508
1-4-83

(2)
I-722 7

Dr. 1099

CONTRACTOR REPORT

SAND82-7037
Unlimited Release

Clay-Based Geothermal Drilling Fluids

N. Guven, L. L. Carney, L. J. Lee, R. P. Bernhard
Department of Geosciences
Texas Tech University
Lubbock, TX 79409

Prepared by Sandia National Laboratories Albuquerque, New Mexico 87185
and Livermore, California 94550 for the United States Department of Energy
under Contract DE-AC04-76DP00789

Printed November 1982

DO NOT MICROFILM
COVER

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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

DISCLAIMER

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

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

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

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A04
Microfiche copy: A01

DO NOT MICROFILM
COVER

SAND--82-7037

DE83 005198

**FINAL REPORT
for
SANDIA CONTRACT # 13-5104
SAND 82-7037**

CLAY-BASED GEOTHERMAL DRILLING FLUIDS

DISCLAIMER

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

By

**N. Guven, L. L. Carney, L. J. Lee,
and R. P. Bernhard**

**Department of Geosciences
Texas Tech University
Lubbock, Texas 79409**

Submitted to

**SANDIA NATIONAL LABORATORIES
Division 4741
Albuquerque, New Mexico 87185**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

I

fy

1944-1945

1946-1947

1948-1949

1950-1951

1952

1953-1954

1955-1956

1957-1958

1959-1960

1961-1962

1963-1964

1965-1966

1967-1968

1969-1970

II

TABLE OF CONTENTS

Introduction	1
Methods for the Characterization of the Solid Particles in the Drilling Fluids	9
I. Attapulgite-Based Fluids	14
1. The Pure Attapulgite Fluid	23
2. Attapulgite/Chloride Fluids	31
3. Attapulgite/Hydroxide Fluids	52
II. Sepiolite-Based Fluids	76
1. The Pure Sepiolite Fluid	76
2. Sepiolite/Chloride Fluids	103
3. Sepiolite/Hydroxide Fluids	121
III. New Fluid Formulations	138
1. Conventional Drilling Fluids	138
2. Addition of Polymers to Attapulgite and Sepiolite Fluids	143
3. Sepiolite/English Mica/SPA Fluids	148
4. Sepiolite/Bentonite/SPA Fluids	151
IV. Effects of the Sepiolite-Based Fluids on the Formation	161
V. Summary and Conclusions	166
References	177
Acknowledgements	177

ABSTRACT

The rheological properties of fluids based on fibrous clays such as sepiolite and attapulgite have been systematically examined under conditions similar to those of geothermal wells, i.e. at elevated temperatures and pressures in environments with concentrated brines. Attapulgite- and sepiolite-based fluids have been autoclaved at temperatures in the range from 70 to 800°F with the addition of chlorides and hydroxides of Na, K, Ca, and Mg. The rheological properties (apparent and plastic viscosity, fluid loss, gel strength, yield point, and cake thickness) of the autoclaved fluids have been studied and correlated with the chemical and physical changes that occur in the clay minerals during the autoclaving process. Both attapulgite and sepiolite particles start out with fibrous morphology and electrostatically neutral structures, and above 300°F, both begin to convert into a smectite with a flaky morphology and with an electrostatically charged structure. The conversion rate increases with the higher temperatures and at 600°F attapulgite becomes fully converted to a smectite, whereas, at that temperature about 20% of the sepiolite still survives the reaction. Smectites formed below 600°F consist of thin films which are often epitaxially grown on the attapulgite or on the sepiolite fibers. These smectites (below 600°F) increase the viscosity of the fluid in the 400-500°F range, and the promoting effect of the cations on the conversion seems to be $Mg > Ca > Na > K$ for both attapulgite/chloride and attapulgite/hydroxide fluids. Similarly the order of the promoting effect of the cations is $Na > K > Ca > Mg$ for the sepiolite/chloride and $Na > Ca > Mg > K$ for the sepiolite/hydroxide fluids. The attapulgite and sepiolite fluids, when autoclaved at or above 600°F,

become extremely thin. The smectites formed at these temperatures have a platy morphology and occur in mosaic aggregates of platelets. In addition other mineral phases such as talc, tremolite, and illite (tri-octahedral-magnesian) also develop. Neither these new mineral phases nor platy smectites add much viscosity to the fluids. The attapulgitite and sepiolite fluids do not show any sign of the gellation that conventional bentonite-based fluids experience at temperatures above 400°F. However, both fluids demonstrate rather poor fluid loss control, especially the attapulgitite-based fluids.

New fluids have been formulated by adding to the sepiolite fluid first polymers and then other clays for reducing fluid loss. The sepiolite/Na-polyacrylate (low and high molecular weight) fluid shows rather satisfactory rheology up to 500°F. The sepiolite/English Mica Clay/Na-polyacrylate fluid displays extremely stable rheology and low fluid loss when subjected to high temperatures. Two other fluids were based on the addition of Wyoming bentonite to the sepiolite fluids. The fluid "GDF-1" based on the formula: sepiolite/Wyoming bentonite/low and high molecular weight Na-polyacrylates was found to function as a good drilling fluid even after it was autoclaved at 800°F. The fluid "GDF-2" is made by adding KOH and English Mica to the fluid "GDF-1", and this new fluid is recommended as the best geothermal drilling fluid in this study.

The possibility that the formation damage may be caused by the invasion of fibrous sepiolite particles into the formation has been examined in a sandstone core exposed to a sepiolite-based mud, and no sepiolite was found to invade the core; therefore no special formation damage is expected from the sepiolite-based muds.

INTRODUCTION

The instability of common drilling fluids in the high temperature and chemically complex environment of geothermal wells is a frequent and costly geothermal drilling problem. It is essential to have fluids that can perform adequately at elevated temperatures and pressures, and in the chemically complex (due to brines) environments. The conventional drilling fluids currently used for hydrocarbon production will not perform at temperatures above 400°F. Drilling fluids based on fibrous clays such as sepiolite have been found by Carney and Meyer (1976), Guven and Carney (1979), and Carney and Guven (1980) to be promising fluids for geothermal drilling. A systematic study of the rheological properties (viscosity, fluid loss, gel strength, yield point, and cake thickness) of the fluids based on fibrous clays (sepiolite and attapulgite) has been carried out in the temperature range from 70°F to 800°F. The rheological behavior of these fluids has been correlated with the chemical and physical changes in the clay minerals caused by the high temperature. Based upon the results obtained from the fluids using pure sepiolite or attapulgite, geothermal drilling fluids have been formulated by adding Wyoming bentonite and various polymers to the sepiolite fluids. The present studies have been carried out in the following systems:

I. ATTAPULGITE-BASED FLUIDS:

1. The pure attapulgite fluid
2. Attapulgite/chloride fluids
3. Attapulgite/hydroxide fluids

II. SEPIOLITE-BASED FLUIDS

1. The pure sepiolite fluid
2. Sepiolite/chloride fluids
3. Sepiolite/hydroxide fluids

III. NEW FLUID FORMULATIONS

1. Conventional base fluids:

- A. Bentonite fluid (Wyoming bentonite and Texas bentonite)
- B. Bentonite/Quebracho/NaOH fluid
- C. Bentonite/Unical/NaOH fluid
- D. Bentonite/Spersene/XP-20/NaOH fluid

2. Attapulgit (or sepiolite)/polymer (SPA) fluids:

- E. Sepiolite/High Mol. SPA/Low Mol. SPA fluid
- F. Attapulgit/High Mol. SPA/Low Mol. SPA fluid

3. Sepiolite/English Mica fluids:

- G. Sepiolite/English Mica/High and Low Mol. SPA's/fluid
- H. Sepiolite/English Mica fluid
- I. Sepiolite/English Mica/High Mol. SPA fluid
- J. Sepiolite/English Mica/Low Mol. SPA fluid

4. Sepiolite/Bentonite/SPA fluids:

- K. HTM-1 fluid
- L. Geothermal drilling fluid "GDF-1"
- M. Geothermal drilling fluid "GDF-2"

METHODS OF INVESTIGATIONS

Clay based fluids have been prepared at 4% concentrations below 500°F and at 5% concentrations above this temperature. These fluids have been autoclaved in the temperature range of 300-800°F under the appropriate confining pressures up to 20,000 psi. After autoclaving, the rheological properties of the fluids have been tested by means of FANN 50C high-pressure/high-temperature viscometer, FANN 35A viscometer, Baroid high-pressure/high-temperature filter press, Baroid standard (API) filter press, and Baroid 600-20 pH meter. Subsequently the fluids were prepared by the addition of chlorides or hydroxides of Na, K, Ca, and Mg at 1% concentrations. These fluids were also autoclaved and tested in order to evaluate the effects of the salts and hydroxides on the fluid properties. The specifics of these experiments are briefly described in the following.

High Temperature and High Pressure Autoclave

The autoclave was designed and manufactured by Autoclave Engineers, Erie, Penn. The cell itself has a sample capacity of 500 ml and is capable of reaching 1,000°F and 20,000 psi. The autoclave uses Autoclave Engineers self-sealing closure metal seals, which seal against high pressure by the use of unsupported area principle. This principle enables internal pressures to force the cover against the seal ring, which presses the seal ring against the body. Slight variation of the angles between contact surfaces of the body and the seal ring results in a line contact between the two surfaces. The cell was used for static heating at

high temperatures (300-800 °F) under confining pressures up to 20,000 psi. The pressure is initially produced by a Haskel air driven liquid pump #DHW 300. The temperature is maintained by an Autoclave Engineers temperature controller which consists of Barber-Colman, Model 520 analog and digital set point controllers. Temperature and pressure are monitored and recorded automatically by a Barber-Colman single pen strip chart recorder, in degrees Fahrenheit and pounds per square inch. The sample was heated at a rate of 250°F/hour to the desired temperature and the temperature was maintained for 6 hours, when this was accomplished the autoclave was cooled in air for 14 hours. The sample was then transferred for further testing.

