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PROGRAM: TECHNOLOGY TRANSFER

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Republic Geothermal, Inc.
Santa Fe Springs, California

U. S. DEPARTMENT OF ENERGY
Geothermal Energy

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GEOHERMAL RESERVOIR WELL
STIMULATION PROGRAM

TECHNOLOGY TRANSFER

VOLUME III

Prepared for:

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by: Vetter Research

May 1980

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1.0 SUMMARY

Realization of the need for additional developmental work in the area of geothermal reservoir stimulation, led the U.S. Department of Energy, Division of Geothermal Energy (DOE/DGE) to award a contract reviewing the various technological disciplines evaluating those processes that offer direct and indirect application to the geothermal industry. Republic Geothermal, Inc. (RGI) was awarded the primary contract (Contract No. DE-AC32-79AL10563) to carry out this assignment.

This volume presents a literature search by Vetter Research (VR) on reservoir and/or well stimulation techniques suitable for application in geothermal fields.

2.0 CONCLUSIONS

Our main findings based upon a literature search and evaluation are:

- 1) Our understanding of high-temperature behavior of materials involved in geothermal reservoir stimulation jobs is limited. There is little information as to the chemical and physical reactivity of injected fluids with reservoir fluids and/or matrix rock at higher temperatures.
- 2) None of the frac fluid additives used to adjust the critical viscosity possess the hydrothermal stability required for geothermal reservoir stimulation.
- 3) A direct "carry-over" of oil-gas technology to geothermal cannot be made. However, knowledge gained in the oil/gas technology is useful in yielding insights to geothermal technology.
- 4) New experimental concepts and analytical procedures should be encouraged in experiments that take into consideration temperature-pressure problems encountered in geothermal operations. This new experimental work (lab and field) may turn out to be extremely costly.
- 5) It is not enough to simply stimulate a geothermal well. Economics dictate that a stimulated well's productivity be maintained after all well work.
- 6) In the design of geothermal stimulation, the project must be designed so that there is sufficient increase in production to cover the cost of stimulation.

- 7) Clays can play a critical role in the production of lower temperature geothermal fields. The terminology and general description of clays found in literature can be directly transferred to geothermal reservoirs. However, some critical aspects of high temperature clay behavior are not fully understood at this time. In particular, the high-temperature phase transitions and chemistry of clays should be known in much more detail.

3.0 SUGGESTIONS AND RECOMMENDATIONS

New field evaluation techniques as well as new experimental and analytical procedures for field and laboratory work should be developed. These new techniques and procedures should be tailored to the specific conditions found in geothermal reservoirs. Of particular interest should be a comprehensive study of the high-temperature reactions of stimulation fluids and geothermal reservoir materials under the conditions of various stimulation techniques.

It is beyond the scope of this report to outline all the specific suggestions and recommendations to study the various types of physical and chemical reactions. These will be the subject of additional reports issued over a period of time as part of the specific tasks identified in the contract "Statement of Work".

4.0 INTRODUCTION

This report contains a literature search on reservoir and/or well stimulation techniques suitable for application in geothermal fields. The literature on stimulation techniques in oil and gas field applications was also searched and evaluated as to its relevancy to geothermal operations.

In the body of this report, we cite the equivalent low-temperature work documented in the open literature and try to evaluate how relevant this information could be as far as high-temperature stimulation work is concerned.

Clays play an important role in any stimulation work. Therefore, special emphasis has been placed on clay behavior anticipated in geothermal operations.

It is our opinion that only general concepts can be transferred from oil and gas fields to geothermal operations due to (a) the higher temperatures, (b) the tremendously larger flow rates and (c) the different economics in geothermal operations. These parameters (temperatures, flow rates and economics) differ so drastically between the oil/gas and geothermal industries that even some basic concepts of stimulation techniques in geothermal operations may need to be changed. Critical details and design criteria of various stimulation techniques appear to be quite different in geothermal applications.

The temperature appears to play the key role as a "road block" in the transfer of stimulation technology from oil and gas fields into geothermal operations. Problems are not only generated by the unknown high-temperature reactions between known stimulation fluids and known reservoir materials, but also by the fact that the chemical and physical behavior of some high temperature reservoir materials are either not known or very ill-defined.

The various types of stimulation techniques studied were (a) fracturing, (b) chemical stimulation (such as acidizing) and (c) mechanical/chemical methods (such as acid fracturing). None of these techniques can be directly transferred into geothermal operations without considerable adjustments because of the temperature, flow rate and economic conditions.

4.1 GEOTHERMAL RESERVOIR STIMULATION: AN ART OR A SCIENCE?

The literature reviewed has little information regarding the effect of high temperature on the behavior of the various fluids and materials used in conventional stimulation jobs. This lack of information extends from the high-temperature hydrothermal stability of fracturing fluids and proppants to the chemical reactions between acids and various rock phases. Neither critical thermodynamics nor pertinent kinetics of any of the basic reactions are defined. Without this basic knowledge, any stimulation technique will quickly turn into an art instead of a science. Major failures will most likely occur during developing the "art of geothermal reservoir stimulation". These future failures can be kept at a minimum if a serious attempt is made to study, in detail, the basic mechanical and chemical reactions involved in all proposed stimulation projects.

It is not believed that the lack of knowledge regarding the basic reactions during high-temperature stimulation work is due to a general lack of interest. On the contrary, we found some rather serious attempts in the literature to study these critical high-temperature reactions. However, the useful information distilled from these attempts is rather limited. The reason for this critical lack of information on the high-temperature behavior of fluids and other materials appears to be due to the lack of suitable instrumentation and experimental designs

to study this behavior. It is simple to conduct experiments to study the low temperature behavior of materials (below 100°C), i.e., below the boiling point of water. Therefore, the low temperature behavior has been studied very extensively. On the other hand, the situation is quite different when it comes to studying high-temperature reactions. Few attempts have been made to overcome the conceptual and experimental problems encountered in high-temperature stimulation work to be designed for geothermal environments. The laboratory and field procedures and equipment required to gather the needed high-temperature data are not readily available.

Major research efforts are required to design both experimental instrumentation and procedures before data gathering can be started. Considerably more effort is required for high-temperature work than is needed for the low-temperature equivalent. This represents a major cost and time effort to obtain even rather rudimentary types of information. For these reasons, even seasoned and "hard core" researchers shy away from this complex, time-consuming and expensive high-temperature work.

4.2 ROLE OF CONVENTIONAL SERVICE COMPANIES

Major stimulation service companies such as Halliburton, Dowell, B.J., etc. will not make the investments required for this high-temperature work. These companies are not only aware of the cost and time efforts required for the developmental work but are also suspicious of the future of geothermal energy. They are hesitant to make investments required for high-temperature work unless they are assured of a "reasonable" return of their investment or, at least, of the future of hydrothermal reservoirs as we see them today. Although these companies will attempt to apply their equipment and chemicals in geothermal fields, both equipment and chemicals have been developed for oil and gas fields.

The DOE/DGE decision of contracting work with companies which have a pronounced interest in geothermal reservoirs in general and stimulation work in particular, is a wise one. The equipment, materials and/or accumulated experience of the service companies working on geothermal projects can be shared by the industry during each individual stimulation job. There will be no retainment of critical information to maintain a better competitive position. In addition, shortcomings and failures of equipment and/or materials used in the stimulation jobs will be analyzed and published. Again, the competitive position of the service company plays no role. Another advantage is that the prime and subcontractors, and not the service company and its profit situation, determine what equipment and materials to use in any individual job.

5.0 MAJOR TASKS OF THIS LITERATURE EVALUATION

Nicholson, et al.,¹ described the major tasks and motivations for the entire scope of work under this DOE/DGE funded contract. The emphasis of these tasks is on stimulation of geothermal production wells through hydraulic fracturing even though other stimulation methods will also be reviewed and evaluated. Any one, or combination of, the stimulation methods listed in Table 1 could find application in many geothermal wells.

The various stimulation methods listed in Table 1 can be applied to increase the productivity of geothermal wells. Selecting the stimulation method, or methods, best suited for a specific well, or reservoir, depends on the wellbore and reservoir conditions. The stimulation method must be chosen after determining the reasons for the low well productivity, which may vary greatly as shown in Table 2.

This report is primarily concerned with a comprehensive search of the literature regarding various aspects of geothermal well stimulation technology in general and the geothermal reservoir fracturing technology in particular. In addition, personal visits to the research centers of major service companies reveal additional work in progress. The initial visits to the research centers of Halliburton, Dowell, and B.J. were made in 1979.

An attempt has been made to evaluate the pertinent oil/gas literature references. This search and concurrent evaluation of the existing literature were the bases for a laboratory work plan and schedule required for fulfilling the goals and objectives as defined in the Statement of Work for this subcontract. Emphasis is placed on the chemical aspects of the various stimulation processes except for some basics needed to maintain continuity.

6.0 TRANSFER OF STIMULATION TECHNOLOGY FROM OIL AND GAS INDUSTRIES TO THE GEOTHERMAL INDUSTRY

In this report, we define a geothermal reservoir as a subterranean reservoir which:

- 1) Produces tremendous amounts of aqueous fluids at high production rates and at temperatures sufficiently high for economic exploitation, and
- 2) Is normally located at a depth shallower than oil and gas reservoirs of equal temperatures.

Within the oil/gas literature are fields with temperatures similar to those found in geothermal reservoirs. Some high temperature gas reservoirs (e.g., the Hunton Dolomite in the Anadarko Basin, Oklahoma/Texas) have temperatures in excess of 400°F. By our definition, these reservoirs could be called "geothermal reservoirs" if they would produce substantial amounts of water.

The various reservoir stimulation techniques that are developed in the higher temperature oil and gas fields, in principal, can be transferred to the geothermal industry. However, there can be major differences between the high temperature technologies developed for oil/gas and geothermal stimulation work, even though there are many similarities.

Some of these differences between the oil and geothermal operations arise because of the differences in such factors as (1) temperature, (2) pressure, (3) reservoir fluid composition, (4) type of reservoir rocks, (5) type of clays and (6) flow rates (see Table 3). These differences may necessitate a thorough investigation of the various chemical and physical damages found before, during and after a stimulation job.

In addition to those differences caused by technical conditions, we may also find some major differences in the economics of stimulation jobs in the oil/gas industries on the one side and the geothermal industry on the other. In particular, a fairly small productivity increase of an oil or gas well has a large impact on the economics for a stimulation job in the oil industry due to the higher value of gas and/or oil. The same small productivity increase in a geothermal well may have only a negligible impact on the economics for a stimulation job in the geothermal industry. For example, doubling of the production rate of a given well from 25 gallons per minute to 50 gallons per minute represents a present day monetary value of approximately \$20,000 per day for the additional production in an oil well. Doubling the productivity of a geothermal well under the same conditions (from 25 GPM to 50 GPM) may result in an incremental value of only \$120/day (vs. \$20,000/day in the oil well). This means that the economics of a stimulation job in the geothermal industry may be quite different from that in the oil and gas industries. This difference in the economics, in turn, may favor certain stimulation techniques and may suggest the deletion of others.

Some of the factors related to the chemical aspects which should be studied in detail for most geothermal frac stimulation jobs are outlined in Table 4. The relative importance of these chemistry-related factors may be different in the two industries (oil/gas and geothermal). Therefore, the direct transfer of stimulation technology from the oil or gas industry into the geothermal industry cannot always be direct. A considerable number of adjustments may be required before the stimulation technology developed for oil and gas reservoirs is acceptable for geothermal reservoirs.

7.0 POTENTIALLY VALUABLE STIMULATION TECHNIQUES FOR GEOTHERMAL OPERATIONS

As outlined in Table 1, there are several mechanical and chemical stimulation techniques having a potential value for geothermal operations. Some of these well stimulation methods, such as explosive and thermal fracturing, will not be treated in this report. The main emphasis of the DOE/DGE program is toward hydraulic fracturing. However, other stimulation methods such as acidizing, acid-fracturing and various other chemical techniques have been considered for actual field work under this contract.

7.1 HYDRAULIC FRACTURING

This technique appears to offer the solution to a number of productivity problems (see Table 2). However, geothermal reservoir fracturing technology is by no means a readily available and proven stimulation method. There are numerous shortcomings and "pitfalls for the unwary". The literature search indicates that known frac fluids and proppants deserve a more thorough and critical investigation than previously expected. Reservations concerning the basic concept of fracturing and the chemical and physical behavior of the frac fluids and proppants are described in the following paragraphs.

The idea of hydraulically fracturing the rock of a subterranean reservoir to increase its fluid productivity is not new. Pros and cons of this well stimulation technique in the fairly cool oil and gas reservoirs have been described in the literature. We will outline some of the more pertinent arguments for and against fracturing in oil and gas fields in this present report.

The technical and economic aspects of fracturing a geothermal reservoir will require considerations quite different from those commonly applied in the oil and gas industry. These differences must be kept in mind during a literature search and critical evaluation as described in this present report. The pertinent characteristics and requirements of a frac job in a geothermal reservoir are constantly emphasized in this present report. Unfortunately, this may result in some redundancies, for which we apologize at this point.

7.1.1 BASIC CONCEPTS OF HYDRAULIC FRACTURING

Hydraulic fracturing may be defined as the process of creating a fracture, or fracture system, in a reservoir rock by pumping a fluid under pressure, thereby inducing mechanical material failure.²⁻⁴

At some pressure on the formation, a crack is initiated at the wellbore in a plane perpendicular to the maximum principal total stress at that depth. Fracturing is a dynamic process and the growth of various

dimensions of a crack is controlled by such factors as (1) fracturing speed, (2) fluid properties, (3) rock properties in the producing zone, and (4) rock properties of the boundary strata. The resulting fractures can be hundreds of feet long, tens of feet high and a fraction of an inch wide.

In order for the fracture not to close after being generated, proppants may be introduced into the fracture to hold the fracture open.

After the fracturing process, the fracturing fluid is removed to allow the producing geothermal waters to flow into the wellbore. The back flow of the proppants by the geothermal waters should be controlled to avoid washing the proppants out of the fractures, thus permitting the fracture to close.

7.1.2 BACKGROUND INFORMATION FOR HYDRAULIC FRACTURING

The basic concepts and terminology presented in this section are briefly summarized in the following sections as a review of hydraulic fracturing. This short review may not be sophisticated enough for the engineers among our readers. However, this report is mainly directed toward chemists who may not be thoroughly familiar with these basic concepts of hydraulic fracturing.

