/DGE Report, 1981.
18. Vetter, O.J. and Kandarpa, V., "Prediction of Salt Precipitation Due to Injection of Foreign Waters into Geothermal Reservoirs", Geothermal Resources Council, Transactions, Vol. 5, pp. 341-344, October, 1981.
19. Krueger, R.F., "Advances in Well Completion and Stimulation During JPT's First Quarter Century", Journal of Petroleum Technology, pp. 1447-1462, 1973.
20. Millar, R.H.G., and Buckles, R.S., "Tritiated Water as a Drilling Mud Tracer in Beufort Exploration Wells", paper presented at the 25th Annual Technical Meeting of the Petroleum Society of CIM, Calgary, May 1974.
21. Muskat, M., and Coggeshall, N.D., "Method of Determining the Fluid content of Well Cores", U.S. Patent 2,458,093, January, 1949.
22. Armstrong, F.E., and Lovelace, K., "A Study of Core Invasion by Waterbase Mud Filtrate Using Tracer Techniques", API Drilling and Production Practice, API, New York, 1961.
23. Taylor, G.E., "Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube", Proc. Royal Society 219, pp. 186, 1953.
24. Frankel, S., "Mixing of Fluid Flowing in a Porous Medium", Conference on Theory of Fluid Flow in Porous Media", U. of Oklahoma, March 23-24, 1957.
25. Brigham, W.E., Reed, P.W. and Dew, J.N., "Experiments in Mixing During Miscible Displacement in Porous Media", Society of Petroleum Engineers Journal, pp. 1-8, March 1961.
26. Levich, V.G., Markin, V.S., and Chismadzlev, Y.A., "On Hydrodynamic Mixing in a Model of Porous Medium with Stagnant Zones", Chem. Eng. Sci., 22, pp. 1357-1367, 1967.
27. Brigham, W.E., "Mixing Equations in Short Laboratory Cores", Society of Petroleum Engineers Journal, pp. 91-99, February 1974.

28. Velde, B., Clays and Clay Minerals in Natural and Synthetic Systems, Elsevier, New York, 1977.
29. Fan, P., "Mineral Assemblage of Hydrothermal Alterations of Basalts from Hawaii", Geothermal Resources Council, Transactions, Vol. 2, pp. 185-187, 1978.
30. Kristanansdottir, H., "Hydrothermal Alteration of Basaltic Rocks in Icelandic Geothermal Areas", Geothermal Resources Council, Transactions, Vol. 2, pp. 441-445, 1978.
31. Hoagland, T.R., and Elders, W.A., "Hydrothermal Mineralogy and Isotopic Geochemistry in the Cerro Prieto Geothermal Field, Mexico. I: Hydrothermal Mineral Zonation", Geothermal Resources Council, Transactions, Vol. 2, pp. 283-286, July 1978.
32. Young, B.M., and McLaughlin, H.C., "Clay Stabilization Agents - Their Effectiveness in High Temperature Steam", SPE 7895, paper presented at the SPE Symposium of Oilfield and Geothermal Chemistry of SPE-AIME, Houston, January 22-29, 1979.
33. Von Olphen, H., An Introduction to Colloid Chemistry, Wiley-Interscience, New York, 1963.
34. Annis, M.R., "High Temperature Flow Properties of Water-Based Drilling Fluids", SPE 1698, preprint 1967.
35. Mumpton, F. A., and Roy, R., "New Data on Sepiolite and Attapulgite", Prod. 5th Nat. Conf. on Clays and Clay Minerals, Urbana, Ill., pp. 136-143, 1956.
36. Frank-Kamenetsky, V.A., Kotov, N.V., and Klechkova, G.N., "Phase Transformations of Sepiolite and Polygorkite under Hydrothermal Condition at Elevated Pressure in the Presence of KCl and NaCl", Geochem. Int. 7, pp. 934-942, 1970.
37. Frank-Kamenetsky, V.A., Kotov, N.V., and Klochkora, G.N., "Phase and Structural Changes in Sepiolite Under Hydrothermal Conditions in the Presence of Ca and Mg Chlorides", Geochem. Int. 9, pp. 818-826, 1972.
38. Otsuka, R., Sakamoto, T., and Hara, Y., "Phase Transformations of Sepiolite Under Hydrothermal Conditions", Nendo Kagaka, 14, pp. 8-19, 1974.
39. Faust, G. T., and Murata, K.T., "Stevensite, Redefined as a Member of the Montmorillonite Group", Amer. Mineral, 38, pp. 973-987, 1953.

40. Faust, G.T., Hathaway, J. C. , and Millot, G., "A Restudy of Stevensite and Allied Minerals", Amer. Mineral, 44, pp. 342-370, 1959.
41. Randall, B.A.O., "Stevensite from the Whin Sill in the Region of the North Tyne", Mineral Mag., 32, pp. 218-225, 1959.
42. Guven, N. , and Carney, L.L., "The Hydrothermal Transformation of Sepiolite to Stevensite and the Effect of Added Chlorides and Hydroxides", 27, pp. 253-260, 1979.
43. Carney, L.L., Guven, N. , and McGraw, G.T., "Investigation of High-Temperature Fluid Loss Control Agents in Geothermal Drilling Fluids", SPE 10736, paper presented at 1982 California Regional of SPE-AIME, San Francisco, March 24-26, 1982.
44. Vetter, O.J. ,and Kandarpa, V., "Scale Prevention and Injection Design Work", DOE/DGE report being prepared, 1982.
45. Copeland, C.T., Coulter, A.W. ,and Harrisburger, W.H., "Designed Application of Clay Stabilizer Improves Performance", SPE 6759, presented in Denver, Colorado, October 9-12, 1977.
46. Vetter, O.J., "Stimulation of Geothermal Operations, Part I: Literature Search and Literature Evaluation of Stimulation Methods in Geothermal Production Reservoirs", RGI-DOE/DGE report prepared under contract No. DE-AC32-AL10563-VR, 1980.
47. Vetter, O.J., "An Evaluation of Scale Inhibitors", Journal of Petroleum Technology, pp. 997-1006, August 1972.
48. Vetter, O.J., and Kandarpa, V., "Scale Inhibitor Evaluation for Oilfield and Geothermal Operations", SPE Paper No. 7864, prepared for the International Symposium on Oilfield and Geothermal Chemistry, Houston, Texas, January 22-24, 1979.
49. Kandarpa, V. , and Vetter, O.J., "Degradation Characteristics of Cotton Seed Hulls and Saw Dust in High Temperature Geothermal Brines", Geothermal Resources Council, Transactions, Vol. 4, pp. 297-299, Sept. 1980.
50. Tyssee, D.A. ", Caenn, R., and Vetter, O.J., "Laboratory Tests of Polymer Fluids at Geothermal Temperatures", SPE paper No. 10619, prepared for the International

Symposium on Oilfield and Geothermal Chemistry, Dallas,
Texas, January 25-27, 1982.

51. Tyssee, D.A., and Vetter, O.J., "Chemical
Characterization Problems of Water Soluble Polymers",
Journal of Petroleum Technology, pp. 721-730, December
1981.