FANN 50C Viscometer

The FANN viscometer model 50C is a concentric-cylinder, rotational type viscometer. The viscometer is equipped with a standard rotor cup with a sample capacity of 50 ml and rotor cup speed of 0-600 RPM. The viscosity is calibrated by shearing a thin film of the liquid between concentric cylinders. The outer cylinder can be rotated at a constant rate and the shear stress measured in terms of the deflection of the inner cylinder (or bob), which is suspended by a torsion spring. The sample can be heated up to 500 °F by an oil bath which is also used for cooling the sample. Pressures in the sample cup reach 1,000 psi and are produced by a nitrogen gas cylinder which is controlled by a pressure regulator. The temperature and viscosity of the mud are automatically recorded by a Houston Instruments' two-pen, bichannel strip recorder. The

viscosity/temperature variations are given in the form of a rheogram for each fluid.

FANN 35A Viscometer

Gel strength, yield point and plastic viscosity are measured at room temperature and atmospheric pressure with a FANN 35A viscometer, a concentric-cylinder, rotational type viscometer, which operates on the same principle as the FANN 50C. The FANN 35A is operated by a two-speed, 110 volt synchronous motor. The instrument is direct reading viscometer that enables the plastic viscosity and yield point to be calculated very simply from two dial readings, one at 600 RPM and the other at 300 RPM. Savins and Roper (1954), have shown the plastic viscosity to be the dial reading at 600 RPM minus the dial reading at 300 RPM. The yield point may be calculated by subtracting the plastic viscosity from the 300 RPM reading. The equations below give plastic viscosity in centipoise and yield point in pounds per 100 square feet:

The apparent viscosity (shear stress divided by shear rate) may also be calculated when the following information is known:

$$1 \text{ dial unit} = 5.11 \text{ dynes/cm}^2 \text{ (shear stress)}$$

$$1 \text{ RPM} = 1.7033 \text{ reciprocal seconds (shear rate)}$$

with 300 centipoise per unit per RPM

so:

$$\text{apparent viscosity} = \frac{300 \times \text{Units read at RPM}}{\text{RPM}}$$

The standard method of measuring apparent viscosity is with rotation speed of 600 RPM so the equation is simplified to:

$$\text{Apparent viscosity} = \frac{\text{Units read at 600 RPM}}{2}$$

Plastic viscosity is the resistance of flow caused by mechanical friction between the particles in a drilling fluid and by shearing of the liquid phase of the mud. So in general, plastic viscosity depends on the concentration of the solids put into the mud. The yield point is dependent on the electro-chemical charges in the mud under flowing conditions. Particles may be charged so that they attract each other giving way to a high yield point, or particles may repel one another making the yield point lesser. In either case a yield point may be regulated by the use of chemical additives. If the parameters are maintained for the yield point and the plastic viscosity, proper treatments can be derived, and the apparent viscosity may be easily regulated.

Gel strength is the measure of thixotropic properties of a drilling fluid under non-flow conditions, while the yield point measures these properties under flow conditions. However, both the yield point and gel strength deal with the attractive forces between solid particles in the mud.

Generally, gel strengths are of two types, a weak-fragile gel strength or a strong-progressive gel strength. A weak gel strength seems to be associated with a thin mud and initially may have a high gel strength that is very easily broken and will increase only slightly with increase of stagnation time. A strong gel strength is associated with

thicker muds and is hard to break on initial rotation. The longer the stagnation time the greater the gel strength becomes.

Both yield point and gel strength result from flocculation forces and are related to thixotropic properties, so as the yield point decreases, the gel strength generally decreases. Gel strengths are determined by the FANN 35A viscometer at 3 RPM. Mud is allowed to stagnate for 10 seconds, then the outer cup is rotated at 3 RPM - by observing the dial on the viscometer the maximum deflection (before the gel breaks) is recorded. The same procedure is repeated after allowing the mud to stand for 10 minutes, the gel strengths are reported in pounds per 100 square feet.

Baroid High-Pressure/High-Temperature Filter Press

The filter press is designed for testing fluids at elevated temperatures and pressures. Mud is placed into a 250 ml filter cell and is heated to 300°F. Pressure is increased to 600 psi by pressurized nitrogen gas. A back pressure receiver is maintained at 100 psi as filtrate is collected. The filtrate test is run for 30 minutes or until blow-out. In the latter case the time is recorded when the blow-out occurred. A blow-out is completely loosing the fluid and the air starts blowing through the filter cake. The volume of filtrate and the filter cake thickness are measured.

Baroid Standard Filter Press

This unit consists of a fluid cup supported by a frame, a filtering medium, a pressurized nitrogen gas cylinder and regulator. A graduated

cylinder is used to catch and measure the discharged filtrate.

The filter test requires 100 psi pressure for 30 minutes, or until blow-out occurs, upon which the filtrate is measured and recorded. The filter paper with the mud cake deposited on it is removed from the pressure cell and the mud cake thickness is recorded in thirty seconds of an inch. The filtration properties of drilling muds are a measure of the ability of the solid phase of a fluid to form a thin, low-permeability cake of filtered solids. The less permeability the cake has, the thinner the cake will form.

METHODS FOR THE CHARACTERIZATION OF THE SOLID PARTICLES IN THE DRILLING FLUIDS

The solids in the fluids have been examined before and after autoclaving and/or after testing with the high-temperature/high-pressure FANN 50C viscometer. The characterization of the solid particles has been done with x-ray diffraction and analytical microscopy as described in the following.

X-Ray Diffraction

Oriented clay films on glass slides were prepared from the fluids before and after autoclaving or other testing at high temperature. The excess salts and hydroxides were washed off by centrifugation and dialysis of the fluids before the x-ray diffraction or electron microscopic analysis. The oriented slides were x-rayed after having been air-dried at room temperature and at a relative humidity of 40-50%. The same slides were then saturated with ethylene glycol and x-rayed again. The quantitative x-ray diffraction analysis of the high-temperature reaction products was performed by comparing the intensity of the $17\text{\AA}$ glycolated smectite reflection with the intensity of the $12\text{\AA}$ sepiolite (or $10.6\text{\AA}$ attapulgite) reflection. Reference mixtures of the sepiolite (or attapulgite) and a smectite (from Cheto, Arizona) were prepared with ratios separated by 10% intervals. The Cheto smectite was chosen because of its morphological similarity with the smectite formed in the fluids during the autoclaving. The x-ray diffraction patterns on these synthetic mixtures as well as on the reaction products were obtained by Phillips

Norelco and Diano x-ray diffractometers using Cu-K α radiation.

Analytical Electron Microscopy

Interactions between high-energy electrons and a specimen generate numerous photons and electrons, most of which are characteristic of a given material. Much information can be obtained from these particles about morphology, chemistry and atomic structure of sub-micron size particles in drilling fluids. These micro-features of the clays often determine the rheological behaviors of a drilling fluid. The following signals, generated by the interaction of electrons with solid particles, have been used in this work:

- transmitted electrons
- secondary electrons
- characteristic x-rays

Transmitted electrons form high-resolution (2-4 $\text{\AA}$) images of thin particles like clay crystallites. These images are referred to as "TEM" images. If the incident electrons are scanned and the transmitted electrons are collected for image formation, this mode of transmitted electron imaging is referred to as "STEM" mode. In this mode electrons have higher penetrating power which can reveal the internal structure of solids. The STEM image has a resolution of about 15 $\text{\AA}$. Secondary electrons form the image of the surface topography of a solid with a resolution of 30-100 $\text{\AA}$. These SEM images are formed by the electrons originating from within a few 100 $\text{\AA}$ of the top surface. Characteristic x-rays are produced by inelastic collision of primary electrons with the inner shell electrons of the atoms. These x-ray spectra are used for microanalysis of

elements in the particles. The excitation volume (R_x) of x-rays and the penetration depth (R_e) of primary electrons determine the resolution for the detection of the characteristic x-rays. The product of the density (ρ) of a solid with the x-ray excitation volume (R_x) is known as the x-ray mass range. The penetration depths (R_e) of primary electrons are listed in Table 1.1 for some clay minerals of relevance to this work. Similarly the x-ray mass ranges for the K lines of the relevant elements (Si, Mg, Al, Na, K, Ca, and Fe) are given in Table 1.2. Considering these data in Table 1.2, it becomes obvious that the x-ray excitation volumes are on the order of one micron or more at 10 keV. Therefore a large discrepancy may exist between the SEM images and the corresponding x-ray spectra due to the large differences in penetration depths. In order to obtain a closer relationship between the electron image and the x-ray spectra, particles need to be extremely thin. Since silicon is a major element in all these minerals, all the x-ray spectra are normalized with reference to Si-K line. Furthermore x-ray spectra are obtained in two modes:

- a) the "area" mode in which a selected area is scanned with the electron probe and the x-rays generated from this area are measured,
- b) the "spot" mode in which the electron probe has been held stationary on a given spot and x-rays generated from this spot are measured.

Often x-ray intensities do not agree closely in "area" and "spot" modes. Furthermore the reproduction of intensities is better in "area" mode than in "spot" mode. A JEM-100 CX electron microscope has been used

Table 1.1

Electron ranges in microns (depth of penetration) R_e for various clay minerals at operating voltages of 10, 20, and 100 keV.

mineral	10 keV	20 keV	100 keV
seopilite	1.6	5.1	75.5
attapulgitite	1.4	4.8	70.6
saponite	1.3	4.3	62.9
Na-montmorillonite	1.4	4.3	63.4

Table 1.2

X-ray mass ranges ($\rho \times R_x$), critical excitation energies (E_c), and fluorescence yield of the major elements in clay minerals at operating voltages 10, 20, and 100 keV.

Characteristic x-ray line	critical excitation potential keV	X-ray fluorescence	mass ranges ($\rho \times R_x$) at operating voltages		
	E_c	yield	10 keV	20 keV	100 keV
Na-K	1.041	.013	2.99	9.75	146.55
Mg-K	1.251	.019	2.97	9.72	146.52
Al-K	1.486	.026	2.94	9.69	146.49
Si-K	1.736	.036	2.71	9.65	146.46
K-K	3.312	.118	2.58	9.34	146.14
Ca-K	3.690	.142	2.49	9.24	146.04
Fe-K	6.398	.324	1.61	8.37	145.17

for this work. Electron-microscope grids which were coated with Formvar films were prepared from the fluids. These grids were subsequently coated with gold and carbon. In a few instances Holey carbon films were also used which allowed examination of the particles without any coating on them.