7.1.2.1 PRESSURE CONCEPTS: (SOME DEFINITIONS)

1) Hydrostatic Pressure: (P_{hy})

The hydrostatic pressure created by a fluid column is given by:

$$P_{hy} = (0.00695) \rho D$$

where P_{hy} = Hydrostatic pressure (psi)

ρ = Fluid column density (lb/ft³)

D = Vertical height of fluid column (ft)

0.00695 = Conversion factor to convert from lb/ft² to psi

Then, hydrostatic pressure gradient, p, is given by:

$$p = \frac{P_{hy}}{D} = (0.00695)\rho$$

For fresh water, $\rho = 62.43 \text{ lb/ft}^3$ at 68°F (or 20°C)

$$\therefore p = 0.433 \text{ psi/ft}$$

In general, the hydrostatic pressure gradient is given by:

$$p = (0.433)S$$

S = Specific gravity of the column

2) OVERBURDEN PRESSURE (P_o)

The overburden pressure originates from the combined weight of the formation matrix (rock) and the fluids in the pore space overlying the formation.

$$P_o = D[(1-\phi)\rho_{ma} + \phi\rho_{fl}] \times .00695$$

Where P_o = Overburden pressure (psi)

D = Vertical height of geologic column (ft)

ϕ = Porosity of the formation

ρ_{ma} = density of rock matrix (lb/ft³)

ρ_{fl} = density of fluid (lb/ft³)

The overburden pressure gradient, p_o , is given by:

$$p_o = [(1-\phi)\rho_{ma} + \phi\rho_{fl}] \times .00695$$

In general, the overburden pressure gradient is a function of depth. At shallow depth, p_o is substantially smaller than 1.0 psi/ft.

3) FORMATION PRESSURE (P_f)

Formation pressure (P_f) is the pressure acting upon the fluids in the pore space of the formation.

$$P_o = P_f + \delta$$

P_o = Overburden pressure (total vertical stress)

P_f = Formation pressure

δ = Grain-to-grain pressure (matrix stress, vertical rock frame stress, etc.)

4) FRACTURE PRESSURE (P_{Fr})

Fracture pressure is the pressure necessary to create fracture in the formation at a depth.

Fracture pressure gradient:

$$P_{Fr} = \frac{dP_{Fr}}{dD}$$

7.1.2.2 PREDICTION METHODS FOR FRACTURE PRESSURE GRADIENTS

1) THE HUBBERT AND WILLIS APPROACH⁵

The general condition of the subsurface stress is characterized by three unequal principal stresses. For hydrostatic fracturing, the hydraulic injection pressures must be nearly equal to the least principal compressive stress. The fracture occurs on the plane perpendicular to this least principal stress.

For normal situations, the greatest stress should be approximately vertical and equal to the effective pressure of the overburden. The least stress should be horizontal and should be most probably between 1/3 and 1/2 of the effective pressure of the overburden.

The effective vertical stress (σ) is given by:

$$\sigma = P_o - P_f$$

$$\text{and } \sigma_H = (1/3 \text{ or } 1/2)\sigma$$

Fracture propagation pressure has to overcome the pore pressure (P_f) and the horizontal rock matrix stress (σ_H). Thus:

$$P_{Fr} = P_f + \sigma_H = P_f + (1/3 \text{ or } 1/2)(P_o - P_f)$$

$$\text{and } p_{Fr} = \frac{P_{Fr}}{D} = \frac{P_f}{D} + (1/3 \text{ or } 1/2) \left(\frac{P_o - P_f}{D} \right)$$

Therefore,

$$p_{Fr}^{\min} = \frac{1}{3D} (P_o + 2P_f).$$

or,

$$p_{Fr}^{\max} = \frac{1}{2D} (P_o + 2P_f)$$

For normal sedimentary rocks,

$$\frac{P_o}{D} = 1.0 \text{ psi/ft}$$

For normal hydrostatic condition,

$$\frac{P_f}{D} = 0.46 \text{ psi/ft}$$

Based on the above values, either,

$$p_{Fr}^{min} = 0.64 \text{ psi/ft}$$

or,

$$p_{Fr}^{max} = 0.73 \text{ psi/ft}$$

However, it should be noted that the fracture pressure gradient has been found to vary with depth.

2) METHOD OF MATHEWS AND KELLY⁶

$$p_{Fr} = \frac{1}{D}(P_f + k_i \sigma)$$

where k_i = matrix stress coefficient for the depth at which the value of σ would be the normal matrix stress.

The value of k_i has to be determined from empirical field data of fracture initiation pressures.

3) METHOD OF EATON⁷

Assuming that the earth's formation is elastic and using Hooke's law, Eaton arrived at the following equation for the fracture pressure gradient,

$$p_{Fr} = \frac{1}{D}[P_f + \frac{\nu}{1-\nu} \sigma]$$

where $\sigma = P_o - P_f$

ν = poisson's ratio

Further, Eaton assumed that the overburden load is a function of depth and expressed as

$$P_o = 0.4335 \int_0^D \rho_b(h) dh$$

where $\rho_b(h)$ = formation bulk density as a function of depth (h).

4) TAYLOR AND SMITH'S FIELD DATA⁸

Taylor and Smith compared the field data with various theoretically calculated values for fracture pressure gradient and concluded that the theoretical methods can only provide the necessary guidance for field operations.

5) METHOD OF MacPHERSON AND BERRY⁹

MacPherson and Berry investigated the possibility of predicting fracture pressure gradients from well loss and concluded that (1) fracture pressure gradients appear to be related to the sand shale ratio, depth of overpressures, geologic age, and the location in the basin; and (2) a quantitative relationship exists between the ratio of sand elastic modulus to overburden pressure and fracture pressure.

6) METHOD OF ANDERSON, INGRAM AND ZANIER¹⁰

- a) Using Terzaghi's concept of effective stress, the fracture pressure gradient can be expressed as

$$P_{Fr} = \frac{2\nu}{1-\nu} \left(\frac{P_o}{D} \right) + \frac{1-3\nu}{1-\nu} \left(\frac{P_f}{D} \right)$$

- b) Using Biot's stress-strain relationship, one derives the following fracture-pressure gradient expression:

$$P_{Fr} = \frac{2\nu}{1-\nu} (P_o/D) + \alpha \cdot \frac{1-3\nu}{1-\nu} \left(\frac{P_f}{D} \right)$$

7.1.2.3 FRACTURE ORIENTATION AND DIMENSIONS

Several calculation methods⁵⁻⁹ are available to "predict" the critical pressure to create a desired hydraulic fracture in subterranean formations. Because of the complex nature of the underground formation, these methods are based on many simplifying assumptions. None of these methods can predict with certainty the exact surface pressures for fracturing. The situation is the same regarding the prediction of the fracture direction, orientation and geometry. However, certain generalizations can be made from the cases where the orientation of the fractures have been determined with certainty. The generalizations are that the majority of the fractures in deep wells are vertical¹¹ and that horizontal fractures mostly occur in shallow wells.¹² It has been generalized from the various reports in the oil industry that horizontal fractures result in reservoirs less than 2000 ft. having fracture gradients of 1.0 psi/ft or higher and vertical fractures are generally formed in zones below 4000 ft. having fracture gradients of 0.7 psi/ft or lower. For fracture gradients between 0.7 psi/ft and 1.0 psi/ft, no evidence is available to predict the exact inclination of the fracture. This generalization, however, contradicts the results of Fraser and Pettitt¹² who concluded that the fractures can be vertical even at very shallow depths. Their conclusion is based on a field test to determine the type and orientation of a hydraulically induced fracture.

Powers et al.¹³ used the technique of acoustic emissions from fractures to determine the orientation and dimensions of fractures. They concluded that these methods may offer a promise for post-fracture determination of direction, orientation and geometry of the fracture but a substantial amount of additional work needs to be done.

Other related work¹⁴⁻¹⁶ in the area of acoustic emission monitoring arrived at similar conclusions. The several studies¹³⁻¹⁶ reported in the literature on the acoustic emission from fractured rocks definitely warrants investigation for its use in the geothermal reservoir fracturing as a monitoring tool.

Several theoretical models¹⁷⁻²¹ are available in the literature to predict or determine hydraulic fracture dimensions. Many simplifying assumptions were made in developing these models. In general, it can be concluded that the simultaneous determination of the orientation and the dimensions of the hydraulically induced fractures is a complicated problem. The only fact definitely known is that the fracture width and length are determined by the force exerted on the fracture walls and the rate of fluid loss to the formation.² Further basic work is needed in this area. It is our opinion that the mathematics need no further development as opposed to the basic physics and chemistry involved in rock fracturing.

7.1.2.4 CALCULATION OF FRACTURE DIMENSIONS

The concepts for determining the dimensions of hydraulically generated fractures are well developed and are reported in several publications.^{2,22-23} However, the application of these concepts to actual field jobs is difficult and involves a considerable number of assumptions and simplifications. These methods can be used for geothermal operations with the same limited use as in the oil industry.

7.1.2.4.1 FRACTURE WIDTH

Fracture width is necessary to determine the injection rate for placement of a given size proppant and to determine fracture conductivity. In general, fracture widths equivalent to two or three times the maximum diameter of proppant particles are required. In developing the equation for the fracture width, assumptions are made on the mechanical properties of the rocks as well as the rheological properties of the fracture fluid. The width calculation also includes such factors as: (1) whether the fracturing fluid flow is laminar or turbulent during injection, (2) whether the resulting fracture is vertical or horizontal, and (3) whether the fluid is Newtonian or non-Newtonian. In all cases reported in the literature, the chemical or physical interactions of the fracturing fluid with the formation rock are not considered.

In hydraulic fracturing, the energy needed for the extension of hydraulic fracture is provided by the kinetic energy from the treatment fluid. In traveling through the narrow region of the fracture, the fluid experiences a friction due to its viscosity resulting in a pressure gradient. The resulting fracture width is related to this pressure gradient which is a result of the fluid injection rate, the rheological properties of the fluid (viscosity) and the mechanical properties of the formation. The mechanical properties under consideration are Young's modulus and Poisson's ratio. The rock is assumed to be isotropic, homogeneous and linearly elastic. For example, Perkins and Kern²³ gave relationships for fracture width for the case of laminar flow in a vertical fracture. These are:

For a Newtonian flow:

$$W = 0.25 \left[\frac{i\mu L}{E} \right]^{0.25}$$

For non-Newtonian flow:

$$W = 8 \left[\frac{2n'}{3\pi} (n'+1) \left(\frac{2n'+1}{n'} \right)^{n'} \left(\frac{0.9775}{144} \right) \left(\frac{5.61}{60} \right)^{n'} \right]^{1/(2n'+2)} \cdot \left(\frac{i^{n'} k' L h_f^{1-n'}}{E} \right)^{1/(2n'+2)}$$

Where i = injection rate (BBL/Day)

L = fracture length (Ft)

μ = viscosity (Cp)

E = Young's modulus (psi)

n', k' = rheological properties of the fluid

h_f = height of fracture (Ft)

Other authors have given equations which are similar except for the constant factors only.

From these equations, it may be concluded that the fracture width increases with increase in viscosity of the fluid, increase in injection rate and decrease in the elastic modulus of the formation.

7.1.2.4.2 FRACTURE AREA

The areal extent of hydraulically induced fracture is one of the important parameters in determining the post-fracture well productivity. Howard and Fast² referenced Carter who made several assumptions and derived expressions for the areal extension of fractures. The derivation is based on mass flow

equations which simply states that the rate of injection of the fracturing fluid equals the rate at which the fluid is lost to the formation ("leak-off" rate) plus the rate of volume increase of the fracture itself.

Using the above concept, the area of a produced fracture is given by:

$$A = \frac{1w}{4\pi c^2} (e^{x^2} \operatorname{erfc}(x) + \frac{2}{\pi 0.5} - 1)$$

$$\text{Where } x = \frac{2c(\pi t)^{0.5}}{w}$$

w = fracture width (in)

t = time (sec)

c = fracturing fluid coefficient

In the development above, three flow mechanisms that control fluid loss from the fracture to the formation are considered each having a different value of C. They are, (1) viscosity effects of the fracturing fluid (C_I), (2) viscosity and compressibility effects of the fracturing fluid (C_{II}) and (3) wall building effects of the fracturing fluids (C_{III}).

The equations for fracture area described above give values that are too large. Hall and Dollarhide^{20,21} considered the dynamic fluid loss effects and derived expressions for the fracture area as:

$$A = \frac{1}{2V_L} \left(\frac{e^{yt} - 1}{e^{yt}} \right)$$

$$\text{Where } y = \frac{2V_L}{w + 2L_{SP}}$$

$$V_L = \frac{\text{Leak-off rate (cu ft/min)}}{\text{Filter area (sq ft)}}$$

$$L_{SP} = \text{Spurt Distance (ft)}$$

$$i = \text{Injection Rate (cu ft/min)}$$

$$A = \text{Fracture Area (sq ft)}$$

In developing these equations for the areal extent of the fracturing, none of the reports included any physical or chemical effects of the fracture fluid on the formation. It is not known whether such chemical and physical interactions have any effect on the fluid loss and areal extent of the fracture.

7.1.3 FRACTURING FLUIDS AND PROPPANTS

A primary problem in transferring the hydraulic fracturing technology from the oil and gas industry to the geothermal industry lies in the availability of data on suitable fracturing fluids and proppants in high temperature environments. An exhaustive search through the published literature demonstrated to us that there are no fracturing fluids that can withstand the high temperature and other severe conditions encountered in geothermal reservoirs. Several fracturing fluids have been developed by various service companies and by oil companies which are suitable for lower temperature oil field use. However, there is not enough information on the properties of the existing fracture fluids in a high temperature environment to judge their usefulness for geothermal application. In addition, there is no information available on the chemical and physical interactions of the various available fluids with either the formation matrix or the formation brines at the high temperatures encountered in geothermal operations. This lack of information is similar for the chemical behavior of proppants and additives. Additives include fluid loss additives, diverting agents, corrosion inhibitors, scale inhibitors, friction reducers, breaking agents, etc.

7.1.3.1 FRACTURING FLUID CONSIDERATIONS

An important parameter for a successful hydraulic fracture job is the fracturing fluid properties. Proper fluid design for frac jobs in geothermal wells may be much more difficult than generally expected. Ideally, the fracturing fluid should have the following properties:

- 1) The fluid to be used in matrix type formations should possess a low leak-off rate. Fluid loss control is generally obtained by adding particulate and/or gelatinous materials to form a filter cake on the fracture faces in order to control fluid loss to the porous medium.
- 2) It should have the ability to carry a propping agent. The addition of concentrated polymer solutions to water-base fluids improves proppant transportability because it thickens the fluid.
- 3) It should possess a low friction loss which will result in lower surface pumping horsepower and consequently lower job costs.
- 4) It should be easily removable from the formation, preferably by thermal degradation or by the addition of breakers.
- 5) It should be compatible with natural formation fluids at reservoir temperatures.

- 6) It should be compatible with the formation rock matrix. If water-sensitive clays are present in the rock matrix, it should be treated to prevent excessive clay swelling or shrinkage.

The fracture dimensions, especially the fracture width, are dependent upon the fracture fluid viscosity. The higher the viscosity, the greater the fracture width. With greater width and appropriate proppants to hold the fracture open, the greater the fluid conductivity for the fracture. The viscosity of water-base fracturing fluids may be increased by the addition of water soluble polymers. There is a direct relationship between the polymer concentrations and the viscosity of the fracturing fluid. Polymers commonly used are guar gums, guar derivatives, modified cellulose, polyacrylamides, cross-linked polymers, etc.