I. ATTAPULGITE-BASED FLUIDS

Starting Material

The attapulgite was obtained from International Minerals and Chemicals. It is the commercially available sample from the deposits in Georgia and Florida and carries the trade name "Floridan attapulgite 150". The chemical composition and the particle size distribution of the attapulgite sample are given in Tables 1.3a and 1.3b. The x-ray diffraction analysis of the original sample indicates the presence of considerable amounts of impurities. There are 15-20% smectite, 5% illite, and 5% calcite in the clay fractions (<2 microns) of the sample. In addition, quartz occurs as a major impurity in the coarser fractions of the sample.

Electron microscopic examination of the original sample shows that attapulgite occurs as fibers or as aggregates of these fibers. Individual fibers are shown in Figure 1.1. These fibers have a length less than one micron and a width ranging from 300 to 500 Å. An electron micro-diffraction pattern of fiber gives the following a and b unit cell dimensions: $\underline{a} = 5.16 \pm 0.01$ Å and $\underline{b} = 17.97 \pm 0.01$ Å. A typical aggregate of the attapulgite fiber is given in Figures 1.3 and 1.4. As shown in Figure 1.2, these aggregates contain small rhombs of calcite and small platelets of illite. Thick attapulgite aggregates look rather fluffy and possess an irregular morphology as shown by the SEM image in Figure 1.4. The latter gives a three-dimensional surface topography of the attapulgite aggregate. The x-ray spectra are obtained randomly from a number of attapulgite fibers both in STEM/area and SEM/area mode. Tables 1.4a and 1.4b, Figures 1.5 and 1.6 display such x-ray spectra. The x-ray spectral data

Table 1.3a

Chemical analysis of the bulk attapulgite sample
(on the basis of the ignited sample).

	Wt%
SiO ₂	68.0
MgO	10.5
Al ₂ O ₃	12.0
Fe ₂ O ₃	5.0
CaO	1.7
K ₂ O	1.0
Na ₂ O	0.7
P ₂ O ₅	n.d.
TiO ₂	0.7
Li ₂ O	n.d.

Table 1.3b

Particle size distribution of the attapulgite powder

size range	weight%
> 149 micron	2.2%
148 - 125 micron	4.6%
124 - 105 micron	6.5%
104 - 88 micron	12.2%
87 - 74 micron	8.1%
73 - 63 micron	4.9%
< 62 micron	61.5%

Figure 1.1 - Attapulgite fibers in the starting material.

Figure 1.2 - An aggregate of attapulgite fibers with the impurities of calcite, feldspars, and apatite entrapped in the aggregate.

Figure 1.3 - Another attapulgite aggregate in the original sample.

Figure 1.4 - SEM image of a thick and fluffy attapulgite aggregate.

Table 1.4a

X-ray spectra obtained from randomly selected attapulgite fibers which were excited at 100 keV in "STEM/area" mode.

Particle designation	Integrated intensities (Counts/100 secs)						Intensity ratios/Si					
	Al	Mg	Si	Ca	Fe	Na	Al	Mg	Si	Ca	Fe	Na
TA1	939	1132	11009	887	424	244	.09	.10	1.00	.08	.04	.02
TA2	1769	2112	16726	1184	708	215	.11	.13	1.00	.07	.04	.01
TA3	6499	7724	62065	4782	2516	145	.10	.12	1.00	.08	.04	.00
TA4	2580	2473	19389	2778	1121	-	.13	.13	1.00	.14	.06	-
TA5	2030	1982	18790	1287	789	-	.11	.11	1.00	.07	.04	-
TA6	456	709	5373	441	237	82	.08	.13	1.00	.08	.04	.02
TA7	501	673	5132	398	228	25	.10	.13	1.00	.08	.04	.00
TA8	707	813	7436	592	487	32	.10	.11	1.00	.08	.06	-
TA9	674	745	6232	481	321	-	.11	.12	1.00	.08	.05	-
TA10	1613	1964	15699	1169	815	82	.10	.13	1.00	.07	.05	.01
Mean							.10	.12	1.00	.08	.05	-
Standard deviation							.01	.01	-	.01	.01	-

Intensity
counts/100 secs

2K

18

Figure 1.5
X-ray spectra obtained in "STEM/area" mode from the
attapulgite fiber in Figure 1.1.

0.00

Energy in keV

10.00

Table 1.4b

X-ray spectra obtained from randomly selected attapulgite fibers which were excited at 20 keV in "SEM/area" mode.

Particle designation	Integrated intensities (Counts/100 secs)						Intensity ratios/Si					
	Al	Mg	Si	Ca	Fe	Na	Al	Mg	Si	Ca	Fe	Na
SA1	407	429	3623	275	104	182	.11	.12	1.00	.08	.03	.05
SA2	2870	3267	20597	2123	664	176	.14	.16	1.00	.10	.03	.01
SA3	955	1105	6726	248	212	6	.14	.16	1.00	.04	.03	-
SA4	874	1054	8817	265	195	85	.10	.12	1.00	.03	.02	.01
SA5	700	1106	6936	308	168	35	.10	.16	1.00	.04	.02	.01
SA6	755	952	7429	323	171	62	.10	.13	1.00	.06	.02	.01
SA7	1116	1244	7769	377	153	77	.14	.16	1.00	.05	.02	.01
SA8	1140	1302	8530	364	196	48	.13	.15	1.00	.04	.02	.01
SA9	640	748	7773	359	102	40	.08	.10	1.00	.05	.01	.01
SA10	1148	1222	9398	357	140	275	.12	.13	1.00	.04	.01	.03
Mean							.12	.14	1.00	.04	.02	.01
Standard deviation							.02	.02	-	.01	.01	.01

Intensity
counts/100 secs

in Table 1.4a and 1.4b show rather small variations of x-ray intensities for the major elements (Mg, Al, Si, Ca, Fe, Na) making up the attapulgite fibers.

In summary, attapulgite occurs in three morphologically different forms:

- a) individual fibers and parallel sets of them (Figure 1.1).
- b) clusters of fibers often with radial arrangement of fibers (Figures 1.2 and 1.3).
- c) thick and fluffy aggregates (Figure 1.4).

Impurities in the Original Floridan Attapulgite

Smectite occurs as fluffy ill-defined aggregates with a cloudy appearance as shown in Figure 1.7a. The x-ray spectra obtained from the data in smectite indicate a significantly large amount of aluminum and very small amounts of magnesium. Furthermore selected area electron diffraction (SAD) data on these aggregates give the following cell dimensions: $\underline{a} = 5.28\text{\AA}$ and $\underline{b} = 9.16\text{\AA}$.

Illite occurs in flakes with irregular outlines (Figure 1.7b). The x-ray spectra obtained from this flake indicate aluminum as the major octahedral cation. The SAD data give the following cell dimensions:

$$\underline{a} = 5.27 \pm 0.01\text{\AA} \text{ and } \underline{b} = 9.10 \pm 0.02\text{\AA}.$$

Other impurities consist of minute crystallites of calcite and apatite which are often entrapped in the attapulgite aggregates.

Attapulgite based drilling fluids have been autoclaved in the temperature range 300–800 °F with and without the addition of chlorides and hydroxides of Na, K, Ca, and Mg. The most characteristic features of the

Figure 1.7a - Smectite aggregate in the original attapulgite sample.

Figure 1.7b - A typical illite flake in the original attapulgite sample.

Figure 1.9 - Thin smectite films developing around the attapulgite fibers autoclaved at 500°F.

Figure 1.10 - An aggregate of attapulgite fibers autoclaved at 500°F displaying the growth of smectite films at the edges of the aggregate.

x-ray diffraction patterns of the solids of these fluids are graphically shown in Figure 1.8 for the attapulgite/H₂O, attapulgite/KCl, and attapulgite/NaCl fluids within the temperature range 70 to 700 °F. The results of the 800 °F runs are very similar to those at 700 °F except for the attapulgite/KCl fluid. The dark-shaded reflections in Figure 1.8 represent the first basal (001) reflection of smectite upon glycol saturation. The 10.5-10.6 Å reflection belongs to the attapulgite. The basal spacings of the smectites before glycolation are also marked with dotted lines in Figure 1.8. The results are described in the following for various attapulgite fluids along with the rheological characteristics of these fluids.

1. THE PURE ATTAPULGITE FLUID

The x-ray diffraction data in Table 1.5 show that about 30% of attapulgite converts to a smectite at 400 °F and the conversion is rather insignificant at 300 °F. The conversion rate increases to about 60% at 500 °F and it is nearly complete at 600 °F. Similarly at temperatures 700 °F and 800 °F no attapulgite remains in the fluid and it is completely converted to smectite. The basal spacings of the smectites formed in the attapulgite fluid range from 14.5 to 15.8 Å in the air-dried state but they all fully expand upon glycolation to 17 Å. Morphological features and the chemical nature of the smectites formed as the reaction products in the attapulgite/H₂O system are examined with the analytical electron microscope. Smectites formed at 400 °F and 500 °F consist of thin films which are often grown around the attapulgite fibers as shown in Figures

Figure 1.8 - X-ray diffraction patterns of the attapulgite fluids which were autoclaved with and without the addition of NaCl and KCl.

Table 1.5

High-temperature reaction products of the attapulgite/H₂O fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	Smectite (+)	thin films
400	Smectite (30%)	thin films
500	Smectite (60%)	thin films + platelets
600	Smectite (80%) + silica spheres	platelets + thin films
700	Smectite (100%) + silica spheres	platelets
800	Smectite (100%) + silica spheres	platelets

Table 1.6

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/H₂O fluid.

Particle designation	Elements				
	Mg	Al	Si	Fe	Ca
Smectite/600°F	.16 ± .05	.16 ± .04	1.00	.08 ± .02	.03 ± .02
Smectite/700°F	.21 ± .14	.24 ± .03	1.00	.14 ± .01	-
Smectite/800°F	.19 ± .04	.22 ± .05	1.00	.11 ± .03	.05 ± .02

1.9 and 1.10. The latter figure displays an attapulgite aggregate of crisscrossing fibers. A large number of minute crystallites in the form of rhombs, rectangles, and plates are also entrapped in the aggregate. The x-ray spectra from these crystallites show large quantities of calcium and phosphor, indicating that they are phosphate impurities in the original sample. Around the edges of the attapulgite aggregate, smectite films are developing. The attapulgite fibers entirely disappear from the fluid after autoclaving at 600°F. The smectites make up about 80% of the sample and they appear in two forms:

- a) thin aggregates of folded films (Figures 1.11 and 1.12),
- b) thick and larger aggregates (Figure 1.13).