As the fracture is initiated and propagated, several things happen:

- 1) The fluid temperature increases with increasing contact-time within the reservoir.
- 2) The fluid "leaks off" into the formation unless material has been added to form a filter case, then "leak-off" decreases with contact-time.
- 3) The shear rate of the fluid changes with changes of fluid temperature.

The fluid loss may be controlled by addition of fluid loss control agents. In a high temperature environment these are generally mixtures of silica flour and commercial additives composed of particles coated with soluble polymers. Both the temperature and shear rate effect the viscosity of the fracture fluid containing polymers. With increase in temperature, the viscosity decreases. The effect of shear rate on viscosity at various temperatures is rather complex and depends upon time, degree of cross-linking and polymer degradation.

After the fracture treatment is finished, the design of the fracture fluid should be such that the fluid is easily removed from the formation. This may be accomplished by viscosity decreases, as a result of the thermal degradation or by addition of polymer breakers. Several studies discuss the temperature profile in a fracture and its effect on the viscosity of the fluid as well as the effect of shear rate on viscosity.²⁹⁻³⁴ All of the publications emphasize the importance of chemical compatibility of the fracture fluids with the formation and formation fluids, but more work is required in this area in a high temperature environment. These effects are particularly important for geothermal fracturing because of the (1) high temperatures found in geothermal reservoirs and (2) complexity of the geothermal fluid compositions.

7.1.3.2 SOME LITERATURE STUDIES ON FRACTURING FLUID PROPERTIES

Water-base fluids with polymers, appear to be the most satisfactory system for geothermal fracturing. Several papers have been published that treat the interrelationships between temperature, shear rate, and viscosity as well as other "mechanically" related fracturing fluid properties. Very few papers deal specifically with the chemical aspects of these fluids. However, there are publications which describe the thermal stability of polysaccharides^{35,36} and sulfonates.^{39,40} Even though the sulfonates have only a very limited use as fracturing fluids, the importance and complexity of the chemistry on the fracturing fluids is clearly stated in these papers.

White and Means³⁵ discussed fracturing fluids formulated by the addition of a specially formulated polysaccharide derivative (PSD). Some of these data were compared with the data obtained with guar gum and cellulose derivative. They concluded that fracturing fluids can be formulated with PSD to handle bottom-hole temperatures up to 250°F or even higher depending on "cool-down" during the treatment.

White and Means³⁵ also measured friction reduction relative to water for PSD addition and compared it with the addition of an equivalent amount of guar gum. PSD thickeners were found to possess several advantages over guar gum thickeners. At 40°C, with PSD addition, a 55% reduction in friction is observed within 15 seconds. Whereas with guar gum addition, it takes more than 60 seconds to obtain the same percentage of friction reduction. White and Means³⁵ have also studied the viscosity of an aqueous fluid with PSD addition and compared it with that of fluids containing equal concentrations of guar gum and modified cellulose. For a temperature of 40°C, at two minutes, the PSD viscosity is four times that of guar gum and 1.5 times that of the modified cellulose. As the temperature increases, this advantage is less significant. They reported the viscosity change up to 175°F. The viscosity of PSD thickeners fall off rapidly with increase in temperature. For a 30-minute fracture job with fluid temperature of 100°F or less, PSD fluids maintain a good viscosity followed by rapid breakdown. No data were published at higher temperatures. Higher temperature data at higher concentrations of PSD is needed to determine if it would work for geothermal applications. Extrapolation of the data is more than questionable because of the uncertain role that degradation kinetics play in determining physical properties. Also, there are only limited data on the viscosity variation with shear rate.

White and Means also presented data on the damage to fracture permeability by the PSD frac fluids. Laboratory tests with 40-60 mesh sand showed a reduction of 1025% to the fracture conductivity with PSD addition, however, the damage to fracture conductivity using guar gum is 45% while with modified cellulose, it is 10%. PSD with silica powder was found to provide effective fluid-loss control.

The paper by White and Means gives data on PSD which can be used for treating wells with temperatures less than 150°F. The paper does not give data at higher temperatures and high shear rates. No rheological properties of this fracturing fluid were reported. In addition, there were no chemical or physical interaction studies of this fluid with the formation rock or the formation fluids. Some useful data was given on residues formed from these polymer additions. However, the chemical nature of these residues may drastically change with a large increase of the temperature.

Free, et al.³⁶ presented information on cross-linked guar gels used as viscosity enhancers of frac fluids. The addition of cross-linked gel increases the viscosity. For example, at 90°F, cross-linked guar additions develop a viscosity which is about 5 times that of a noncross-linked guar solution. This high viscosity was developed in less than two minutes. Cross-linked guar derivatives have been shown to contain less residue than guar, thereby reducing the formation permeability and fracture conductivity damage. The fluid loss parameters of the cross-linked guar derivatives are low, especially at lower temperatures. They had good proppant transport characteristics. They contained reliable breaker mechanisms that cause a positive viscosity break and a better return of the fluid from the well. The paper presents some rheological properties of the cross-linked guar and guar as a function of temperature and shear rate. The viscosity dropped by a factor of ten for the cross-linked guar derivative as the temperature increased from 170°F to 200°F. No information was available on the rheological properties at higher temperatures and at higher concentrations of the polymer. Further study is needed on the chemical interaction of these fluids with the formation matrix and the formation fluid which are important for geothermal application.

Seidel and Stahl³⁷ studied a high viscosity non-Newtonian fracture fluid for use in gas wells with bottomhole temperatures from 240°F to 300°F. The particular fluid additives were not identified. The paper does give data on viscosity as a function of temperature and composition. The viscosity stability of the fluid at 260°F was also presented. After an initial drop in viscosity, viscosity reaches a value that is constant over the range of 200-400°F. For example, at 260°F the loss in viscosity was less than 30 percent in 10 hours. Viscosity versus the gel concentration data indicate that higher additive concentration yields higher viscosity for all temperatures. This type of information is useful for geothermal application and provides a basis for the selection of the proper fluid for the bottomhole temperature. The temperature profile in the fracture can vary from well bore temperature cooled by surface fluids to the reservoir temperature at the leading edge of the fracture. Thus, one would encounter a range of temperatures under which the fracture fluids must function. This dictates a detailed study of the rheological properties of the fracture fluid not only as a function of temperature and shear rate

but also as a function of time. In addition, the leak-off rate and the breaker activity must be understood. Finally, the chemical stability and interaction of these fluids with formation matrix and formation brines should also be correlated as a function of time, temperature, shear rate and concentration of the additives.

Hannah, et al.³⁴ presented several concepts regarding fracturing fluids. They proposed a method of scheduling polymers, breakers or other material additions. This permits placement of fracture fluids with desired properties within the fracture so as to obtain optimum fracture generation. Their method considers fracture area and temperature profile. The fracture fluid temperature starts at the matrix surface and increases to the reservoir temperature at the fracture tip. Different portions of the fluid along the fracture length are exposed to a different temperature environment for different lengths of time. This dictates variable requirements for thermal, physical and chemical properties along the fracture. Based on this analytical method and the rheological properties of the fracture fluids, they proposed varying polymer addition at scheduled intervals to maintain the viscosity above a certain prescribed value (a viscosity of 50 cp or above was utilized in their example). A similar schedule was suggested for breaker addition to reduce the shut-in time. This method appears to offer interesting and useful possibilities for geothermal applications. No data on the rheological properties of these fluids or on the chemical interaction of the fluids with the formation brine or matrix was presented in the paper.

The qualitative information from technical publications on fracturing fluids may be summarized as follows:

- 1) Several fracturing fluids have been developed by various service and oil companies for various fracturing techniques to be used in lower temperature oil and gas fields.
- 2) All the fracturing fluids have been developed to specifically satisfy the requirements for application in low temperature oil and gas production.
- 3) For some fracturing fluids, the rheological data, particularly the apparent viscosities, as a function of temperature and shear rates was available. The range of temperature is limited in all cases to the relatively low temperatures commonly encountered in oil fields.
- 4) For most fluids, the viscosity data were available only for low temperature conditions.
- 5) The physical properties of fracturing fluids given as a function of the polymer concentrations are available only in a few studies.

- 6) Data on the chemical or physical interaction of the fracturing fluids with formation rock material and formation brines was not readily available.

From the available literature on the fracturing fluids, it is concluded that additional studies are required on the properties of the existing fracturing fluids at high temperatures for geothermal fracturing. In addition, information on the chemical and physical interaction of the existing fracturing fluids with the formation matrix and formation brines at the high temperatures encountered in geothermal operations is required.

7.1.3.3 PROPPANTS

The fracture conductivity is an important factor contributing to successful stimulation results. Proppants are used to maintain high fracture conductivity during fracture operations and prevent fracture closure after treatment. Several factors which influence the conductivity of the propped crack are:

- 1) Size and concentration of the propping particle.
- 2) Effect of fracture closure stress on the conductivity.
 - a) Ability of proppant to withstand crushing.
 - b) Resistance of embedding of proppant into the fracture walls.
- 3) Permeability reduction due to the frac fluid residues left in the propped fracture after fluid break-down.
- 4) High temperature chemical reactions resulting in unwanted solid materials trapped in the fracture.

In general, propping particles should exhibit good mechanical strength, good chemical stability, acceptable density, be pumpable downhole when suspended in the fracturing fluid, and be readily available in large quantities at a reasonable cost.

7.1.3.3.1 FRACTURE CONDUCTIVITY IMPROVEMENT WITH PROPPANTS

The conductivity of fracture proppants has been proposed by Darin and Huitt⁴¹ for a partial monolayer of proppants. They have taken into consideration such factors as crushing of the proppants under closure stress and the embedment of the proppant particles in the fracture walls. The fracture conductivity was measured by placing proppants between slabs of reservoir rocks, applying mechanical stress

on the proppants and flowing fluid through the proppant. These methods are described in various publications,^{42,43}

Cooke⁴³ studied the effect of environment on the conductivity of brittle proppants and the effect of flow rate on the conductivity. This paper and related articles⁴⁴⁻⁴⁶ clearly demonstrate the influence of the environment on the mechanical behavior of a proppant. Swolfs⁴⁷ examined the chemical aspects of the mechanical properties of consolidated sandstone and noted that water promotes the fracturing of sandstone at elevated temperatures and also the solutions of aluminum and ferric ion promote the fracturing of quartz at low temperatures. These reports suggest that a detailed study on the mechanical properties of proppants in the presence of various brine components at high temperatures under reservoir conditions is important.

Cooke⁴⁸ tested particles of sintered bauxite as a high-strength proppant in the laboratory and field. This proppant showed physical stability to about 300°F temperature. Neel, et al.^{49,50} developed a ceramic, aluminum-oxide containing proppant. The conductivity of fractures propped with this material was then laboratory tested under a closure pressure of up to 10,000 psi. This type of proppant appeared to work well. They also tested the effect of 10% HCl on this proppant at 85°C. After one week of exposure to the acid, the proppants did not show any decrease in fracture flow capacity.

McDaniel and Willingham⁵¹ studied the permeability of various proppants (both low strength and high strength) as a function of fracture closure pressure. At high closure pressures, sintered bauxite was the only one among the proppants tested that could maintain high permeabilities at closure pressures of up to 10,000 psi. This investigation did not report on the chemical and high temperature effects upon proppant behavior.

Sarda and LeTirant⁵² developed high-strength proppant ceramic beads that can withstand a high compression strength of 15,000 psi. Sarda⁴² reported laboratory studies testing these ceramic beads under various environmental conditions. The measured conductivities using these ceramic beads remained unchanged when subjected to brine (3% NaCl and 0.5% CaCl₂) at 300°F for 24 hours. The field tests using these proppants also showed good success.

Further data on these proppants under the more severe temperature conditions of geothermal wells is required as any extrapolation from the low temperature data to high temperature conditions could lead to false conclusions and very costly failures in the field.

7.1.3.3.2 PROPPANT TRANSPORT IN VERTICAL FRACTURES

The prediction of proppant transport is complex. Novotny⁵³ described the transport of proppants in vertical fractures as follows:

- 1) Prediction of dynamic vertical fracture geometry, i.e., the length and width of fracture as functions of time.
- 2) Loss of fluid to the formation as the proppant-fluid slurry flows along the fracture. This loss of fluid decreases the fluid velocity and increases the concentration of the proppant. Another effect leading to fluid loss is the dragging of the fluid and proppant along the fracture walls.
- 3) Fluid temperature behavior. As the fluid is injected through the wellbore into the fracture, the fluid temperature may drastically change which alters the fluid loss and viscosity which in turn may result in a change of the settling velocity of the proppant.
- 4) Decrease of conductivity due to fracture closure pressure. As soon as the fracturing treatment is completed, the fracture begins to close, thus changing the "packing" (i.e., the compaction and geometry of the pore space) of the proppants within the fracture. This may have decreasing effects on the resulting fracture conductivity.

7.1.3.3.3 PROPPANT SETTLING IN A VERTICAL FRACTURE

For Stokes-law region ($N_{Re} < 2$), the single particle settling velocity (V_s) in an infinite Newtonian fluid medium is given by:

$$V_s = \frac{g(\rho_p - \rho)d^2}{18\mu}$$

Most of the fracturing fluids are non-Newtonian and their viscosity is a function of the shear rate.

Here ρ_p = density of the proppant (gm/cc)

ρ = fluid density (gm/cc)

d = proppant diameter (cm)

μ = fluid viscosity (poises)

g = acceleration due to gravity (cm/sec²)

V_s = proppant settling velocity (cm/sec)

For settling in a stagnant non-Newtonian fluid, the shear rate ($\dot{\gamma}$) has been shown to be given by⁵⁴

$$\dot{\gamma} = \frac{V}{d}$$

Assuming a power law fluid,

$$\mu = K \dot{\gamma}^{n-1}$$

where K, n = the rheological constants for the fluid.

The particle settling velocity in a quiescent power-law fluid can be predicted by:

$$V_s = \left[\frac{g(\rho_p - \rho)d}{18K} \right]^{1/n} d$$

The fluid motion imposes a horizontal shear rate on the particle. Novotny⁵³ showed that the horizontal component of the shear rate is important for non-Newtonian fluids. Using the combined shear rates, the settling velocity would be:

$$V_s = \frac{980(\rho_p - \rho)d^2}{18K} \left[\left(\frac{V}{d} \right)^2 + \gamma_H^2 \right]^{\frac{1-n}{2}}$$

In addition, the fluid velocity varies from zero at the fracture walls to a maximum midway between the walls.

The theoretical and experimental studies of Novotny⁵³ and the experimental work on viscous fluids by Hannah, et al.⁵⁵ demonstrated that the determination of settling velocities measured in stagnant non-Newtonian fluids are not reliable for predicting proppant transport under actual flow conditions. Settling should be determined as a function of fluid shear rate.

7.1.4 DESIGN CRITERIA FOR A HYDRAULIC FRACTURING JOB

The hydraulic fracturing process may be described by a five-step process, namely (1) selecting all materials required for a frac job, (2) preparing and pumping of the fracturing fluid, (3) fracture initiation and propagation, (4) proppant placement and (5) fracture fluid removal (see Table 5). Each of these steps involves the computation of various parameters and the consideration of various interactions. (see Tables 6 to 10.)