The smectite aggregate of thin folded films in Figure 1.14 displays the traces of a fibrous texture related to the remnants of the original attapulgite fibers. Otherwise all the smectites formed at 600°F are the precipitates from the solution following the dissolution of the attapulgite. The x-ray spectral data obtained from several of these smectite films are averaged with respect to their intensities and listed in Table 1.6. The intensities of the x-ray data show that Mg/Si and Al/Si intensity ratios are significantly higher in these smectites compared to those in the original attapulgite. The natural smectites do not contain high Mg and Al at the same time in their structures. Thus the smectite formed during the autoclaving of the attapulgite fluid does not have a natural analog. The smectite aggregates often contain a large number of spherical, rectangular, or rhombic particles as shown in Figure 1.12. The x-ray spectra obtained from spherical particles (Figure 1.12) record mainly silicon indicating that these are silica spheres. The x-ray

Figure 1.11 - Aggregates of thin smectite films formed at 600°F in the attapulgite fluid.

Figure 1.12 - Another aggregate of thin folded smectite films formed at 600°F in the attapulgite fluid.

Figure 1.13 - Typical thick smectite aggregates formed during the autoclaving of the attapulgite fluid at 600°F.

Figure 1.14 - A thin smectite film with the original attapulgite fibers embedded.

spectra from rectangular particles give Ca, Si, and P lines suggesting a mixture of silica with calcium phosphate. Calcium is obtained as the only spectra from the rhombohedral particles, indicating that they are calcite rhombs.

Smectites formed at 700 °F display different morphological features. These smectites occur as small platelets as shown in Figures 1.15 and 1.16. The chemical composition of these smectite platelets, as indicated by the x-ray spectra in Table 1.6, includes high amounts of magnesium and aluminum. Therefore, the chemistry of these smectites is again unusual because of their high Mg and Al contents.

A considerable number of silica spherules are also observed to form at 700 °F. Figure 1.17 shows the typical features of these spheres. Smectites formed from attapulgite at 800 °F temperature consist mainly of platy forms and their mosaics as shown in Figure 1.18. Again a large number of silica spheres are also precipitated at this temperature. It is noteworthy to point out that the original montmorillonite in the starting material remains in the system without any changes except the flakes seem to be extremely rolled and curled.

The Rheological Properties of the Pure Attapulgite Fluids

The rheogram of the attapulgite fluid with no pretreatment shows a viscosity "hump" at about 450 °F (Figure 1.19). Similarly, the fluids autoclaved at 400 and 500 °F reveal a viscosity "hump" at 400 °F but the maximum reaches only 3.2 and 2.5 centipoise respectively. The fluids autoclaved at temperatures 600, 700, and 800 °F show very low viscosities which are decreasing with the increasing temperatures. The other

Figure 1.15 - Platy smectites which form at 700°F in the attapulgite fluid.

Figure 1.16 - A platy smectite aggregate developed at 700°F in the attapulgite fluid.

Figure 1.17 - Typical silica spheres which precipitate at 700°F in the attapulgite fluid.

Figure 1.18 - Platy and disc-shaped smectites formed at 800°F in the attapulgite fluid.

Figure 1.19 - THE FANN 50C rheograms of the pure attapulgite which were autoclaved at the temperatures marked on the curves.

rheological properties (plastic viscosity, yield point, gel strength, filtrate loss, cake thickness) are listed for the pure attapulgite fluids in Table 1.7. The API fluid loss is measured to be 182 ml for the attapulgite at 70°F. The fluid loss increases drastically with higher temperatures. The fluid autoclaved at 600°F has a filtrate loss of 306 ml, and therefore offers no fluid loss control at all.

The viscosity "humps" displayed in these rheograms in Figure 1.19 are related to the conversion of attapulgite to smectite at temperatures above 400°F. The morphological features of the smectites formed at temperatures 600°F and above are rather different than those formed at lower temperatures. Thus, the platy smectites seem to give lower viscosities to the fluids than do the thin films of smectite. The other measurements in Table 1.7 indicate that the pH of the fluids decreases with higher temperatures. This suggests that the attapulgite-to-smectite reaction increases the hydrogen concentration in the fluid.

2. ATTAPULGITE/CHLORIDE FLUIDS

Chlorides of Na, K, Ca, and Mg have been added at 1% concentrations to the attapulgite fluids. Their effects on the hydrothermal reactions of attapulgite and on the rheology of attapulgite fluids are discussed in the following.

Attapulgite/NaCl Fluid

The addition of NaCl slightly increases the conversion rate of attapulgite to smectite at the temperatures 400°F and 500°F (Table 1.8a).

Table 1.7

Rheological measurements with FANN 35A Viscometer on the attapulgite fluid autoclaved at high temperatures.

Parameter	70	400	500	600 °F
Apparent Viscosity (centipoise)	8.5	6	14.5	5.5
Plastic Viscosity (centipoise)	3	5	7	5
Yield Point (lbs/100 sq ft)	11	2	15	1
Gel Strength (lbs/100 sq ft)	7/8	3/9	4/5	1/2
pH	9.5	7.8	7.0	7.5
API Filtrate (ml/7.5 min.)	182	320	182	304
HP-HT Filtrate (ml/30 min.)*	120/5	115/4	100/7	105/5
Cake Thickness (inches)	7/32	17/32	22/32	20/32
HP-HT Cake Thickness (inches)	5/32	7/32	17/32	9/32

*A blow-out occurs after the minutes marked following the slash.
A blow-out is completely loosing the liquid and the air starts blowing through the filter cake.

Table 1.8a

High-temperature reaction products of the attapulgite/NaCl fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	mophology of smectite
300	Smectite (10%)	thin films
400	Smectite (40%)	thin films
500	Smectite (65%)	thin films + platelets
600	Smectite (90%)	platelets + thin films
700	Smectite (100%) + silica spheres	platelets
800	Smectite (100%) + silica spheres	platelets

Table 1.8b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/NaCl fluid.

Particle designation	Elements			
	Mg	Al	Si	Fe
Smectite/700 °F	.17 ± .01	.19 ± .03	1.00	.12 ± .02
Smectite/800 °F	.18 ± .10	.23 ± .02	1.00	.11 ± .01

At higher temperatures the reactions of attapulgite are similar to those in the pure water; attapulgite is completely replaced by a smectite at 600 °F in the fluid. The basal spacings of these smectites vary between 15.1 to 15.8Å and they are very different from those expected from Na-smectites which have a basal spacing of about 12Å. This discrepancy suggests that some of the Mg ions occur as interlayer cations of the smectites. All these smectites, however, expand to 17Å upon glycolation as expected (Figure 1.8).

The new smectites formed at the temperatures 400 °F and 500 °F consist of thin films similar to those in the pure attapulgite fluid. The smectite particles develop both thin films and platy forms at 600 °F. The observed basal spacings of the smectites formed in the attapulgite/NaCl fluid vary from 15.1 to 15.8Å.

At 700 °F smectites seem to grow as thin and small platelets with regular outlines as shown in Figure 1.20a. These minute platelets often form a mosaic with edge-to-edge associations of the particles (Figure 1.20b). Amorphous silica spheres precipitate in appreciable quantities at 700 and 800 °F. Such silica spherules are shown in figure 1.21. The platy morphology of the smectites becomes rather distinct with regular pseudo-hexagonal outlines at 800 °F as indicated in Figure 1.22. The x-ray spectra in Table 1.8b are obtained from these newly formed smectites at 700 and 800 °F and they again show the increased Al and Mg content of these smectites as compared with the original attapulgite chemistry.

Rheological Features of the Attapulgite/NaCl Fluids

The rheological data on the attapulgite/NaCl fluids are given in

Figure 1.20a - Platelets of smectites formed at 700°F in the attapulgite/NaCl fluid.

Figure 1.20b - A typical aggregate consisting of a mosaic of smectite platelets formed at 700°F in the attapulgite/NaCl fluid.

Figure 1.21 - Amorphous silica spheres which form in appreciable quantities (10-15%) at 700°F in the attapulgite/NaCl fluid.

Figure 1.22 - Typical smectite platelets and a silica sphere which form at 800°F in the attapulgite/NaCl fluid.

Figure 1.23 and Table 1.9. The FANN 50C rheograms in Figure 1.23 show that the addition of NaCl greatly decreases the viscosity of the attapulgite fluid except after autoclaving at 400 and 500°F. At these temperatures the viscosities of the fluids are considerably higher than at the other temperatures (Figure 1.23). This is probably due to the fact that a large portion of the attapulgite has been converted to a smectite with thin film morphology. The development of the platy smectite morphology at and above 600°F seems, however, to be detrimental for the viscosity of the fluid. The filtrate loss of these fluids shows a significant decrease up to 500°F and it increases again after autoclaving at and above 600°F (Table 1.9). The HP/HT filtrate loss is extremely high up to 800°F. Thus the conversion of the attapulgite to smectite does not decrease the fluid loss and therefore the attapulgite/NaCl fluid does not have much practical value. The pH of the fluid becomes neutral to slightly acidic with the temperature increase up to 600°F and it significantly increases again at 700°F.

Attapulgite/KCl Fluid

In the presence of 1% KCl the attapulgite-to-smectite conversion seems to be slowed down at 400°F but at 500°F about 70% of the attapulgite is converted to smectite (Table 1.10a). These smectites are characterized by a thin film morphology. At temperatures of 600°F and above attapulgite is completely dissolved in the fluid and a new set of clay minerals is formed, which consists of smectite, illite, and illite/smectite mixed-layers. At 600°F and 700°F the amount of illite is rather small (about 5%) as indicated by the x-ray pattern in Figure 1.8. At

Figure 1.23 - The FANN 50C rheograms of the attapulgite/NaCl fluids which were autoclaved at the temperatures marked on the curves.

Table 1.9

Rheological measurements with Fann 35A on the attapulgite/NaCl fluids autoclaved at high temperatures.