The lists of design criteria given in Tables 5-10 cover the parameters and interactions that need to be known for a proper frac job design in a geothermal well. The mechanical aspects of the hydraulic fracturing process developed for the oil and gas industry can be transferred into a geothermal field if the parameters are similar. The chemical aspects of the fracturing process, particularly the interactions between the various fracturing fluid and reservoir materials and the proppant behavior at the high geothermal temperatures need further study. The importance of this present lack of knowledge cannot be overemphasized.

7.1.5 HYDRAULIC FRACTURING IS HIGH-RISK BUSINESS

The results of hydraulic fracturing are unpredictable. Reasons for frequent failures are a lack of understanding of almost all the parameters involved in a stimulation project.

A few of the reasons why fracturing of a reservoir can be unsuccessful are:

- 1) Generated fractures in a locally tight rock do not intercept the fluid bearing zones of high permeability. Generated fractures will most likely follow the direction of the largest stresses in the reservoir which tend to run parallel to naturally occurring fractures. If natural and artificially introduced fractures run parallel, the opportunity to produce new drainage paths from the reservoir into the wellbore are lessened or even non-existent.
- 2) The generated fractures may not propagate into the reservoir, but rather the hydraulic fluid may channel behind the casing and go up or down the borehole.
- 3) The frac fluids may be chemically unstable under high reservoir temperatures. Changes in the chemical composition will lead to drastic changes in the rheological behavior of the fluid, thus decreasing the efficiency of the fluid as a fracturing fluid.
- 4) The hydraulic fluids may be chemically incompatible with the reservoir matrix or fluid. The plugging damage caused by this incompatibility may fully or partially offset the benefits derived from the actual frac job.
- 5) An initially generated and well-placed fracture may close for various, proppant-related reasons after the field job is finished.
 - a) The proppants may crush, thus closing the fractures and leading to a rapid decrease of fracture productivity.

- b) The rock matrix may be plastic enough to "flow" into the fracture space supported by the proppants thus leading to a "healing" of the fracture and a subsequent loss of productivity.
- c) After creation of the fracture, the back flowing fluid may carry the same proppants back into the wellbore, thus reducing fracture support and partial closure of the fracture.
- 6) Some of the solids (proppants, formation fines or precipitated materials) may flow back into the wellbore and may plug the critical perforation holes or even the entire wellbore, thus reducing the productivity of the well.

7.1.6 PRODUCTION LONGEVITY AND ECONOMIC JUSTIFICATION OF SOME FRACTURE STIMULATION MAY BE QUESTIONABLE

Vetter ^{119,120} described some of the "pitfalls for the unwary" related to fracturing through shallow formation damage. Assuming this formation damage is caused by scale build-up as frequently encountered in geothermal wells, a corrective fracturing job may offer no permanent solution to the problem. On the contrary, the new flow paths initially created by a shallow frac job may soon be plugged again. Subsequent jobs will show a decreased efficiency because the newly formed deposits may now form further out in the reservoir. Eventually, the formation damage will be moved from a near wellbore region into a location far out in the reservoir where it becomes less and less accessible for an efficient damage removing job. In this case, a simple hydraulic fracturing job was definitely the wrong means of correcting a bad situation, despite the fact that the initial job may have been very successful for a short period of time.

It is critical that we understand what problems we are attempting to correct. If the problem is that of scale build-up, and subsequent plugging around the wellbore, a fracture treatment may re-open communication between the formation and wellbore, but the new flow channels would again plug, thus reducing production. If the period of time for increased flow were short, and the economic value of increased flow did not exceed the cost of treatment, the project would be economically unjustifiable.¹¹⁹

7.2 CHEMICAL STIMULATION METHODS

Chemically reactive fluids can be used to increase the well productivity by dissolving materials plugging the formation around the wellbore. Typical chemicals for the removal of solids in geothermal producing reservoirs are acids. Acidizing geothermal reservoirs follows the same principal concepts as acidizing in oil and gas operations, however, two major differences are:

- 1) Temperatures in geothermal reservoirs are usually much higher than in oil or gas operations. The high temperature-chemical reactions of acids with rock material (or any other solid deposits) may differ drastically from low temperature reactions. In addition, there may be major differences in the (a) chemical reaction rates and (b) chemical and physical behavior of the reaction products.
- 2) Production rates and lengths of producing intervals are usually much greater in geothermal wells than in oil wells. In order to stimulate the longer section of a geothermal wellbore by chemical removal of solids to increase dramatically the productivity of a geothermal well may require economically prohibitive volumes of acids.

Although matrix acidizing does not appear to be economically attractive, small acid jobs aimed at removal of acid-soluble materials around the wellbore may offer a large potential to improve the well productivity. Before one considers acidizing, a thorough knowledge of the type of materials to be dissolved and the effects of temperature and pressure on the acid reaction must be understood. From a safety viewpoint, the by-products of the reaction should be checked to insure no dangerous gases such as H_2S are produced in larger quantities.

7.2.1 VARIOUS ACIDIZING TECHNIQUES

There are at least three basically different acidification methods:

- 1) Matrix acidizing designed to remove rock or other solid materials from the rock matrix to increase the rock permeability.
- 2) Wellbore acidizing designed to remove scale and solids from within and around the casing and tubing to restore a free flow of produced fluids within the well.
- 3) Acid-fracturing methods designed to generate fracture walls with an etching pattern permitting the production of reservoir fluids without the need for proppants.

The first two methods are described below, whereas the third method (acid-fracturing) is described in Section 7.3 of this report.

Reviews of Williams, et al.,⁵⁶ Fitzgerald, et al.,⁵⁷ and Hendrickson⁵⁸ are typical of the various articles available on numerous aspects of acidizing in oil and gas reservoirs. References on the general aspects of acidizing and matrix acidizing are found in the references.⁵⁹⁻⁸⁵ Other references⁸⁶⁻⁹² are concerned with the technique of acid fracturing. A paper addressing directly the high temperature aspects of acidizing (maximum 300-400°F) was prepared by Dill and Keeney.⁸⁵

Important requirements for an acid to be useful in a geothermal environment are:

- 1) The acid must react with the formation rock and only form soluble reaction products.
- 2) The acid should not form sludges by reacting with the formation brines found in the matrix.
- 3) The additives used at high temperatures of the geothermal environment should be thermally stable and should not react with the acid to form unwanted reaction products.
- 4) Heat-stable inhibitors should be used to prevent excessive reaction with the metal parts used in building the system. These inhibitors must be effective at the high temperatures found in geothermal reservoirs.
- 5) The reaction rate between the acid and the formation rock should be slow enough so that a reasonable amount of acid penetration into the formation is accomplished.

Several requirements listed above for acidizing of a geothermal well are difficult to fulfill. The design of an acidization job, however, should take all the above factors into consideration and should optimize the above factors.

7.2.2 HIGH TEMPERATURE ACIDIZING

The "rock removal power" is the important aspect of acids in matrix acidizing and wellbore acidizing. The "etching power" is a critical parameter in acid fracturing even though the "rock removal" and dissolution kinetics also play an important role even during acid fracturing because they determine the "spending length" or depth of active acid penetration into the reservoir. Table 11 shows the major parameters of any acid job design as a function of temperatures, pressure and compositions (of all liquid, gaseous and solid phases).

Unfortunately, the published literature⁸⁵ contains very little information related to the high temperature acidizing which can be directly applied to geothermal operations. Admittedly, many wells can be cooled before any highly reactive liquid such as acids are injected into any well. However, this cooling process is (a) limited to certain wells and time durations and (b) cannot be applied during numerous phases of even very typical acid jobs. For example, cooling of the wellbore cannot be applied during times when the spent acid is produced back. This spent acid may be low enough in its pH value to cause severe damage to the wellbore hardware, particularly if the corrosion inhibitor is either diluted or adsorbed or otherwise retained by the formation. Also, cooling cannot be applied when the acid reactions take place in locations further away from the wellbore.

The lack of high temperature data on acidizing is particularly difficult when it comes to the formation of secondary deposits. We have reason to believe that the high temperature chemistry of the acid reaction products is quite different from the equivalent low temperature chemistry. For example, the high temperature behavior of secondary fluorides (reaction products of hydrofluoric acids) may drastically differ from their low temperature behavior. Calcium fluorides and kryolite-type compounds may have an extremely low solubility at high temperatures, thus leading to severe formation damage if hydrofluoric acid is applied. During one recent acid job in East Mesa we noticed that almost none of the spent HF was produced back, whereas the spent HCl was contained in the returned fluids as expected even though both acids were injected almost simultaneously. This may prove our suspicion regarding the low solubility of the fluorides at high temperatures and with that, the danger of using HF/HCl mixtures for acid stimulation jobs in geothermal reservoirs.

Field data, a number of publications on solubilities, and laboratory observations lead us to believe that the high temperature chemistry of acidizing is filled with "pitfalls for the unwary". Extending low temperature acidizing practices indiscriminantly into geothermal operations is bound to be met by disaster. Previous field experiments in East Mesa and laboratory experiments to be conducted under this contract will be the topic of a special report to be issued soon. It would lead beyond the frame of this present report to treat these subjects in great detail at this time.

7.3 COMBINED MECHANICAL/CHEMICAL STIMULATION METHODS

A different situation is encountered when the major advantages of chemical and mechanical stimulation methods are designed into a combination method. The most typical example is the method of acid-fracturing. Instead of using a frac fluid which is chemically inert (by all practical means) when it comes to rock dissolution during a hydraulic frac job, one chooses a highly reactive chemical fluid such as an acid for the frac job.⁸⁶⁻⁹²

The mechanical (hydraulic) action of fracturing the rock matrix is combined with the chemical dissolution of rock material from the newly generated face of a fracture. A uniform removal of the solids from these fracture faces is definitely not attempted. Instead, a rather non-uniform etching by the acid is desired during the process of fracturing. This extremely non-uniform chemical etching pattern may generate flow channels on the fracture faces which will remain open even after the fracture closes immediately upon completion of the stimulation job. In a sense, the acid replaces the need for proppants by generating these non-uniform etching patterns. The tips and valleys on the etched fracture faces provide the flow paths for the fluids, thus guaranteeing a residual fracture conductivity similar to that generated through the placement of proppants.

As mentioned previously in this report, the placement of proppants in a fracture may offer serious problems, particularly if the proppants must be placed at large distances from the wellbore. Acid fracturing eliminates these placement problems. However, the generation of suitable flow channels within the fracture through acid-fracturing is also not without many technical problems and "pitfalls for the unwary". Some of these problems are outlined below:

- 1) The rock composition must be suitable as far as reaction rates with acids at reservoir temperature are concerned. Suitable rocks for conventional acids are, e.g., limestone and dolomite.
- 2) The rock matrix cannot be too uniform or too heterogeneous as far as chemical composition is concerned. For example, calcium carbonate embedded in sand grains will be dissolved and the sand grain will not be attacked at a sufficiently high rate by the acid. If full or partial dissolution of the calcium carbonate does not generate new flow channels, the acid-frac job will end up with a failure.
- 3) To obtain a suitable etching pattern in a fracture within a suitable reservoir, an almost perfect optimization of the fracturing job design is required. Of prime importance is the relationship between: fracturing fluid composition, fracture geometry (particularly length and height), injection rate, injected volume, temperature, time parameters, chemical reaction rates and flow patterns within the freshly generated fracture. Obviously, it is nearly impossible to know all these parameters needed for the design of a perfect acid/fracturing job.

7.4 EVALUATION OF STIMULATION JOBS

Conventional "evaluation" methods often consist of a simple monitoring of the production rate after finishing the well stimulation jobs. A better job evaluation method is rate measurements combined with pressure transient testing although it should be noted that this often used combination may also prove to give inadequate data for a proper job evaluation.

The problem of evaluating a stimulation method cannot be solved adequately by simple and conventional means of rate monitoring and pressure transient testing. A fairly simple situation may illustrate this statement. Assuming a reservoir is hydraulically fractured and a sufficiently large flow path has been established between the wellbore and the fluid bearing portions of the reservoir. The proppants are placed properly. However, the closure stress of the fracture is high enough

to cause the proppants to crush. As a result, very little fluid is produced and the job must be considered a failure. The method itself and all design features of the job except the selection of the proppant material were correctly chosen. Dropping this method as a potential candidate for stimulating this reservoir based on the job "evaluation" through rate monitoring would be an improper reservoir management procedure.

Another example illustrates one of the many personal experiences of the author with this specific operational problem. A number of oil wells were "successfully" stimulated with highly expensive aqueous solutions of EDTA (ethylene diamine tetra acetic acid). The EDTA was chosen because of a suspected BaSO_4 scale problem in the field. As it turned out later on, the usage of EDTA was a total waste of dollars despite the huge increases of well productivity resulting from the stimulation jobs. The solvent (fresh water) and not the EDTA, removed some NaCl precipitations and hardly any BaSO_4 within or close to the wellbore, thus increasing drastically the productivity. Here again, judging a stimulation method based on well performances subsequent to stimulation jobs proved to be extremely wrong.

The complexity of stimulation evaluations increase for chemical stimulations such as the various types of acidification. Every time an acid is introduced into a reservoir, a large number of vigorous and competitive reactions may start. These reactions will proceed or stop depending upon the numerous thermodynamic conditions in the system. Pressures, temperatures and concentrations at any given instant may vary with reaction rates (acceleration or deceleration) or may even initiate a new type of reaction. Some of these chemical reactions and their vital rates will cause a physical situation beneficial for increasing the well productivity. For example, removal of even small amounts of solid material from a tight pore space may drastically increase the critical permeability within the reservoir at locations close to the wellbore. On the other hand, over-reacting may cause the detrimental removal of all formation cementing materials, thus leading to a matrix collapse in the same locations which could have disastrous consequences for the same permeability. In addition, the various chemical reactions occurring concurrently during the process of acidification may start the formation of undesired secondary acid by-product deposits may be more harmful to the well productivity than the original damage. Some of these secondary deposits (e.g., the siliceous materials) can be very fluffy and can occupy a large portion of the critical pore space within the close vicinity of the wellbore. The resulting skin damage reduces flow of the reservoir fluids into the wellbore.

Evaluating a certain stimulation technique for its suitability in geothermal operations can and will offer many problems as outlined above.

Two additional evaluation methods besides production rate monitoring and pressure transient testing should be considered:

- 1) Use of naturally occurring tracers before and after an individual stimulation job. The chemical compositions of the native formation fluids often change drastically due to physical (mixing) and chemical reactions. A very close and comprehensive monitoring of the produced fluids for some of the critical chemical constituents will permit a sophisticated job evaluation.
- 2) Use of artificially introduced special tracers in the acid will allow the extraction of a considerable amount of information. Radioactive tracers are particularly useful.

Both methods, i.e., (a) conventional pressure testing and (b) monitoring through tracer analyses, should be combined in some future stimulation jobs. These evaluation methods will be the main subject of future reports to be issued by VR.

7.5 MAINTENANCE OF INCREASED PRODUCTIVITY

A set of problems quite different from that related to increasing the well productivity is encountered during maintaining the productivity. This productivity maintenance can be viewed as an integral part of a stimulation job. Achieving an increase of productivity is only a portion of the entire job, maintaining this productivity can be considered the remainder of the overall job.

Quite often, productivity maintenance jobs have to be designed into the stimulation job itself. For example, if the productivity of a geothermal well is decreasing because of scale formation within the reservoir, a combination "stimulation/productivity maintenance" job seems to be the most logical choice for a field job. A hydraulic fracture job employing scale inhibitors in the fracturing fluid could achieve both the desired increase of the productivity and its maintenance for an extended period of time. The properties of this fracturing fluid may not be the best choice possible for a "pure" stimulation job. However, the technical and economical advantages by performing this combination job may outweigh the disadvantages related to the productivity stimulating properties of the fluid.

Our literature search regarding productivity maintenance aspects of stimulation jobs did not yield any useful information.

8.0 CLAYS AND THEIR ROLE DURING STIMULATION JOBS

Clays play an important role during a number of oil and gas field operations. There is sufficient reason to believe that clays also play an important role in geothermal operations. Clays can cause

problems during (a) regular production periods of a well and (b) during or after stimulation or work-over jobs in a certain well. Clay related production problems may require a stimulation job with specific job design features to handle the clay problems.

The impact of clays on specific stimulation design varies as clays also vary greatly in their chemical and physical composition and behavior. Clays are generally defined as hydrated aluminum silicates and are found in reservoir rocks in varying percentages, structures, forms and compositions. We will discuss only the basic structural principles and terminology necessary to understand the phenomena which contribute to clay damage and its prevention. It is beyond the scope of this report to even list the numerous types and forms of clays which could be present in geothermal reservoirs. It is suspected that the normally high temperatures in geothermal reservoirs may lead to the formation of clays or clay related products not often found in the cooler oil and gas reservoirs.⁹³

The clays found in a producing subterranean reservoir can pose a variety of problems during a stimulation job. The following clay properties may lead to many of these problems:

- 1) Changes in the volume of clay-sorbed-fluid volume. This change can be an increase of sorbed waters (swelling) or decreased (shrinkage). Either can adversely affect the pore channels by loosening solids and plugging pore throats, thus hindering fluid flow.
- 2) Breakdown of reservoir matrix and/or cementing material, freeing the clays and the plugging of the pore channels with these fines.
- 3) Removal or partial removal of cementation and clays. This removal may result in a partial collapse of the pore channels with (a) a subsequent loss of productivity and (b) sand (free-moving) problems within the pore channels, wellbores, and surface equipment.
- 4) Clays often separate various reservoir portions through clay layers (stringers). The stress and rock properties within the productive zones and the generally non-productive clay stringers may impact the effectiveness of a hydraulic fracture stimulation job. Any fracture may or may not penetrate through a stringer.
- 5) The chemical reactivity of clay particles may be quite different from that of the remaining rock materials. The chemical reactions between stimulation fluids (particularly acids) and clays must be carefully considered for all stimulation jobs. In addition, this chemical reactivity may also lead to chemisorption of additives of stimulation fluids on clays, thus altering the clay particle.

- 6) The clays may strip certain chemicals from the stimulation fluid thus altering the fluid itself.

The primary question is to what degree these problems can be anticipated during stimulation jobs in geothermal reservoirs. The reasons for problems may be associated with the following unique characteristics of clays such as: (1) they are normally smaller than 2 μm , or break up easily to this size under the slightest stress, e.g., when in contact with water; (2) they are usually much smaller than any other mineral in the matrix; and (3) their ability to readily react is due to their crystal structure, which is a layered lattice with weak interlayer forces and sometimes high surface area over which the reaction can take place.

8.1 GENERAL CLAY STRUCTURE AND TERMINOLOGY

The basic structure of clay minerals has been determined to consist of layers with substitution of various cations in the clay lattice to give various different properties to the clays. In general, the structural units of clay layers are sheets with different structure and cations:

- 1) One is a silicate sheet composed of SiO_4 - tetrahedra interconnected over three of the four corners. The corresponding three oxygens of all tetrahedra in the sheet lie in one plane. The sheet has a composition of $\text{SiO}_{2.5}$ and, thus, is negatively charged. It is called the tetrahedral sheet or (T) unit.
- 2) The other type of sheet is a neutral, stoichiometric, and can exist as minerals brucite, $\text{Mg}(\text{OH})_2$, or gibbsite, $\text{Al}(\text{OH})_3$, with the cations in octahedral coordination. This then is the octahedral sheet or (O) unit.

The valence of the cation in the octahedral sheet allows us to distinguish between the two basic groups of sheet silicates:

- 1) Dioctahedral, where trivalent aluminum occupies two out of every three available octahedral sites, and
- 2) Trioctahedral, with divalent magnesium in all octahedral positions.

The variety of sheet silicates is controlled by two features:

- 1) The different combinations in which these sheets are combined to form layers which are then stacked in regular and mostly simple sequences, and
- 2) The substitutions of cations into the lattice structure (e.g., Al, Mg, Fe, etc.).

A more detailed examination of clay structure shows that:

- 1) There are three potential combinations of tetrahedral and octahedral sheets which form most types of layers for sheet silicates. These are TO-, or 1:1 layers, TOT-, or 2:1 layers, and TOT-O-, or 2:1:1 layers. Because of the composition and the resulting charge, the tetrahedral sheet (T) cannot exist by itself, but only in connection with the octahedral sheet (O): stable layers are formed by substituting apical oxygens of the tetrahedral sheet with hydroxyls of the octahedral sheet. Thus, an octahedral sheet can combine with a tetrahedral sheet on one side (TO- layer), or with two of them, one on each side (TOT- layer). The third kind of layer is formed by insertion of a separate octahedral layer between consecutive TOT- layers.
 - a) TO- layers form diphormic minerals, i.e., the trioctahedral antigorite (a serpentine), or the dioctahedral kaolinite (a clay mineral).
 - b) TOT- layers form triphormic minerals, i.e., the trioctahedral talc or the dioctahedral pyrophyllite.
 - c) TOT-O- layers form tetraphormic minerals, also known as chlorites.

Clay minerals other than kaolinite and the related kandites are triphormic, based on the talc and pyrophyllite layers, as are the micas. These clay minerals include illites, smectites, and vermiculites. One group which has chain structure rather than sheet structure is the palygorskite group which includes sepiolite.

TO^o-layers have a repeat distance of 7Å. TOT-layers about 10Å, and TOT-O-layers about 14Å. Sometimes, two or all three of these layers occur together in the same mineral. These so-called mixed-layers usually have rather large repeat distances.

- 2) Substitutions may take place in both the octahedral sheet (Al for Si) and tetrahedral sheet (Al, Mg for each other, and by similar ions like Fe). Substitution occurs because of the similar size of the ions regardless of their charge. In most cases a lower charged ion replaces a higher charged one: Al^{3+} for Si^{4+} , Mg^{2+} for Al^{3+} , and similar. The resulting negative charge in the layer is compensated by other ions between the layers, mostly K^+ , Na^+ , or Ca^{2+} . These interlayer cations change the character of the forces between the layers. Neutral layers are bonded by van-der-Waals forces or hydrogen-bridging, while interlayer cations can introduce ionic bonding,

i.e., K^+ in the mica muscovite. The clay minerals, as a rule, do not show regular substitution with stoichiometric composition but rather compositional ranges and, thus, rather complicated and generally weak interlayer forces.

As a consequence of their structural similarities and easy substitutions, clay minerals, chlorites, and micas are often transformed into similar minerals under given chemical and thermodynamic conditions.

8.2 GENERAL CLAY PROPERTIES

The general properties of the most clays are described below:

8.2.1 CLAY SWELLING

The volume of sorbed water will vary on the clay-fluid particle dependent upon the type and concentration of cation in the sorbed fluid and the type of clay present.

8.2.1.1 KANDITES

Kandites have the most stable crystal structure of all clay minerals. Their lattice structure permits only surface sorption of cations and not interlayer sorption which will cause internal or surface changes. They are, thus, only slightly affected by cation changes. In physical form, they are generally hexagonal flakes with crystals small and poorly formed.

8.2.1.2 ILLITES

Illites are, structurally, closely related to micas. They are the most common clay minerals in nature. They do not take up interlayer water and cation exchange takes place on the surface of the clay mineral. Physically, they are found as small, poorly defined flakes commonly grouped in irregular aggregates without distinctive outline.

8.2.1.3 SMECTITES

Smectites, including montmorillonites, however, are characterized by the phenomenon of swelling, that is the uptake of water in variable quantity between the clay lattice layers. Some of this water can be considered hydration water of the small interlayer cations. Calcium smectites usually take up two layers of water molecules. Sodium smectites take a variable and, usually, greater amount of water during swelling. The smectites have great surface areas, permitting sorption of water and surface chemical reactions. Due to the variable volume of the clay-fluid particle, this is the primary clay family that is considered in oil, gas or geothermal reservoirs.

8.2.1.4 VERMICULITES

Vermiculite is a mineral resembling mica that, when heated, has the appearance of little worms. Its structure shows it to be composed of mica layers separated by water molecules. The swelling capability is similar to that of Ca-Smectites.

8.2.1.5 ATTAPULGITE, SEPIOLITE AND Palygorskite Groups

The palygorskite group, including sepiolite has chain rather than sheet structure. They contain water in channels between the chains. The sepiolite has gained some importance only recently as a drilling mud additive. The physical shape tends to be needle-like. One characteristic is their fibrous habit. These clays have low sorption values.

8.2.1.6 CHLORITES

The chlorites though not generally classified as clay minerals are often considered in this context. Some "swelling chlorites" have been reported which probably have incomplete, discontinuous brucite layers in the form of islands. Chlorites have been well known in crystalline shists, in hydrothermal rocks and in the alteration products of silicates.

8.2.2 ION EXCHANGE CAPACITY OF CLAYS

The ion exchange capacity of clays depends upon the number of broken bonds around their edges. This capacity increases with increasing surface area.

8.2.2.1 KANDITES

Kandites, including kaolinite, halloysite and others, are diphormic and dioctahedral. They deviate very little from the ideal formula $Al_4[Si_4O_{10}](OH)_8$, plus hydration, so that there are few exchangeable cations, all positioned on exterior surfaces. The cation exchange capacity is only about 3-20 meq/100 gram.

8.2.2.2 ILLITES

Illites are triphormic and mostly dioctahedral. The cation exchange capacity is somewhat greater than that of kaolinite ranging from 10 to 40 meq/100 gram.

8.2.2.3 SMECTITES

Smectites including montmorillonite are triphormic and both dioctahedral and trioctahedral. Substitutions take place in both the tetrahedral positions (Si by Al) and the octahedral positions (Al by Mg, or Mg

by Li, and similar), mostly by ions of lower valence. The charge deficiency is mostly made up by Na^+ and Ca^{2+} ions between layers and on exterior surfaces. These relatively small cations are easily exchanged for other cations. Thus, the cation exchange capacity of smectite can be very high, ranging from 80 to 150 meq/100 gram.

8.2.2.4 VERMICULITES

Vermiculites are also triphormic and mostly trioctahedral. The substitutions are mainly in the tetrahedral sites (Si by Al), with charge compensation by Mg^{2+} (and Ca^{2+}) ions. Cation exchange capacity ranges from 100 to 150 meq/100 gram.

8.2.2.5 PALYGORSKITE GROUP

The palygorskite group, which includes sepiolite, is different from most clay minerals. It is the only group which has a chain structure with open channels. These minerals have a considerable base exchange range with relative amounts of Al and Mg. The cation exchange capacity ranges from 20-30 meq/100 gram.

8.2.2.6 CHLORITES

The chlorites differ from normally considered clay minerals. They are tetraphormic with regularly alternating talc-like and brucite-like layers. Substitution is mainly Al^{3+} , simultaneously for Si^{4+} in the talc layer and for Mg^{2+} in the brucite layer, balancing the charge. This makes the interlayer bonding partly electrostatic. The other important bonding mechanism is similar to that in diphormic kaolinites. This arises from pairs of adjacent oxygen (in the talc layer) and hydroxyl ions (in the brucite layer). The cation exchange capacity ranges from 10-40 meq/100 gram.

8.3 CLAY STRUCTURES

Clay minerals are formed during weathering, sedimentation, burial, and by diagenetic and hydrothermal alteration of other minerals.⁹⁴ The clay mineral formed during weathering is dependent upon composition of the parent rock and surrounding fluids. Upon shallow burial (less than 1 meter) an important change takes place, the partial exchange of sodium and calcium for magnesium. Throughout burial until the production of metamorphic rock, a chemical and mineralogical reorganization of geologic material occurs. Depending on pressure and temperature, there are transformations in the montmorillonite-illite series which can be used to define different zones of mineral assemblages. For details see Velde.⁹⁴

8.3.1 CLAY STRUCTURES IN OIL FIELDS

Montmorillonites are commonly found in oil and gas fields. They play an important role in the production history of a well as, through swelling or migration, they can decrease the size opening or constrict the pore channel through which reservoir fluids flow. This "plugging" action will reduce the potential production of the well.

8.3.2 CLAY STRUCTURES IN GEOTHERMAL FIELDS

Geothermal reservoirs range through temperature and depth zones which can be defined by stability boundaries of certain phyllosilicate assemblages.⁹⁴ For practical reasons, authors use different nomenclatures more suited to the local circumstances, because the boundaries are normally not as clear cut, and equilibrium mostly has not been established.

Fan⁹⁵ noted that the first zone of alteration in Hawaiian basalt is characterized by montmorillonite, between 675 and 1350m. The temperature at the lower depth ranges from 290 to 325°C. The second zone below is the "chlorite zone" ranging from 1350 to 1894m with temperatures from 307 to 340°C.

In Icelandic geothermal areas (basaltic rocks), Kristmannsdottir⁹⁶ established three zones for clays according to temperature. The first zone, below 200°C was characterized by smectites. Next, a transition zone between 200 and 230°C where smectites were altered to chlorites, with swelling chlorites occurring as intermediate products, followed by the third zone characterized by primarily chlorites.

At the depths of sandstone reservoirs, the transformation of illite to chlorite appears to take place at lower temperatures: Hoagland and Elders⁹⁷ place the transition from the "diagenetic" to the "illite-chlorite" stage around 150°C at the Cerro Prieto geothermal field. The diagenetic zone is defined by the presence of kaolinite and montmorillonite.

8.3.3 CRITICAL DIFFERENCES BETWEEN OILFIELD AND GEOTHERMAL CLAYS

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 at high-temperature areas where they 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 should be considered in design of work-overs or stimulation jobs.

8.4 PRODUCTION PROBLEMS DUE TO FORMATION CLAYS

Clay related fluid production problems can lead to the need for extensive stimulation jobs or well work-overs. Some of these clay related production problems are well recognized in the oil industry. Similar problems can be anticipated for the geothermal industry. It is our opinion that the geothermal industry may also experience additional problems due to the different and more complex behavior of clays at high temperatures. These anticipated but still unrecognized problems may require considerable research and field experimentation to reduce "plugging" of the reservoir about the well core.