Parameter	70	400	500	600	700	800 °F
Apparent Viscosity (centipoise)	2.25	19.5	17	10.5	2.5	3.5
Plastic Viscosity (centipoise)	2	13	10	7	2	3
Yield Point (lbs/100 sq ft)	1.5	10	14	7	1	1
Gel Strength (lbs/100 sq ft)	2/2	12/25	10/14	4/8	1/2	1/2
pH	9.0	7.0	6.4	6.0	7.8	n.d.
API Filtrate (ml/7.5 min.)*	280	200	180	210	192	270
HP-HT Filtrate (ml/30 min.)*	125/7	100/5	102/5	105/6	121/2	66/4
Cake Thickness (inches)	6/32	24/32	19/32	22/32	2/32	2/32
HP-HT Cake Thickness (inches)	5/32	16/32	15/32	12/32	4/32	8/32

*A blow-out occurs after the minutes marked following the slash.

Table 1.10a

High-temperature reaction products of the attapulgite/KCl fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	smectite (20%)	thin films
500	Smectite (70%)	thin films
600	Smectite (80%) + I/S mixed-layer	thin films + platelets
700	Smectite (80%) + illite, I/S	platelets
800	Smectite (10%) + illite, I/S	platelets

Table 1.10b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/KCl fluid.

Particle designation	Elements				
	Mg	Al	Si	Fe	K
Smectite/700°F	.18 ± .03	.12 ± .02	1.00	.08 ± 0.3	0.07 ± .04
Illite/800°F	.16 ± .03	.25 ± .01	1.00	.14 ± .03	.23 ± .01

700°F, a 10.9Å reflection is observed on the x-ray pattern of the air-dried sample. This reflection shifts back to 10.0Å upon glycolation. This behavior indicates the presence of illite/smectite mixed-layering in the fluid. After autoclaving the fluid at 800°F, a strong reflection appears at 10.5Å which splits upon glycolation to a strong 10.0Å reflection and a weak 17Å reflection. This suggests that illite becomes the predominant clay mineral in the fluid and the amount of smectite is drastically reduced. The illite is the trioctahedral magnesium and iron variety as indicated by its x-ray spectra in Table 1.10b. The smectites formed at 600°F and 700°F display a distinct platy morphology as shown in Figure 1.24a. The x-ray spectra from these smectite platelets (Table 1.10b) indicate high magnesium and aluminum in their compositions. Unusually large amorphous silica spherules (Figure 1.24b) also form in the fluid at 700°F and 800°F. Illites with pseudo-hexagonal platelets form at 800°F in this fluid. Such illite particles are shown in Figures 1.25 and 1.26.

Rheological Properties of the Attapulgit/KCl Fluid

The rheological measurements on the attapulgit/KCl fluids are given in Figure 1.27 and Table 1.11. The addition of KCl to the attapulgit fluid at 70°F drastically decreases its viscosity. The fluids seem to regain some of their viscosity upon autoclaving at 400 to 600°F. This may be related to the formation of thin smectite films at the expense of some of the attapulgit. The fluids subjected to temperatures of 700 and 800°F become extremely thin as shown by their FANN 50C rheograms. The formation of illite (mica) at these temperatures seems to be detrimental for the rheology of the fluid.

Figure 1.24a - A mosaic aggregate of smectite platelets formed at 700°F in the attapulgite/KCl fluid.

Figure 1.24b - Large silica spherules formed at 700°F in the attapulgite/KCl fluid.

Figure 1.25 - A mosaic of illite platelets formed at 800°F in the attapulgite/KCl fluid.

Figure 1.26 - Illite platelets with pseudo-hexagonal outlines formed at 800°F in the attapulgite/KCl fluid.

Figure 1.27 - The FANN 50C rheograms of the attapulgite/KCl fluids which were autoclaved at the temperatures marked on the curves.

Table 1.11

Rheological measurements with FANN 35A viscometer on the attapulgite/KCl fluids autoclaved at high temperatures.

Parameter	70	400	500	600	700	800 °F
Apparent Viscosity (centipoise)	4.5	7.5	8.5	12.5	4.5	3.5
Plastic Viscosity (centipoise)	2	5	6	7	3	3
Yield Point (lbs/100 sq ft)	0.5	5	5	11	3	1
Gel Strength (lbs/100 sq ft)	1/1	4/15	3/9	9/14	2/4	1/3
pH	9.2	6.5	6.0	5.9	6.5	n.d.
API Filtrate (ml/7.5 min.)*	346/5.5	274	216	150	224	262/4.5
HP-HT Filtrate (ml/30 min.)*	125/2.5	108/5	70/7	110/12	114/3.5	108/3
Cake Thickness (inches)	3/32	21/32	21/32	19/32	10/32	4/32
HP-HT Cake Thickness (inches)	6/32	10/32	9/32	8/32	5/32	6/32

*A blow-out occurs after the minutes marked following the slash.

The API filtrate loss of the attapulgite/KCl fluid is extremely high at 70°F (Table 1.11) but it steadily decreases with temperature up to 600°F. Nonetheless fluid loss of 150 ml/7.5 min at 600°F is still very high. The fluid losses of the fluids autoclaved at 700 and 800°F again become very high. The pH values of the fluids show a steady decrease with the higher temperatures (Table 1.11). Thus both the rheology and the fluid loss control of the attapulgite/KCl fluids are rather poor for any practical use of this fluid.

Attapulgite/CaCl₂ Fluid

Upon the addition of 1% CaCl₂, the attapulgite to smectite conversion proceeds at much higher rates as indicated by the x-ray diffraction data in Table 1.12a. The amount of attapulgite which transforms to smectite is about 60% at 400°F and 90% at 500°F. The newly formed smectites consist of thin films and they have a basal spacing of 15.3Å as expected from a Ca-smectite. Attapulgite completely dissolved in the fluids which were autoclaved at 600 to 800°F. The morphological features of these smectites are rather different and they consist of platelets often with pseudo-hexagonal morphology (Figures 1.28 through 1.31). The x-ray spectra in Table 1.12b are obtained from these smectites. They indicate a high magnesium variety of smectite. There are also significant amounts of amorphous silica spheres in the fluids which are autoclaved at temperatures 600 to 800°F. Such silica spheres are seen in Figure 1.28.

Figure 1.28 - Platy smectites forming an aggregate with a mosaic texture and large silica spherules in the attapulgite/ CaCl_2 fluid autoclaved at 700°F.

Figure 1.29 - A closer look at the smectite platelets and laths formed at 700°F in the attapulgite/ CaCl_2 fluid.

Figure 1.30 - Platelets of single smectite layers formed at 800°F in the attapulgite/ CaCl_2 fluid.

Figure 1.31 - Smectite platelets with pseudo-hexagonal morphology, which are formed at 800°F in the attapulgite/ CaCl_2 fluid.

Table 1.12a

High-temperature reaction products of the attapulgite/ CaCl_2 fluid and the morphological features of the smectites formed in them.

Temperatures ($^{\circ}\text{F}$)	reaction products	morphology of smectite
400	Smectite (60%)	thin films
500	Smectite (90%)	thin films
600	Smectite (100%) +	thin films + platelets
700	Smectite (100%) + silica spheres	platelets
800	Smectite (100%) + silica spheres	platelets

Table 1.12b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/ CaCl_2 fluid.

Particle designation	Al	Elements Mg	Si	Fe
Smectite/700 $^{\circ}\text{F}$	.18 $\pm$.01	.25 $\pm$.05	1.00	.12 $\pm$.02
Smectite/800 $^{\circ}\text{F}$	.18 $\pm$.01	.27 $\pm$.03	1.00	.12 $\pm$.02

Rheological Properties of the Attapulgate/ CaCl_2 Fluid

The rheological measurements of the attapulgate/ CaCl_2 fluids are summarized in Table 1.13 and in Figure 1.32. The FANN 50C rheograms in the later figure show that the fluid at 70°F has rather low viscosities after the addition of CaCl_2 . The fluid regains its viscosity upon autoclaving at 400°F and 500°F; which may be related to the formation of smectites with thin film morphology. When the temperature is increased further to 600°F, the fluid becomes practically useless. The filtration losses of these fluids are extremely high, ranging from 300 ml at 70°F to 280 ml at 600°F (Table 1.13). The pH values drop from slightly alkaline at 70°F to neutral at 700°F. Thus the attapulgate/ CaCl_2 fluid has rather unacceptable rheological properties for a drilling fluid.

Attapulgate/ MgCl_2 Fluid

The x-ray data on the high-temperature products of the attapulgate/ MgCl_2 fluids in Table 1.14a show that the addition of 1% MgCl_2 greatly enhances the conversion of the attapulgate to smectite, in fact, 45% of attapulgate converts to smectite at 400°F and 95% of the attapulgate transforms to smectite at 500°F. After autoclaving at temperatures 500 through 800°F all the attapulgate dissolves in the fluid. The basal spacings of these smectites in the air-dried state steadily decrease from 15.8Å at 400°F to 15.0Å at 800°F; they all expand to 17Å upon glycolation. Smectite and appreciable amounts (10-20%) of amorphous silica precipitate at the expense of attapulgate at and above 600°F. Smectites formed below 500°F consist of thin films growing around the attapulgate fibers as typically shown in Figure 1.33. Smectites formed at and above

Table 1.13

Rheological measurements with FANN 35A viscometer on the attapulgite/CaCl₂ fluids autoclaved at high temperatures.

Parameter	70	400	500	600	700	800°F
Apparent Viscosity (centipoise)	2	11	10	9	3	3.5
Plastic Viscosity (centipoise)	2	6	8	6	2	3
Yield Point (lbs/100 sq ft)	0	10	4	6	2	1
Gel Strength (lbs/100 sq ft)	1/1	11/17	4/7	7/7	1/2	1/2
pH	8.8	7.0	6.8	6.8	7.0	n.d.
API Filtrate (ml/7.5 min.)*	300	310	292	280	300/2.5	280/2
HP-HT Filtrate (ml/30 min.)*	120/2.5	105/4	95/4	120/6	110/2	140/2
Cake Thickness (inches)	7/32	17/32	31/32	21/32	6/32	4/32
HP-HT Cake Thickness (inches)	4/32	8/32	16/32	8/32	6/32	5/32

*A blow-out occurs after the minutes marked following the slash.

Figure 1.32 - The FANN 50C rheograms of the attapulgite/CaCl₂ fluids which were autoclaved at the temperatures marked on the curves.