8.4.1 KNOWN DAMAGE MECHANISMS IN OILFIELD OPERATIONS

Clays may cause damage to the permeability of reservoir rocks by reducing the pore volume and restricting flow channels. There are two mechanisms generally recognized:

- 1) The swelling of expandable clays.
- 2) The break-up, transport, and deposition of all clays.

In addition to these damage mechanisms, clays may also cause problems during or after stimulation jobs because of their ion exchange capacities.

8.4.1.1 SWELLING OF EXPANDABLE CLAYS

While dry, smectite has a translation period of about 9.6 Å along the crystallographic c-axis, the uptake of water between layers can increase this cell height to 21.5 Å, more than doubling the volume of the crystallite. This spacing is due to four molecular layers of water which are very ordered with properties different from those of liquid water.⁹⁸ This water is considered most resistant to removal.⁹⁹ Hydrated smectite can take up additional interlayer water. Mixtures and mixed-layer clays containing smectite are also expandable. Expanding of the clay component can result in disrupting the fabric or pore structure of the matrix rock, releasing fines that can also migrate and plug pore throats, resulting in further "plugging".

8.4.1.2 DISINTEGRATION AND DEFLOCCULATION OF CLAYS

Clays such as kaolinite, illite, and chlorite which are considered non-expanding nevertheless adsorb enough water between the platelets to make them easily slip and cleave into smaller particles. Illite and chlorite, normally bonded by potassium ions, can degrade and lose the ions by leaching when exposed to slightly acidic fresh water. After potassium removal degraded illite will expand to 14 Å (normally 9.5 Å).¹⁰⁰ Potassium leaching will help alter micas. Reed¹⁰¹ demonstrated that this results in the expansion and fraying of the edges of mica, thereby releasing small particles.¹⁰⁰

Even if the individual particles do not disintegrate, all clays are subject to deflocculation (or peptization), a condition wherein agglomerated masses of clay (flocs) are broken up and dispersed. When salt water flows through the rock, the clay is in a flocculated condition. Neasham¹⁰² has shown, with Scanning Electron Microscope (SEM) photomicrographs, the physical appearance of clay flocs. He found that kaolinite exists in discrete, platy particles scattered throughout the pore system and does not form intergrown crystal frameworks on pore walls or within intergranular pores. Illite, chlorite, and montmorillonite, on the other hand, are attached to pore walls to form a relatively continuous and thin (<12 μ m) coating ("pore-lining") or extend far into or completely across a pore or pore throat to create a bridging effect ("pore-bridging"). This microporous structure is comparatively easily broken down. When fresh water flows through the rock, the clays will be in a deflocculated condition. The individual particles will be entrained by the fluid, transported, and deposited as microscopic filter cakes plugging narrow pore openings. Such filter cakes reduce the permeability of the rock considerably.¹⁰³

The largest differences between salt-water and fresh-water permeability occur when the rocks contain montmorillonite clays. Because of the exceptional swelling capacity of these clays it was long believed these differences are related to the corresponding differences in swelling. However, montmorillonites are also known as efficient filtration-rate reducers. This property is probably a result of the particular size and shape of the particles. They are very thin, and possibly somewhat flexible. These flakes may be expected to close small pore openings effectively by building a compact impervious sheath of flakes across the openings. Thicker clay particles, such as those of kaolinite, are far less effective in building impermeable filter cakes.¹⁰³ It has, therefore, repeatedly been pointed out, that clay expansion in situ is far less important a damage mechanism than is dispersion and deposition. It is, however, acknowledged that the expandable clays are the most damaging.

8.4.2 EXPECTED DAMAGE MECHANISMS IN GEOTHERMAL PRODUCTION OPERATIONS

Damage in geothermal operations can be expected to be somewhat different from that experienced in oilfield operations. This is due to in-situ and flow conditions which are partly advantageous, partly disadvantageous. The major disadvantages are:

- 1) Clay minerals found in hydrocarbon bearing structures are in a flocculated or less damaging state when exposed to the formation brine,
- 2) High velocities associated with geothermal fluid can physically disintegrate weaker clay masses and facilitate their movement within the pores which can result in blockages or "plugging".

- 3) Formation fluids which contain clay attracting polar components such as geothermal fluids may create "drag" forces on the clays causing dispersion and movement.¹⁰⁰ The mobile clays can block flow channels.

These are disadvantages of an aqueous system and higher flow velocities. On the other hand, the most damaging clay substance, montmorillonite, is expected to be present only in greatly reduced amounts, or to be completely altered due to temperature to a low swelling form. Generally, a greater amount of less expandable clays can be expected in the high temperature geothermal reservoir. How much this could affect the associated production problems depends on the ability of illite and chlorite to form comparable filter cakes. The shape and structure of the crystallites of these clays is very similar to that of montmorillonite as seen in Neasham's¹⁰² photomicrographs.

The influence of the higher temperature on clays is not fully understood.

8.5 CAUSE AND PREVENTION OF CLAY DAMAGE

Clay damage may be overcome by preventing:

- 1) expandable clays from swelling, and
- 2) all clays from deflocculation.

The causes for these damage mechanisms, and the basic prevention methods are presented below.

8.5.1 EXPANSION OF CLAYS, AND ION EXCHANGE

The swelling of smectite is due to its structure. In the stacking of the layers, oxygen planes of each TOT-layer are adjacent to oxygen planes of the neighboring layers. As a consequence there is a very weak bond and an excellent cleavage between them. Water (and other polar molecules, such as certain organic molecules) can enter between the layers, causing the lattice to expand in the c direction. The c-axis dimension which measures the translatory repeat unit of stacks, therefore, varies from about 9.6 Å, when no polar molecules are between the layers, upwards to over 30 Å with polar molecules present. Substantially complete separation of the individual layers can occur in some cases.⁹⁸ The bond between layers can be strengthened by interlayer cations which in turn influence the hydration of the clay. Norrish (see Grim⁹⁸) investigated in detail the sequence of hydration states of montmorillonite carrying various exchangeable cations. In the case of the common ions, he showed that for sodium montmorillonite there is at first a stepwise increase in c-axis spacing and then (above about 40 Å) complete dissociation of the individual layers. Calcium has a considerable range of stability with two molecular layers of water with a C-axis spacing of about 15.4 Å, and it has substantially no expansion beyond 18 Å. For montmorillonites with potassium and

magnesium there is only very limited expansion.⁹⁸ The swelling of smectite can, therefore, be controlled with cations. Smectite has a considerable cation-exchange capacity of 80 to 150 milliequivalents per 100 g, among the highest of all clay minerals.

8.5.2 DEFLOCCULATION AND FLOCCULATION

The interaction between clay particles in a liquid medium is complicated by the action of both attractive and repulsive forces. According to Van Olphen,¹⁰³ three kinds of forces have to be considered:

8.5.2.1 VAN-DER-WAALS ATTRACTION

The attracting forces are basically of Van-der-Waals nature. Clay particles are, however, not, as a mineral formula would suggest, electrically neutral but carry a negative charge on their surface due to lattice imperfections. This surface charge is the cause for adsorption of cations. These so-called counter ions form a diffuse layer around the particles. The constituents of this "atmosphere" are in diffusion equilibrium with the bulk of the solution in which their ionic concentrations are lower. The negatively charged clay surfaces and the positive counter ion atmosphere form an electric double layer, much like a condenser. The counter ion layers provide for repulsive forces between the clay particles. This phenomenon is called double-layer repulsion.

The double-layer repulsion depends on the concentration of the cation in the bulk solution. The charge density is determined by the imperfections in the interior of the crystal and is, thus, a fixed quantity. If the bulk concentration of the counterion is increased, the concentration difference to the double layer and, thus, the range of the repulsion, is decreased. The double layer is being compressed toward the clay surface. The combined effect of Van-der-Waals attraction and double-layer repulsion varies. Therefore:

- 1) At low bulk cation concentrations, the repulsion dominates. Attraction provides for a minimum in potential energy close to the clay surface, followed by a maximum on the solution side. This maximum constitutes a barrier which clay particles would have to overcome in order to flocculate. Low cation concentrations, therefore, are favorable to deflocculation.
- 2) At higher cation concentrations, the repulsion approaches the same order of magnitude as the attraction and the barrier becomes smaller. Eventually, the barrier will disappear making high cation concentrations favorable for flocculation.

When ions of different valence are compared, it is to be expected that those of higher valence produce a more compressed double layer at comparable bulk concentrations and, thus, promote flocculation

better. Indeed, the valence rather than the type of counter ions predominantly determines the flocculation value (Schulze-Hardy rule) which is the minimum concentration of an electrolyte causing the flocculation of a certain colloidal solution, or sol, in a given time. Counter ions can be mutually exchanged. Between ions of the same valence the ratio of the concentrations in the counterion atmosphere is the same as that in the bulk equilibrium solution. For ions of different valence, the ion with the higher valence is predominantly accumulated near the clay surface. Therefore, the fractions of ions of highest valence are greater in the counter ion atmosphere than in the bulk solution.

So far, only the ions have been considered. It is, however, obvious that the solvent, too, has some influence on the double-layer. If the double-layer is taken as an electric condenser of molecular dimensions, it is clear that a reduction of the dielectric constant of the medium decreases the "thickness" of the double-layer. Such a compression due to a reduction of the dielectric constant may be achieved by the addition of water-miscible solvents, such as alcohols or acetone, to the solution. Most polar solvents enhance the flocculating power of an electrolyte markedly. Then, the addition of an organic solvent can induce flocculation.

8.5.2.2 ELECTROSTATIC ATTRACTION

The flat layer surfaces are not the only surfaces of the platelike clay particles. They also expose an edge surface area. The atomic structure of the edge surfaces is entirely different from that of the flat-layer surfaces. At the edges, the tetrahedral silica sheets and the octahedral (alumina) sheets are disrupted, and primary bonds are broken. Although the total charge of the particle is negative, there are strong indications that the charge of the edges is positive, at least under certain conditions, such as low pH. Here is a different type of double layer than that existing on the flat surfaces. It is created by the adsorption of potential-determining ions. Thus, double layers of opposite sign are present on the edge and flat surfaces of the clay particles in hydrous systems. The resulting electrostatic attraction leads to mutual flocculation. The result is edge-to-face linkage of particles forming house-of-cards structures.

8.5.2.3 BRIDGING OF PARTICLES IN INTERACTION WITH ORGANIC COMPOUNDS

When clays interact with organic compounds, there are additional factors which can promote flocculation. Principally, these are the bridging of particles by:

- 1) polyfunctional long-chain compounds which may become adsorbed on more than one particle simultaneously and thus bridge several particles, i.e., polyelectrolytes, and

- 2) a second immiscible liquid component, such as traces of water or other polar liquids, in an organic dispersion. If the clay is preferentially wetted by the added polar liquid, they are believed to be enveloped with a thin film. When two particles come together, their water films will flow together at the junction points much like two droplets. This arrangement results in a reduction of the interfacial area and, thus, results in a reduction of the total free energy of the system.

8.6 CLAY STABILIZERS

Clay stabilization agents used in the oilfields are generally of three kinds which are, in order of increasing importance and effectiveness:

- 1) Salts which promote ion exchange and flocculation.
- 2) Inorganic polymers.
- 3) Organic polymers.
- 4) Miscellaneous others.

There has also been an effort to look into the feasibility of utilizing the effects of organic solvents as well as mutually immiscible fluids, mostly based on oil. Since the compounds listed under "miscellaneous others" are not useful in geothermal applications, they will only be briefly considered in this report.

8.6.1 SALTS WHICH PROMOTE ION EXCHANGE AND FLOCCULATION

The stabilizing quality of these salts is due to the fact that the cations they provide enter between the layers, possibly in exchange of other cations, to control expansion and/or adsorb to the surface layers to control flocculation.

The replacing power of cations offered in solution depends on many factors and is not yet understood in any detail. Generally, it seems to increase with:

- 1) the concentration of the cation in the solution,
- 2) the valence of the cation, and
- 3) cation atomic number, or size, at equal valence. (Since the ions are hydrated, the size of these hydrated ions may have to be considered. If the hydration goes generally down with cation size - which is debated - the sequence in size of hydrated ions would just be the reverse of that of the unhydrated ions, and the rule could still hold.)

The expansion of smectite seems to be better controlled by Ca^{2+} and Mg^{2+} than by Na^+ .

The flocculating power of cations adsorbed on the outside layers is subject to the Schulze-Hardy rule. Thus, it increases with valence. The following flocculation values have been observed:

25 - 150 m mol/dm³ for monovalent ions
0.5 - 2.0 m mol/dm³ for divalent ions
0.01 - 0.1 m mol/dm³ for trivalent ions.

Thus, there is a decrease of two orders of magnitude per step, measured in meq/dm³. With increasing concentration, the flocculation power also increases. Among cations of the same valence, the flocculating power increases slightly with ion size.

Thus, cations act qualitatively in the same order, or sequence, whether as exchange - and exchanged - ion or as adsorbed ion. The sorption of water between layers, or on the outside, of expandable clays with cations present can be viewed similar to double-layer repulsion, or deflocculation. What happens is that the water uptake first destroys any ionic bonds between layers, and then the water separates layers with their adsorbed ions. Thus, two double-layers are created which are now held in some equilibrium distance from each other. Clay expansion is the phenomenon seen from a clay-mineralogical point of view as a clay-cation system, to which water is added. The same phenomenon from a colloid-chemical point of view is deflocculation which takes place in a clay-water system into which ions are introduced. In our context, however, we are dealing with a water-ion system (brine, etc.) to which clay minerals are added. The difficulty here is to develop this third possible viewpoint out of the other two. According to the Schulze-Hardy rule, divalent cations are more effective at lower concentrations. Their usefulness was shown by Land and Baptist¹⁰⁴ in laboratory measurements. The water permeability of sands containing sodium clays proved to be lower than that of sands containing calcium clays. The relative permeability of both kinds of sand to gas was almost equal, which implies independence of the nature of the adsorbed ions.

Experiments relating to the relative concentrations of different ions have importance in view of ion exchange. Such experiments were performed by Jones.¹⁰⁵ His results suggest that even small proportions of calcium or other divalent ions, such as magnesium, are capable of controlling clay blocking in formation rocks. Core tests indicate that a sensitive formation can be exposed to water safely if at least one tenth of the salts dissolved in both the native water and the injection water are calcium and magnesium salts. Even less concentrations are often sufficient. These relations correspond to those of the flocculating values.

The use of Ca^{2+} ions, however, has its disadvantages. According to Reed,¹⁰¹ there is field evidence of formation damage near the wells in sands in several Southern California oilfields. In laboratory studies, this behavior was attributed to mica alteration in the sands when leached with neutral NaCl or CaCl_2 solutions. Using potassium salt shows no such ill effects. The use of acidic solutions, however, results in dissolution of calcareous cement. To prevent this, such solutions have to be saturated with respect to CaCO_3 .

The following salts and solutions have been used as clay stabilizer. According to Black,¹⁰⁶ 1-2% KCl water, 8-10% NaCl brine, 1-2% NH_4Cl water, 1-2% CaCl_2 water. KCl water has been most effective of these and most widely used. The application of a XC-Polymer/ KCl system was reported by Kendall and Norton.¹⁰⁷ According to Kubacki,¹⁰⁸ laboratory measurements were performed with $\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ on shaly sand samples from the Lake Maracaibo area containing kaolinite and illite. A minimum concentration of 6% proved to be effective, a 6.5% solution showed the best inhibitor properties. Generally, the performance of these stabilizers follows the Schulze-Hardy rule, with the exception of the potassium salts. Their superiority is credited to the unique role of the K^+ ion in the phyllosilicate lattice due to its larger size.

8.6.2 INORGANIC POLYMERS

With cations of higher valence, actually a qualitatively higher step is taken in clay stabilization. The ions of such metals as iron, aluminum, chromium, lanthanum (all trivalent), zirconium, hafnium, titanium (all tetravalent) can take on even higher charge than their valence indicates: they can polymerize. Veley¹⁰⁹ has outlined the basic processes which take place. The ions, when dissolved in water, first hydrate and then hydrolyze. Hydration is adsorption, where attachment or association of water molecules occurs with other molecules, ions, or surfaces. Hydration of exchangeable cations and clay surfaces is important in the first stages of separation of clay particles. Hydrolysis signifies a chemical reaction wherein bonds in water molecules are broken, and new bonds are formed. Hydrolyzable metal ions react with water to produce acid solution. That is, they tend to reduce their high charge by giving up H^+ to form hydronium, H_3O^+ :

where M is a trivalent, six-coordinated metal ion such as Al^{3+} . Hydrolyzation is the reaction of these ions with each other by forming hydroxyl bridges, and again producing H_3O^+ , i.e.:

In such a polymerization process, polynuclear ions are formed with greater net charge (per ion), but lower charge per metal ion in these ions which can be generalized as $[M_x(OH)_y(H_2O)_{6x-2y}]^{(3x-y)+}$, with $x=1,2$, etc., and $y=0,1,\dots,3x$. The process can continue until H_3O^+ ion concentration becomes high enough to break M-OH-M bonds as rapidly as they are formed. Equilibrium is sometimes reached only after weeks, months, or years of standing.

These metal ions maintain sixfold coordination with H_2O molecules and hydroxyls. Each charged kinetic unit (ion) will consist of an indefinite number of metal atoms linked together by hydroxyl bridges. The total charge per ion will depend on the M:OH ratio and the number of metal atoms per ion. Trivalent metal solutions may contain ions such as $[M_6(OH)_6(H_2O)_{24}]^{12+}$ or $[M_{24}(OH)_{48}(H_2O)_{48}]^{24+}$, whose total charge per ion is much greater than their empirical equals, $[M(OH)(H_2O)_5]^{2+}$ and $[M(OH)_2(H_2O)_4]^+$. The attraction between a negatively charged clay particle and its exchangeable cations is exponentially related to the charge of the cations. Thus, a polynuclear ion with net charge of 8+, or 12+, or more, may be several million times more strongly attracted to a clay particle than monovalent or divalent cations. Consequently, from electrostatic considerations alone, polynuclear ions should almost immediately displace all the exchangeable cations on the surface and be very tightly held. In addition, there is some evidence that the polynuclear metal ions become chemically bonded to the clay surfaces by M-O-Si linkages.

These polymer ions are, therefore, not exchangeable. They block exchangeable positions permanently. The role of Al^{3+} , i.e., can be described as building layers very similar to a separate octahedral layer in chlorites, linking two TOT-layers.

According to Reed,¹¹⁰ aluminum salts when dissolved in water hydrolyze to form an acidic solution, i.e.:

Generally, the reaction proceeds in the presence of NaOH from $Al^{3+} + OH^- \rightarrow Al(OH)^{2+}$ over $Al(OH)^{2+} + OH^- \rightarrow Al(OH)_2^+$ to $Al(OH)_2^+ + OH^- \rightarrow Al(OH)_3$ which is quite insoluble and thus precipitates. $AlCl_3$ solutions are acidic (pH=6) and remain so on addition of NaOH until the NaOH/Al ratio approaches 3. Then, however, the insoluble product $Al(OH)_3$ has little affinity for additional OH and thus the solution pH increases sharply on addition of NaOH (pH=11) (at still higher pH, Al^{3+} redissolves because water-soluble aluminate ions are formed). By stopping the addition of NaOH when the OH/Al ratio is less than 3, water-soluble species commonly known as OH-Al polymers are

formed where each OH forms a bridge between two Al. The polymerization is to 6-membered rings, at OH/Al equal to 2.0 (second step, above): $6 \text{ Al}(\text{OH})_2^+ \rightarrow \text{Al}_6(\text{OH})_{12}^{6+}$. At higher OH/Al ratios (<3), the ring units grow to form multiple rings, and the growth proceeds into the third dimension approaching the structures of gibbsite and bayerite (metastable), the crystalline forms of $\text{Al}(\text{OH})_3$. These structures are layered, with weak bonds perpendicular to the layers, and the rings and multiple rings can all be considered substructures of these layers. In other words, they are flat and two dimensional. They represent portions of gibbsite layers. As mentioned above, gibbsite layers are part of the clay mineral structure. They form the octahedral layer of the dioctahedral minerals.

Thus, the relatively highly charged ring units are not only attracted to the clay surfaces to adsorb tightly. They also fit the crystal structure so nearly perfectly, that they form octahedral structures between layers of clay particles. When they age they grow to form larger and more perfect crystalline sheets. Clays with these virtually non-exchangeable polymers are quite stable structurally and resistant to expansion and dispersion.

Inorganic compounds of several metals were tested for their stabilizing properties, among which Al, La, Fe, Sn, Pb, Ti, Zr, Hf, and others, proved effective. Zr, Hf, Th, and Ti were not affected by strong brines and distilled water showing that these hydrolyzable ions would not be removed by prolonged exposure to ordinary salt concentrations.

Laboratory and field tests have mainly been conducted with two compounds. Hydroxy-aluminum, OH-Al (Reed,¹¹⁰ Coppel, et al.,¹¹¹ Copeland, et al.¹¹²), and Zirconium oxychloride, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (Velej,¹⁰⁹ Peters and Stout,¹¹³ and Copeland, et al.¹¹²).

8.6.3 ORGANIC POLYMERS

The information on organic polymers in literature is scarce. This has two main reasons:

- 1) The mechanisms by which they work are not too well understood. There are a great many of them, and thus their adsorption may act in many ways. Bonds as strong as covalent have been suggested. The main impetus is to find active compounds and test them. As long as they work, the interest for the mechanisms is secondary, especially since these are very complicated.
- 2) The polymers are - probably all - proprietary to the service companies and thus protected by them. They are very effective, and in some applications they out-perform the inorganic varieties.

Organic polymers have been used for clay stabilization for some time. Slobod and Beiswanger¹¹⁴ report on laboratory tests with GAF's CLA-Perm N (nonionic, based on vinyl pyrrolidone) and CLA-PERM A (anionic, based

on vinyl ethers) series. Clay swelling was successfully controlled in Berea cores with concentrations as little as 1 ppm of polymer but does require a minimum amount adsorbed of about 0.03 mg/cc of pore space. For field treatment, indications are that more concentrated solutions of 100 ppm and more will move the polymer through the porous medium. Black¹⁰⁶ mentions a polymer effective at 0.5 ppm concentration.

Laboratory tests were run on two polymers, dimethyldicoco ammonium chloride, and a product of dimethyldiallyl ammonium chloride, in comparison with inorganic polymers, by Copeland, Coulter and Harrison.¹¹² Based on the data published, the zirconium salt was the most efficient clay stabilizer studied on the Frio formation. It provided effective control at a ratio of 100 grams of the clay silt fraction stabilized per milliliter of zirconium salt solution. The comparison figures for the other stabilizers were: DDAC (dimethyldicoco ammonium chloride): 75; polymerization product of dimethyldiallyl ammonium chloride: 50; and hydroxy-aluminum 25. Two and two-tenths (2.2) gallons of zirconium salt solution per foot of vertical height are required to stabilize a cylinder of the Frio formation (assuming 25% porosity) to a radius of five feet from the (eight-inch) wellbore. According to the numbers given above, the corresponding amounts of the other stabilizers are 1.5, 2 and 4 times as high, respectively, in the above order. This highest stabilizer efficiency was obtained by using 5% HCl with either 0.5% water-wetting surfactant (an ethylene oxide adduct of an alcohol blended with a fluorocarbon) or with 10% EGMBE (ethylene glycol monobutyl ether) rather than using fresh water as a carrier fluid, except in the case of hydroxy-aluminum. The solvent and the surfactant are applied, as in matrix acidizing, for cleaning the surfaces and reducing the surface tension. Their effect on the Zr-salt is an improvement by a factor of 4, or better, and somewhat less on DDAC. The acid alone, without additives, proved to be a more effective carrier than fresh water for the Zr-salt in some cases (Frio Formation), in others not (Brazos River sand).

According to McLaughlin, et al.,⁹⁹ certain organic polymers, for short COP's, have been found to be effective and long lasting clay stabilizers. There is a family of COP's which is characterized by multiple nuclei or groups which can react with cation exchange sites on the clay as connected groups. Thus, there are not individual ions occupying the cation exchange sites, but ionic nuclei linked together in a chain-like or polymer structure. X-ray diffraction tests indicated only a single layer of polymer adsorbed between clay layers. The simultaneous occupation of many sites makes the COP's resistant to replacement by monomer cations such as sodium. COP's have several advantages over inorganic polymers and other stabilization agents:

- 1) They can be used in all types of formations since they are not acidic nor do they require an acidic pH to remain in solution. Carbonate components in the formation such as limestone or dolomite have no effect on COP agents while they can interfere with the placement of the inorganic agents because mildly acidic pH conditions are necessary to retain them in solution.

- 2) They are quite tolerant of the fluid used as a solvent to carry them into the formation. Any convenient pH can be used, alkaline, neutral, or acid. Several aqueous fluids have been used such as fresh water, sea water, and solutions of ammonium chloride, potassium chloride, calcium chloride, and hydrochloric acid. Alcohols such as methanol make good solvents allowing full functioning of the COP. But diesel oil or crude oil are not suitable solvents because COP's are not hydrocarbon soluble due to their intense polarity.
- 3) Aside from adsorbing on anionic surfaces, they display minimal surface activity. Flow tests indicate that they tend to allow the clays and sands to remain water set. COP's failed to stabilize emulsions or aggravate emulsion problems with several crude oils.

8.6.4 MISCELLANEOUS OTHERS

There are several attempts to use the properties of other fluids for clay control, such as organic solvents, water-miscible and immiscible fluids. These are mostly, of course, petroleum and petroleum products.

Atwood¹¹⁵ conducted experiments resulting in a satisfactory laboratory method for restoring permeability to clay containing cores damaged by fresh water. Flooding the damaged cores with water-miscible fluids such as salt water, acetone, isopropyl alcohol and ethanol was not successful. Flooding with oil was partly successful. However, when water was removed by distillation in the presence of immiscible fluids, such as air or toluene, permeability was completely restored. This is attributed to the collapse of "brush heaps" of swollen and dispersed clays to their original volume due to strong interfacial and capillary forces. The required forces can be generated with a solvent partially miscible with water such as n-hexanol. Oil and its derivatives can be used in oil producing formations (i.e., Barkman, et al.¹¹⁶: oil-coating process using a cationic surfactant to oil-wet the sandgrains; Clementz¹¹⁷: adsorption of petroleum heavy ends - asphaltenes and resins - in hydrocarbon solution; use of oil-base frac fluids) but not for geothermal stimulation. Alcohol is used as carrier and fracturing fluid.

8.7 CONVENTIONAL METHODS TO OVERCOME CLAY DAMAGE

Conventional methods use one of the clay stabilizing agents described in the previous section. The permanence of the salt treatments is generally inferior to that of the polymers. Polymers are not affected by changes in salinity.

While formation water containing sodium can counter-replace the exchanged potassium or calcium, thus restoring the clay to its original sensitivity, the polymers are more resistant to replacement. However,

an acid treatment later on may remove the inorganic polymer stabilization agent (Coppel, Jennings and Reed¹¹¹).

Thus, the COP's described by McLaughlin, et al.⁹⁹ appear to be better suited to stabilize clays than the inorganic polymers. COP's have been used in injection wells. A penetration of treatment for 10 to 15 feet seems appropriate for waterflooding operations with fresh water to repressure water-sensitive formations. The amount of stabilizing agent generally used for clay control is sufficient for 5 to 8 feet of penetration depth. When water production starts in a hydrocarbon producing formation, sand may be produced which was bound by clay. Sometimes, it is advisable to use alcohol to carry the COP when it is feared that even an aqueous fluid containing a clay stabilization agent may loosen the sand. If remedial treatment is attempted after damage has taken place, the main condition for use of a COP treatment to reopen permeability is that there be some residual permeability so that the treatment fluid can arrive at the source of the blockage.

8.7.1 CLAY STABILIZATION FOR CONTINUOUS PRODUCTION

For continuous production, clay stabilization may be essential. If sufficient salinity is not maintained, stabilization treatment becomes necessary. With the modern polymers, these treatments generally last for years.

8.7.2 CLAY STABILIZATION DURING WORK-OVERS

According to Reed,¹¹⁰ laboratory (on Berea sandstone) and field tests were conducted with hydroxy-aluminum as a clay stabilization agent. Hydroxy-aluminum can be successfully prepared in large quantities by reacting AlCl_3 and NaOH in a high-shear mixing device. The results indicate that it is advantageous to use an OH/Al ratio of 2.0 and age the treated rock for perhaps two days in fresh water. Hydroxy-aluminum has been successfully applied in the field (0.1 m solution injected) for treatment before steam stimulation and as a perforating and gravel-packing fluid (making subsequent HCl - HF acid treatments unnecessary). Coppel, Jennings and Reed¹¹¹ report that more than 200 wells have been treated in this way, many with outstanding success and a few distinct failures. Hydroxy-aluminum could be the best solution for:

- 1) Wells whose production declines rapidly after acid stimulation. Re-acidizing and then applying OH-Al reduced the rate of decline markedly: Four wells had an average oil production rate of 160 BOPD after 60 days compared with 86 BOPD after conventional acid treatment.
- 2) Wells that sand up. After sand is cleaned out, OH-Al retards the migration of sand and clays and keeps wells on production that could not previously maintain production.
- 3) Steam-stimulated wells in water-sensitive formations. OH-Al treatment before steam stimulation has resulted in injectivities nearly double those of untreated wells - 13.3 vs. 7.5 in B/D/psi/ft x 10^3 units. Oil productivity during the first cycle has more than doubled - 3.2 vs. 1.5 in BOPD/ft units.

The hydroxy-aluminum jobs can be carried out with conventional oilfield service company equipment. OH-Al is a slightly acidic (pH 4-5), non-hazardous (nontoxic), colorless, odorless chemical which requires no unusual handling procedures.