Table 1.14a

High-temperature reaction products of the attapulgite/MgCl₂ fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (45%)	thin films
500	Smectite (95%)	thin films
600	Smectite (100%) + silica spheres	thin films + platelets
700	Smectite (100%) + silica spheres	platelets
800	Smectite (100%) + silica spheres	platelets

Table 1.14b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/MgCl₂ fluid.

Particle designation	Al	Elements Mg	Si	Fe
Smectite/700°F	.21 ± .06	.16 ± .04	1.00	.03 ± .02
Smectite/800°F	.22 ± .03	.32 ± .03	1.00	.13 ± .03

Figure 1.33 - Typical growth of thin smectite films around the attapulgite fibers at 500°F in the attapulgite/MgCl₂ fluid.

Figure 1.34 - A mosaic aggregate of smectite platelets formed at 700°F in the attapulgite/MgCl₂ fluid.

Figure 1.35 - Perfectly developed smectite ribbons formed at 800°F in the attapulgite/MgCl₂ fluid.

Figure 1.36 - Well-developed platelets and ribbons of smectite formed at 800°F in the attapulgite/MgCl₂ fluid.

600°F consist of platelets. The morphological features of these platelets significantly improve with the temperature. At 600 and 700°F the platelets aggregate with a mosaic texture (Figure 1.34) but at 800°F smectites develop rather regular forms such as ribbons and pseudo-hexagonal platelets (Figure 1.35 and 1.36). The x-ray spectra obtained from these smectites (Table 1.14b) indicate high amounts of Al and Mg in the chemistry of these smectites.

Rheological Properties of the Attapulgite/MgCl₂ Fluid

The rheological data in Table 1.15 and Figure 1.37 indicate that the initial fluid at 70°F shows rather low viscosities due to the addition of 1% MgCl₂. The fluid regains its viscosity when autoclaved to 400, 500, and 600°F as shown in Figure 1.37. The fluid, however, becomes extremely thin when subjected to the temperatures 700 and 800°F. This may well be related to the morphological changes in smectites from thin films at 400-600°F to a platy structure at higher temperatures. The API filtrate loss and HP-HT filtrate values (Table 1.15) of these fluids again show no fluid loss control, therefore, these fluids are useless for drilling purposes. The pH values also show slight decreases with the higher temperatures.

3. ATTAPULGITE/HYDROXIDE FLUIDS

Hydroxides of Na, K, Ca, and Mg have been added at 1% concentrations to the attapulgite fluids. Their effects on the high temperature reactions of attapulgite and on the rheology of these fluids are

Table 1.15

Rheological measurements with FANN 35A viscometer on the attapulgite/MgCl₂ fluids autoclaved at high temperatures.

Parameter	70	400	500	600	700	800°F
Apparent Viscosity (centipoise)	2.5	12.5	34	12.5	3.5	7
Plastic Viscosity (centipoise)	2	7	11	9	3	5
Yield Point (lbs/100 sq ft)	1	11	46	7	1	4
Gel Strength (lbs/100 sq ft)	2/2	10/29	19/31	7/14	1/10	5/7
pH	8.3	6.6	6.2	7.6	n.d.	n.d.
API Filtrate (ml/7.5 min.)*	260	248	120	130	310/2	270
HP-HT Filtrate (ml/30 min.)*	125/5.5	115/9	82/9	98/15	104/1	108/35
Cake Thickness (inches)	5/32	25/32	17/32	15/32	4/32	5/32
HP-HT Cake Thickness (inches)	4/32	10/32	25/32	15/32	7/32	17/32

*A blow-out occurs after the minutes given following the slash.

Figure 1.37 - The FANN 50C rheograms of the attapulgite/MgCl₂ fluids which were autoclaved at the temperatures marked on the curves.

systematically examined in the temperature range from 70°F to 600°F.

Attapulgitite/NaOH Fluid

Smectite develops at the expense of attapulgitite in appreciable quantities (30%) at 400°F and 500°F (Table 1.16a). The basal spacings of these smectites vary between 15.1-15.5Å and they fully swell to 17Å upon glycolation. The smectite forms as thin films around the attapulgitite fibers (Figure 1.38). The dense disc-like particles in the latter figure give strong Al and Si spectra as indicated in Table 1.16b. These are possibly hydrated aluminum silicates and they also occur in well developed crystals in the form of laths. These laths are often aggregated in stacks as shown in Figures 1.39 and 1.40. More smectite forms during the autoclaving of the fluid at 600°F. These smectites make up about 45% of the sample and they consist of thin films and minute platelets (Figure 1.41). The x-ray spectra of these smectites (Table 1.16b) indicate that they are magnesium-rich trioctahedral varieties. The hydrated aluminum silicates are also found to form in appreciable quantities at 600°F.

Rheological Properties of the Attapulgitite/NaOH Fluid

The rheological measurements of the attapulgitite/NaOH fluid are given in Table 1.17 and in Figure 1.42. The latter represents the FANN 50C rheograms. The addition of NaOH to the attapulgitite fluid at room temperature tremendously increases the viscosity of the pure attapulgitite fluid (Table 1.17). After the attapulgitite/NaOH fluid has been aged at 400 and 500°F this viscosity "hump" disappears and the viscosity steadily decreases from about 20-24 centipoise at 70°F to about 5-7 centipoise at

Table 1.16a

High-temperature reaction products of the attapulgite/NaOH fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (30%)	thin films
500	Smectite (30%)	thin films
600	Smectite (45%) Al-Si-H*	thin films + platelets

*hydrated aluminum silicates

Table 1.16b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/NaOH fluid.

Particle designation	Mg	Elements Al	Si	Fe
Al-Si-H/500°F	-	.18 ± .01	1.00	.05 ± .01
Smectite/600°F	.17 ± .01	.05 ± .01	1.00	.02 ± .01

Figure 1.38 - Thin smectite films developing around the attapulgite fibers at 500°F in the attapulgite/NaOH fluid.

Figure 1.39 - Parallel stacks of laths of aluminum silicates formed at 500°F in the attapulgite/NaOH fluid.

Figure 1.40 - A parallel set of laths of aluminum silicates.

Figure 1.41 - Thin films and platelets of smectites formed at 600°F in the attapulgite/NaOH fluid.

Table 1.17

Rheological measurements with FANN 35A on the attapulgite/NaOH fluids auto-claved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	65	36	31.5	67.5
Plastic Viscosity (centipoise)	14	26	11	31
Yield Point (lbs/100 sq ft)	102	20	41	73
Gel Strength (lbs/100 sq ft)	42/74	12/16	14/15	32/33
pH	12.0	11.0	10.6	9.4
API Filtrate (ml/7.5 min.)	116	80	90	110
HP-HT Filtrate (ml/30 min.)*	78/4	81	55/5	91/15
Cake Thickness (inches)	9/32	12/32	7/32	8/32
HP-HT Cake Thickness (inches)	16/32	26/32	20/32	13/32

*A blow-out occurs after the minutes given following the slash.

Figure 1.42 - The FANN 50C rheograms of the attapulgite/NaOH fluids which were autoclaved at the temperatures marked on the curves.

500°F (Figure 1.42). The fluid which was autoclaved at 600°F shows a steep viscosity decrease with the temperature.

Thus the attapulgite/NaOH fluid becomes thin with the increasing temperature. The API and HP-HT fluid losses are still high for a good drilling fluid.

Attapulgite/KOH Fluid

Small quantities of smectite develop in the system at 400°F (Table 1.18a), which is revealed by a broad reflection ranging from 10 to 14Å. The smectites form as thin films around the attapulgite fibers. More illite and illite/smectite mixed-layers develop at 500°F with a basal spacing of 10.6-10.8Å. The illite and illite/smectite mixed-layers show a platy morphology with a mosaic texture as shown in Figure 1.43. A potassium aluminum silicate is also observed as a new phase formed during the runs at 500 and 600°F. This reaction product occurs in disc-shaped crystals at 500°F and in equant forms at 600°F as shown in Figure 1.44. The attapulgite to illite conversion is almost completed at 600°F with a small amount of illite/smectite mixed-layering. The illite develop large platelets with regular forms as shown in Figures 1.45 and 1.46. The x-ray spectra of illite show a high Mg and low Al content indicating the presence of a trioctahedral illite similar to a hydrated phlogopite.

Rheological Properties of the Attapulgite/KOH Fluid

The rheological data in Table 1.19 and the FANN 50C rheogram in Figure 1.47 show the effects of the KOH on the attapulgite fluid. When KOH is added to the fluid at 70°F, the FANN 50C viscosity increases and

Table 1.18a

High-temperature reaction products of the attapulgite/KOH fluid and the morphological features of the smectite formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (+)	thin films
500	I/S mixed-layer + K-Al-silicate	platy illite
600	I/S mixed-layer + K-Al-silicate	platy illite

Table 1.18b

Average intensities of x-ray spectra obtained STEM/area mode from the high-temperature reaction products of the attapulgite/KOH fluid.

Particle designation	Mg	Elements Al	Si	K	Fe
I/S/600°F	.15 ± .01	.07 ± .01	1.00	.13 ± .01	.03 ± .01
K-Al silicate/600°F	-	.16 ± .01	1.00	.37 ± .01	.04 ± .01
Illite/600°F	.21 ± .01	.10 ± .01	1.00	.18 ± .01	.04 ± .01

Figure 1.43 - Platelets of illites and illite/smectite mixed-layers formed at 500°F in the attapulgite/KOH fluid.

Figure 1.44 - A K-feldspar formed at 600°F in the attapulgite/KOH fluid.

Figure 1.45 - Typical platelets of K-feldspar and illite formed at 600°F in the attapulgite/KOH fluid.

Figure 1.46 - A larger illite particle formed at 600°F in the attapulgite/KOH fluid.

Table 1.19

Rheological measurements with FANN 35A viscometer on the attapulgite/
KOH fluids autoclaved at high temperatures.