The other inorganic polymer in wide-spread use, zirconium oxychloride, was laboratory and field tested by Veley¹⁰⁹. It often had to be applied as a methyl alcohol solution, but this proved to be effective even when steamed at 600°F. Long-term field studies reported by Peters and Stout¹¹³ confirm that the use of hydrolyzed zirconium salts provides effective clay stability in Appalachian formations. This has resulted in higher sustained production rates and greater ultimate recovery after it had been recognized that measures previously taken were not effective. Through September 1976, more than 2000 treatments have been performed with this stabilizer, more than 1000 of which have been fracturing treatments in the Appalachian area. Several case histories are reported based on work performed in the Clinton sand of Ohio. They represent closely controlled field tests where continuous production (2 to 4 years) records were available for analysis. One of the cases provides a comparison to KCl as a stabilizer which proved to be far inferior.

COP's (organic polymers) have been used (McLaughlin, et al.,⁹⁹) in acid and fracturing treatments. COP's are preferably used before the acid treatment but can be used also during or, like other stabilization agents, after the acid treatment when fines are already liberated by the acid. Mutual solvents make COP's compatible with non-emulsifying additives without noticeably impairing the effectiveness of either the additives or the COP's. When hydrofluoric acid is used, COP compounds are stable at least an hour in the presence of 3% HF-12% HCl. COP compounds can treat clay in the presence of spent HF which otherwise causes almost complete removal of all clays in 20 minutes of exposure (at 75°F) as

shown in SEM photomicrographs by Thomas, Crowe and Simpson.¹¹⁸ Fracturing treatments are the major use of COP's (McLaughlin, et al.⁹⁹). Formation damage can occur by the interaction of clays with fracturing fluid lost into the fracture face. Many of the fracturing fluid additives are anionic which make slight changes in technique and use of alternate additives necessary to readily accommodate the use of COP compounds. Most of the wells treated using COP compounds as additives have been low permeability (0.1 to 5 md) gas wells where about 10% of the normal concentration of COP compounds is optimum. The use of COP compounds in frac fluids may be in the pre-pad, pad, the sand laden fluid itself, and/or in an afterflush. Because of the ionic nature of some gelling agents, care should be exercised in selection of the specific gelling agent used. COP compounds are not compatible with anionic gelling agents, but they will not interfere with nonionic gelling agents such as hydroxy ethyl cellulose.

The application of COP's is simple because most of the time they are part of another treatment. Thus, the equipment used as well as pump rate and pressure for placement are governed by the primary treatment. Mixing the COP solution is achieved by stirring it into the miscible carrier fluid which must be clear (i.e., sea water should be filtered). As mentioned, anionic surfactants are incompatible so they should be used with care. Quantity and concentration of a COP depends upon the formation, the clay type, and the length of the interval to be treated. Efficiency and economics dictate the use of an afterflush behind the COP solution to spread it into untreated depths of the formation. The authors report well over 200 field tests. These were, however, underway only for a few months so that results were preliminary and limited. Fracturing treatments using COP as an additive appeared to have a more permanent production increase curve than those without COP. The wells treated with COP also had a faster clean-up rate, 1 to 2 days vs. the untreated well clean-up time of 3 to 6 days in acidizing treatments, two wells had sustained gas production with no water or sand production.

Of particular interest is the applicability at high temperatures. Literature on the retention of clay stabilizing properties at higher temperatures is scarce. Reed¹¹⁰ reports that hydroxy-aluminum has been successfully applied in the field before steam stimulation treatment. According to Veley¹⁰⁹, stabilization with zirconium oxychloride prevented damage by succeeding high temperature (600°F) steam treatment.

The effectiveness of clay stabilization agents at high temperatures was tested by Young and McLaughlin.¹⁰⁰ Several commercial inorganic and organic clay agents were evaluated in the laboratory for retention of clay stabilization properties when exposed from 300°F to 600°F steam. Steam is used for oil recovery in two techniques: cyclic steaming of the producer and steam flooding through injector wells. Three proprietary (Halliburton Services) organic polymers (McLaughlin, et al.⁹⁹) and two inorganic polymers (hydroxy-aluminum, zirconium oxychloride), all field proven at lower temperatures, demonstrated durability and effectiveness

at high temperatures. They vary some in respect to retention of clay stabilization properties and resistance to hydrochloric acid stimulation treatments. While the former is generally good, acid resistance is problematic. The inorganic polymers are not acid resistant. The organic stabilizers work well at 300°F but at the next test point, 500°F, only one of the three (number 1) is still effective after acidizing, retaining its effectiveness also at 600°F.

8.7.3 GRAVEL PACKING

According to Coppel, et al.,¹¹¹ as a gravel-packing fluid, OH-Al has made it possible to bring wells onto production without acid stimulation previously necessary when a low-salinity brine (Ca = 5000 ppm) was used.

Organic polymers (COP's) have been used in sand control operations according to McLaughlin, et al.⁹⁹ The primary goal is to help prevent migration of formation fines back into the established sand barrier. The treating technique is similar for the sand control treatments in use, i.e., gravel packs, most of pressure packs, and sand consolidation. The best technique involves placing the COP compound in a preflush ahead of the sand control materials. In this manner, the sand control materials and associated fluids provide the displacement required. With certain COP compounds and sand consolidation techniques the COP compound must follow the sand consolidation treatment in order to avoid weakening the consolidation compressive strength.

8.8 TECHNOLOGY TRANSFER OF CONVENTIONAL CLAY STABILIZATION INTO GEOTHERMAL FIELDS

8.8.1 CLAY STABILIZATION

Geothermal fields pose less of a problem as far as the clays are concerned, because relatively fewer amounts of the most damaging clay minerals, the smectites, are expected. The difficulties arise from the brines, which have high temperatures, high flowrates, high volume (and maybe low salinity, sometimes). The same stabilizers will probably work under these conditions as long as they are effective at the temperatures encountered.

8.8.1.1 STABILIZATION FOR ROUTINE PRODUCTION

The clay stabilizers tested by Young and McLaughlin¹⁰⁰ showed retention of their stabilization properties at temperatures up to 600°F. Of these, hydroxy-aluminum and zirconium oxychloride have been successfully applied in the field before steam stimulation treatment. It is, however, not yet known how long they will withstand this environment.

8.8.1.2 STABILIZATION FOR WORK-OVERS

The polymer stabilizers will probably work well enough for work-overs since they have been tested to withstand high temperatures for some time. Acidizing requires some consideration, because only one, organic polymer 1, of the five polymers tested by Young and McLaughlin,¹⁰⁰ was still effective over 150°C (300°F) after acid treatment.

8.8.2 GRAVEL PACKING

Hydroxy-aluminum, according to Coppel, et al.,¹¹¹ has worked well as gravel packing agent in the oilfield. McLaughlin, et al.,⁹⁹ report successful application of organic polymers (COP's). As far as geothermal applications are concerned, the reservations are similar as in 7.8.1.

8.9 SUGGESTIONS FOR FUTURE R & D WORK

The last section leaves much room for R & D. Most of the problems have not been addressed yet experimentally. Long-time stability, effect of chemical environment, high stress behavior, all at high temperatures, are unknowns as far as clay stabilizers are concerned.

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TABLE 1

POTENTIAL GEOTHERMAL WELL STIMULATION METHODS

- 1) MECHANICAL:
 - A) MASSIVE HYDRAULIC FRACTURING
 - B) SHALLOW HYDRAULIC FRACTURING
 - C) EXPLOSIVE FRACTURING
 - D) THERMAL FRACTURING

- 2) CHEMICAL:
 - A) MATRIX ACIDIZING
 - B) WELLBORE ACIDIZING
 - C) CLAY STABILIZATION
 - D) OTHER CHEMICAL TECHNIQUES

- 3) MECHANICAL AND CHEMICAL
 - A) ACID FRACTURING
 - B) OTHER CHEMICAL FRACTURING

TABLE 2

REASONS FOR SELECTING LOW PRODUCTIVITY
WELLS UNDER A STIMULATION PROGRAM

- 1) RESERVOIR ROCK NEAR THE WELLBORE HAS INHERENTLY LOW PRODUCTIVITY.
- 2) THE PERMEABILITY NEAR THE WELLBORE MAY BE REDUCED BECAUSE OF INVASION OF DRILLING MUD AND CHEMICALS.
- 3) REGIONS NEAR WELLBORE HAVE DECREASED PERMEABILITY CAUSED BY SCALE FORMATION DUE TO PRESSURE AND/OR TEMPERATURE DROPS..
- 4) PERMEABILITY MAY BE DECREASED BECAUSE OF PARTICLE RELEASE AND SUBSEQUENT PLUGGING.
- 5) NEAR WELLBORE PERMEABILITY MAY HAVE DECREASED DUE TO FAULTY WORK-OVERS OR STIMULATION JOBS.

TABLE 3

FACTORS LEADING TO DIFFERENCES IN
STIMULATION TECHNIQUES BETWEEN OILFIELD
AND GEOTHERMAL OPERATIONS

- 1) TEMPERATURE
- 2) PRESSURE
- 3) RESERVOIR FLUID COMPOSITION
- 4) TYPE OF ROCKS
- 5) TYPE OF CLAYS
- 6) FLOW RATES

TABLE 4

CHEMISTRY-RELATED PROBLEMS OF FRAC
STIMULATION IN GEOTHERMAL RESERVOIRS

- 1) HYDROTHERMAL STABILITY OF STIMULATION FLUIDS
- 2) REACTIONS BETWEEN STIMULATION FLUIDS (INCLUDING ALL ADDITIVES) AND FORMATION ROCK (INCLUDING CLAYS)
- 3) REACTIONS BETWEEN STIMULATION FLUIDS (INCLUDING ALL ADDITIVES) AND FORMATION FLUIDS

TABLE 5

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB

- 1) SELECTING OF FRAC FLUID MATERIALS AND PROPPANTS
BASED ON MEASURED AND CALCULATED CONDITIONS BEFORE,
DURING AND AFTER FIELD JOB
- 2) PREPARING AND PUMPING OF FRAC FLUID:
FLOW OF NON-NEWTONIAN FLUID THROUGH WELLBORE
- 3) FRACTURE INITIATION AND PROPAGATION AS FUNCTION
OF FLOW RATE AND PRESSURES
- 4) PROPPANT PLACEMENT, I.E., DISTRIBUTING OF
PROPPANTS IN FRAC FLUID AND FRACTURE
- 5) FRAC FLUID REMOVAL FOR IMPROVED PRODUCTION
OF FORMATION FLUIDS

TABLE 6

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB:

I. SELECTING OF MATERIALS

1) FRAC FLUIDS:

- A) COMPATIBILITY OF FRAC FLUID (WATER) AND/OR FRAC FLUID ADDITIVES WITH FORMATION FLUID
- B) HYDROTHERMAL AND MECHANICAL STABILITY OF ALL FLUIDS AND ADDITIVES
- C) RHEOLOGICAL PROPERTIES AS FUNCTION OF TEMPERATURE, TIME AND SHEAR RATE

2) PROPPANTS:

- A) MECHANICAL STABILITY: RESISTANCE TO CRACKING, CRUSHING AND DISINTEGRATING
- B) CHEMICAL STABILITY: RESISTANCE TO DISSOLUTION AND CORROSION (PARTICULARLY STRESS CORROSION CRACKING)
- C) SIZE AND SHAPE FOR CARRYING IN FRAC FLUID

TABLE 7

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB:
II. FLOW OF NON-NEWTONIAN FLUID THROUGH WELLBORE

- 1) TEMPERATURE PROFILE AS FUNCTION OF DEPTH
- 2) RESULTING VISCOSITY PROFILE
- 3) FRICTION LOSS ALONG WELLBORE
- 4) CHEMICAL AND PHYSICAL FLUID BEHAVIOR AS FUNCTION
OF SHEAR RATE AND TEMPERATURE
- 5) CHEMICAL INTERACTIONS BETWEEN FRAC FLUID AND
WELLBORE MATERIALS

TABLE 8

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB:
III. FRACTURE INITIATION AND PROPAGATION

- 1) PRESSURE CALCULATIONS FOR FRACTURE INITIATION AND PROPAGATION
- 2) FRACTURE WIDTH, HEIGHT AND LENGTH CALCULATIONS
- 3) CALCULATIONS OF TEMPERATURE PROFILES ALONG THE FRACTURE LENGTH
- 4) RESULTING VISCOSITY PROFILE BASED ON TEMPERATURE AND RHEOLOGICAL PROPERTIES AT CORRESPONDING SHEAR RATES
- 5) FLUID LOSS THROUGH FRACTURE FACES TO FORMATION
- 6) FILTER CAKE FORMATION DUE TO FLUID LOSS ADDITIVES
- 7) FLUID LOSS CALCULATIONS FOR DYNAMIC CONDITIONS
- 8) INTERACTIONS OF FRAC FLUID WITH FORMATION
 - A) PHYSICAL REACTIONS: ERROSION, PARTICLE RELEASE, ADSORPTION/DESORPTION, VISCOSITY CHANGE
 - B) KINETICS OF CHEMICAL REACTIONS BETWEEN FRAC FLUIDS AND FORMATION MATERIALS: PRECIPITATION, DEGRADATION, DISSOLUTION
- 9) KINETICS OF HYDROTHERMAL AND MECHANICAL DEGRADATION OF FRAC FLUID ADDITIVES

TABLE 9

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB:
IV. PROPPANT PLACEMENT

- 1) PROPPANT CARRYING CAPACITY OF FRAC FLUID
- 2) DEGREE/SHAPE OF PACKING AND RESULTANT FRACTURE CONDUCTIVITY
- 3) INTERACTIONS BETWEEN PROPPANTS AND FRAC FLUIDS OR FORMATION FLUID AT HIGH TEMPERATURES:
 - A) STRESS CORROSION CRACKING, DISSOLUTION, ERROSION, PROPPANT
 - B) SOFTENING
- 4) ROCK SOFTENING AND FRACTURE CLOSURE

TABLE 10

DESIGN CRITERIA FOR HYDRAULIC FRAC JOB:
V. FRAC FLUID REMOVAL

- 1) SHUT-IN TIMES FOR POLYMER DEGRADATION OR BREAKING
- 2) DIFFERENTIAL PRESSURES TO START BACKFLOW AND PROCEED WITH FRACTURE AND WELLBORE CLEAN-UP
- 3) FLOW RATES TO AVOID OR MINIMIZE SAND BUILD-UP IN WELLBORE
- 4) DAMAGING EFFECTS FROM RESIDUALS CAUSED BY INTERACTIONS OF FRAC FLUID AND/OR FRAC FLUID ADDITIVES WITH FORMATION MATERIALS

TABLE 11

IMPORTANT VARIABLES FOR DESIGN OF ACID JOBS
(AS FUNCTIONS OF TEMPERATURE, PRESSURE AND COMPOSITIONS)

- 1) "ROCK REMOVING POWER"
- 2) REACTION (OR DISSOLUTION) KINETICS
- 3) REACTIVITY OF FRESH ACID ON STEEL
- 4) REACTIVITY OF SPENT ACID ON STEEL
- 5) FORMATION OF SECONDARY DEPOSITS