Parameter	70	400	500	600 °F
Apparent Viscosity (centipoise)	21.5	5.5	11	25
Plastic Viscosity (centipoise)	3	4	9	2
Yield Point (lbs/100 sq ft)	37	3	4	1
Gel Strength (lbs/100 sq ft)	9/14	2/2	2/4	1/1
pH	12.6	11.2	9.6	10.0
API Filtrate (ml/7.5 min.)	134	115	100	144
HP-HT Filtrate (ml/30 min.)*	88/3	130/10	100/11	105/15
Cake Thickness (inches)	3/32	5/32	4/32	8/32
HP-HT Cake Thickness (inches)	14/32	13/32	18/32	3/32

*A blow-out occurs after the minutes given following the slash.

Figure 1.47 - The FANN 50C rheograms of the attapulgite/KOH fluids which were autoclaved at the temperatures marked on the curves.

the viscosity "hump" becomes much larger. The rheology of the fluid with KOH becomes very poor with the increasing temperatures. The API and HP-HT filtrate losses of these fluids are extremely high both at room temperature and at higher temperatures (Table 1.19). The pH of the fluids change from highly alkaline (12.6) at 70°F to alkaline (9.6-10.0) at 500°F and 600°F. Apparently the formation of illite in the fluid at higher temperatures becomes very detrimental to the rheology of the fluid.

Attapulgite/Ca(OH)₂ Fluid

Large amounts of smectite form in this fluid at conversion rates of 50% at 400°F, 60% at 500°F, and 70% at 600°F (Table 1.20a). The basal spacing of the smectite ranges from 14.3Å in air-dried state and expand to 17Å upon glycolation. An 11Å tobermorite (a cement mineral of hydrated calcium silicate composition) also forms in the fluid and makes up about 30-40% of the solids at 400°F. Figure 1.48 shows thin films of smectite and tabular tobermorite formed at 400°F. An orthorhombic unit cell with $a = 10.85 \pm 0.1 \text{Å}$ and $b = 7.29 \pm 0.05 \text{Å}$ is obtained from the SAD data for the tobermorite. At 500°F and 600°F the tobermorite laths become larger (Figure 1.49). The x-ray spectra (Table 1.20b) with high Ca and Si intensities confirm the identification of these phases as hydrated calcium silicates. Smectites formed at 600°F occur as aggregates of folded thin films (Figure 1.50) and as small platelets as shown in the center of Figure 1.51. Their x-ray spectra (Table 1.20b) indicate a pure magnesium smectite like stevensite.

Table 1.20a

High-temperature reaction products of the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (50%) + CSH*	thin films
500	Smectite (60%) + CSH*	thin films
600	Smectite (70%) + CSH	thin films + platelets

*: hydrated calcium silicate (tobermorite)

Table 1.20b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid.

Particle designation	Mg	Elements	
		Si	Ca
CSH/400°F	-	1.00	.70 ± .01
CSH/600°F	-	1.00	.80 ± .01
Smectite/600°F	.21 ± .01	1.00	-

Figure 1.48 - Thin smectite films and tabular tobermorites formed at 400°F in the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid.

Figure 1.49 - Laths of tobermorite and folded thin films of smectite formed at 500°F in the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid.

Figure 1.50 - Aggregates of smectite thin films formed at 600°F in the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid.

Figure 1.51 - Minute platelets of smectites (in the center) formed at 600°F in the attapulgite/ $\text{Ca}(\text{OH})_2$ fluid.

Rheological Features of the Attapulgite/Ca(OH)₂ Fluid

The attapulgite fluid mixed at 70°F with Ca(OH)₂ gives a viscosity of about 25 centipoise at 70°F, which steeply decreases to about 4 centipoise at 500°F. It does not show any viscosity "hump". The viscosity curves for the attapulgite/Ca(OH)₂ fluids show a temperature induced thinning (Figure 1.52). The API and HP-HT filtrate losses show significant reductions at higher temperatures (Table 1.21). The viscosities and fluid loss values seem to be affected by the formation of cement crystals.

Attapulgite/Mg(OH)₂ Fluid

Smectites develop in large amounts (70-85%) at 400°F and 500°F (Table 1.22a) with a basal spacing of 15.2-15.5Å which expands to 17Å upon glycolation. These smectites consist of thin films around the original attapulgite fibers as displayed in Figures 1.53 and 1.54. Smectites formed at 600°F display a platy morphology (Figure 1.55). Their x-ray spectra in Table 1.22b indicate a pure Mg-smectite. A hydrated calcium silicate (tobermorite) also develops in the fluid at 600°F; these tobermorites occur as sets of laths as shown in Figure 1.56.

Rheological Features of the Attapulgite/Mg(OH)₂ Fluid

The rheological data on the behavior of this fluid at various temperatures are given in Figure 1.57 and in Table 1.23. The viscosity "hump" is more enhanced in this fluid than in the pure attapulgite fluid (curve at 70°F in Figure 1.57). The viscosity "hump" still remains, although at reduced magnitudes, for the fluids autoclaved at 400°F and

Figure 1.52 - The FANN 50C rheograms of the attapulgite/CA(OH)₂ fluids which were autoclaved at the temperatures marked on the curves.

Table 1.21

Rheological measurements on the attapulgite/Ca(OH)₂ fluids autoclaved at high-temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	24.5	16	29.5	18
Plastic Viscosity (centipoise)	17	13	22	14
Yield Point (lbs/100 sq ft)	15	6	15	8
Gel Strength (lbs/100 sq ft)	5/8	3/3	5/6	2/2
pH	12.0	9.0	9.3	8.8
API Filtrate (ml/7.5 min.)	194	122	76	92
HP-HT Filtrate (ml/30 min.)*	42/1	70/8	78/18	80
Cake Thickness (inches)	12/32	16/32	13/32	14/32
HP-HT Cake Thickness (inches)	32/32	32/32	24/32	17/32

*A blow-out occurs after the minutes given following the slash.

Table 1.22a

High-temperature reaction products of the attapulgite/Mg(OH)₂ fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (70%)	thin films
500	Smectite (85%)	thin films
600	Smectite (90%) CSH*	thin films + platelets

*: hydrated calcium silicate (tobermorite)

Table 1.22b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the attapulgite/Mg(OH)₂ fluid.

Particle designation	Mg	Elements Al	Si	Fe
Smectite/600°F	.18 ± .01	.03 ± .01	1.00	.02 ± .01

Figure 1.53 - Typical smectites formed at 400°F in the attapulgite/Mg(OH)₂ fluid.

Figure 1.54 - Attapulgite fibers converting to smectites in the attapulgite/Mg(OH)₂ fluid at 500°F.

Figure 1.55 - Typical platy smectites formed at 600°F in the attapulgite/Mg(OH)₂ fluid.

Figure 1.56 - Tobermorite laths developing in the attapulgite/Mg(OH)₂ fluid at 600°F.

Figure 1.57 - The FANN 50C rheograms of the attapulgite/Mg(OH)₂ fluids which were autoclaved at the temperatures marked on the curves.

Table 1.23

Rheological measurements with FANN 35A viscometer on the attapulgite $\text{Mg}(\text{OH})_2$ fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	21.5	9.5	10	16
Plastic Viscosity (centipoise)	4	8	9	14
Yield Point (lbs/100 sq ft)	35	3	2	4
Gel Strength (lbs/100 sq ft)	20/20	4/8	1/3	2/5
pH	10.2	7.7	7.4	8.8
API Filtrate (ml/7.5 min.)	80	80	122	40
HP-HT Filtrate (ml/30 min.)*	12/0.5	91/7	105/5	46
Cake Thickness (inches)	4/32	17/32	24/32	4/32
HP-HT Cake Thickness (inches)	32/32	17/32	19/32	18/32

*A blow-out occurs after the minutes given following the slash.

500°F, and it becomes more prominent at 600°F. At 600°F the fluid maintains an apparent viscosity of 16 centipoise, and relatively low API and HP-HT filtrate losses compared with the pure attapulgite fluid. Thus the magnesium smectites formed in this fluid seem to give remarkably good rheology to the fluid. The attapulgite/Mg(OH)₂ seems to be the best fluid among the attapulgite-based fluids.

II. SEPIOLITE-BASED FLUIDS

Starting Material

The sepiolite used in this investigation is from the Aschenbrenner deposit, Nye County, Nevada, and it is produced by Industrial Mineral Ventures Company, Golden, Colorado. The impurities detected by x-ray diffraction are about 5% of dolomite, calcite, and illite. The chemical composition and the particle size distribution of a typical sample are given in Tables 2.1 and 2.2. Electron microscopic examination shows that the Aschenbrenner sepiolite particles occur either as individual fibers up to 2.0 microns in length and 200-300^oÅ in width or as birdnest-type aggregates of fibers. Typical sepiolite particles are displayed in Figures 2.1 and 2.2. The x-ray spectra obtained randomly from ten sepiolite fibers are given in Table 2.3. Typical x-ray spectra from a sepiolite fiber are displayed in Figure 2.3.

Sepiolite-based drilling fluids have been autoclaved at temperatures from 300 to 800°F with and without the addition of chlorides and hydroxides of Na, K, Ca, and Mg at 1% concentrations. The changes in the mineral components and in the rheology of these fluids have been systematically examined and described in the following.

1. THE PURE SEPIOLITE FLUID

The x-ray diffraction data of the high-temperature reaction products of this fluid are summarized in Table 2.4a and in Figure 2.4. These data show that sepiolite converts to a smectite in considerable amounts at

Table 2.1

Chemical analysis of the bulk sample of sepiolite (on the basis of the ignited sample).

	Wt%
SiO ₂	67.1
MgO	26.5
Al ₂ O ₃	2.7
Fe ₂ O ₃	0.66
CaO	1.48
K ₂ O	0.55
Na ₂ O	0.32
P ₂ O ₅	n.d.
TiO ₂	n.d.
Li ₂ O	0.11

Table 2.2

Particle size distribution of the sepiolite powder.

Size range	weight %
>420 micron	4.7%
419-250 micron	12.8%
249-177 micron	16.0%
176-149 micron	5.6%
148-125 micron	6.7%
124-105 micron	6.5%
104- 88 micron	8.3%
87- 74 micron	4.5%
73- 63 micron	3.8%
<62 micron	31.03%

Figure 2.1a - Sepiolite fibers and illite impurities in the original sample (prepared on a formvar film with Au/C coating).

Figure 2.1b - Aggregates of sepiolite fibers in the original sample (prepared on a formvar film with Au/C coating).

Figure 2.2a - Sepiolite aggregates resting on a Holey membrane.

Figure 2.2b - A closer look at the sepiolite fibers (prepared on a Holey grid without any coating).

Table 2.3

X-ray spectra obtained from randomly selected sepiolite fibers which were excited at 100 keV in "STEM/area" mode.

Particle	Integrated intensities (Counts/100 secs)						Intensity ratios/Si					
	Al	Mg	Si	Ca	Fe	Na	Al	Mg	Si	Ca	Fe	Na
TA1	112	737	3499	147	92	151	.03	.21	1.00	.04	.03	.04
TA2	112	838	3936	10	19	54	.03	.21	1.00	-	-	.01
TA3	389	2973	14680	113	225	212	.03	.21	1.00	.01	.01	.01
TA4	246	1076	5595	3	88	134	.04	.19	1.00	-	.01	.02
TA5	164	802	3637	147	69	-	.04	.22	1.00	.04	.02	-
TA6	438	2481	10679	130	73	380	.04	.23	1.00	.01	.01	.04
TA7	218	1993	9698	101	92	123	.02	.21	1.00	.01	.01	.01
TA8	8	419	2386	57	43	96	.00	.18	1.00	.02	.02	.04
TA9	315	1514	7686	148	200	326	.04	.20	1.00	.02	.03	.04
TA10	78	1276	6555	41	109	28	.01	.19	1.00	.01	.01	.00
Average							.03	.20	1.00	.02	.02	.03
Standard deviation							.01	.01	.00	.02	.01	.01

Intensity
counts/100 secs

512

80

0.00

Energy in keV

10.00

Figure 2.3
X-ray spectra obtained in "STEM/area" mode from a
sepiolite fiber.

Table 2.4a

High-temperature reaction products of the sepiolite/H₂O fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	-	-
400	Smectite (20%)	thin films
500	Smectite (40%)	thin films
600	Smectite (80%)	thin films + platelets
700	Smectite (60%) + talc, tremolite	platelets + thin films
800	Smectite (40%) + talc, tremolite	platelets

Table 2.4b

Average intensity ratios of the x-ray spectra obtained from the original sepiolite and from the minerals formed at high temperatures in the pure sepiolite fluid.

Particle designation	Elements				
	Mg	Al	Si	Fe	Ca
sepiolite fibers (original)	.20 ± .01	.03 ± .01	1.00	.02 ± .01	.02 ± .02
smectite/600°F	.29 ± .05	.01 ± .01	1.00	.01 ± .01	-
tremolite/700°F	.16 ± .04	.02 ± .01	1.00	.03 ± .01	.19 ± .05
tremolite/800°F	.16 ± .04	.02 ± .01	1.00	.03 ± .02	.16 ± .04
talc/800°F	.33 ± .04	.04 ± .03	1.00	.03 ± .03	-

Figure 2.4 - X-ray diffraction patterns of the sepiolite fluids which were autoclaved with and without the chlorides of Na, Ca, and Mg.

400°F. No smectite was detected by x-ray diffraction when the sepiolite was autoclaved at 300°F under the confining pressure of 475 psi. The sepiolite fibers do not suffer any morphological changes during the autoclaving at 300°F/475 psi as shown in Figure 2.5. When the pressure was increased to 10,000 psi at this temperature, very small quantities (below 5% level) of smectite were found as the reaction product. The amount of this newly formed smectite increases with the temperature up to 80% at 600°F. The smectites formed at 400 and 500°F consist of thin films which are mostly epitaxially grown on the original sepiolite fibers as shown in Figure 2.6. The transition from sepiolite fibers to thin films of smectite can be seen in Figures 2.7a and 2.7b. Smectites formed at 600°F mostly consist of aggregates of folded thin films (Figure 2.8), which do not show any relationship to the original sepiolite fibers. There are still a few sepiolite aggregates with smectite films growing around them at 600°F (Figure 2.9). The x-ray spectra obtained from these newly formed smectites are given in Table 2.4b. Compared with the x-ray data on the original sepiolite fiber the magnesium content of the smectite is significantly higher than that of the original sepiolite; otherwise the chemistry of these two phases is very similar.

After the hydrothermal treatments at 700 and 800°F under a pressure of 16,000 psi, all the sepiolite dissolves and disappears from the system. New minerals such as smectite, tremolite, and talc are found to form in the fluid. Smectite makes up about 60% of the solids after the run at 700°F and about 40% after the run at 800°F. Tremolite content of the sample seems to increase at 800°F. All these minerals (smectite, tremolite, and talc) often occur together as aggregates (Figure 2.10).

Figure 2.5 - Sepiolite fibers after autoclaving of the fluid at 300°F.

Figure 2.6 - Thin smectite films forming around the sepiolite fibers at 500°F in the sepiolite fluid.

Figure 2.7a - Transition of sepiolite fibers to films of smectite at 500°F in the sepiolite fluid.

Figure 2.7b - A closer look at the sepiolite-to-smectite transition (magnified from the previous figure).

Figure 2.8 - Aggregate of folded smectite films formed at 600°F in sepiolite fluid.

Figure 2.9 - Conversion of a sepiolite aggregate to smectite films around the edges at 600°F in the fluid.

Figure 2.10 - Tremolite fibers and laths, and smectite aggregates formed at 800°F in the sepiolite fluid.

Figure 2.11 - Talc and smectite platelets formed at 800°F in the sepiolite fluid.

Tremolite laths occur as bundles or as individuals. These laths have a length of 2 to 6 microns. Sometimes these fibers join each other along their fiber edges. The selected area electron diffraction pattern of a tremolite fiber in Figure 2.12a is given in Figure 2.12b. The b and c unit-cell parameters obtained from this pattern are $\underline{c} = 5.27 \pm 0.03 \text{ \AA}$ and $\underline{b} = 18.12 \pm 0.03 \text{ \AA}$.

The chemistry of these tremolite fibers is indicated by the x-ray spectral data in Table 2.4b. Thus the chemistry, unit-cell parameters, and morphological features confirm the identification of this phase as tremolite. The latter is a fibrous amphibole (an asbestos mineral) with the formal chemical composition: $\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ where parts of magnesium can be substituted by divalent iron.

Talc occurs in well-developed platy forms as shown in Figures 2.11 and 2.13a. The selected area electron diffraction pattern of the talc in Figure 2.13a is given in Figure 2.13b. The following unit cell parameters are obtained from this pattern: $\underline{a} = 5.32 \pm 0.2 \text{ \AA}$ and $\underline{b} = 9.08 \pm 0.02 \text{ \AA}$. The x-ray spectra obtained from the talc platelets are given in Table 2.4b. These x-ray spectra are very similar to those obtained from a standard talc with the formal composition of: $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$.

Nature of the Smectite Formed in the Fluid and the Mechanism of the Sepiolite-to-Smectite Conversion

Smectite first develops in the fluid at 300°F in very small quantities (<5%) and in appreciable quantities at 400 and 500°F. The thin smectite films formed within this temperature range grow epitaxially on

Figure 2.12a - A tremolite fiber formed at 800°F in the sepiolite/water system.

Figure 2.12b - Selected area electron diffraction pattern of the tremolite fiber in Figure 2.12a.

Figure 2.13a - A talc platelet formed at 800°F in the sepiolite/water system.

Figure 2.13b - The selected area electron diffraction pattern of the talc platelet in Figure 2.13a.

the sepiolite fibers (Figures 2.6 and 2.7a). In most of the aggregates the identity of the sepiolite fibers seems to disappear in a gradual manner so that the sepiolite fibers coalesce laterally and develop a thin film of a smectite (Figures 2.7a and 2.9). Thick aggregates of folded smectite films which develop at 600°F (Figure 2.8), and platy smectites, which form at 700 and 800°F, do not show any relationship to the original sepiolite fibers. These smectites are therefore directly precipitated after the dissolution of sepiolite in the fluid at high temperatures. The other type of smectite formed by the coalescing sepiolite fibers can develop through a different mechanism which does not require a total dissolution of sepiolite. This mechanism which was suggested by Güven and Carney (1979) can be easily understood by considering the crystal structure of sepiolite. The crystal structure of sepiolite is shown schematically in Figure 2.14a as projected along the fiber direction. The crystallographic a-axis of sepiolite is set parallel to the fiber direction. The rectangular envelope-like blocks in Figure 2.14a represent the projections of talc-like ribbons in the sepiolite structure. The hatched and dark triangles indicate the directions in which the silica tetrahedra point in these ribbons. The sepiolite structure may thus be described as talc ribbons that are displaced with respect to each other by an n-glide, i.e. by a $(\frac{1}{2}^a + \frac{1}{2}^c)$ glide vector. These talc ribbons are attached to each other only by Si-O-Si bonds at their four corners, which make the sepiolite structure rather delicate. At higher temperature and pressure the ribbons may change to a more stable configuration by undergoing an n-glide, e.g., in a series of dislocations, and by establishing additional bonds between their octahedral networks. This

Figure 2.14a - Schematic representation of the sepiolite structure as projected along the fiber direction (a-axis), and its transformation mechanism to smectite (stevensite) by the n-glide mechanism.

Figure 2.14b - Projection of the sepiolite structure along the c-axis.

mechanism implies that sepiolite can rapidly transform to a smectite under the stress of high temperature. As indicated in Figure 2.14b, the new phase cannot be talc. The magnesium octahedra in the talc-like ribbons are located at $z = 1/4$ in one ribbon and at $z = 3/4$ at the next ribbon in the sepiolite structure. Magnesium positions along the edges of the ribbons at $z = 1/4$ are designated by M1 and M2, and those along the edges of the ribbon at $z = 3/4$ are similarly designated by M1' and M2'. Each of the M1 and M1' metals have two water ligands, whose positions are marked by X in the c-projection of the structure (Figure 2.14b). After the n-glides (or when the ribbons are reassembled), the H₂O ligands superimpose, and a reaction such as that formulated in Figure 2.15 should occur, thereby generating layer charge in the smectite structure. This variety of smectite is known as stevensite. Depending on the number of water molecules that undergo this reaction, the sepiolite-to-smectite conversion can be formulated as:

sepiolite

stevensite

where the zeolitic water of sepiolite is disregarded. If all of the crystalline water ligands become hydroxyls, the layer charge of smectite will reach a maximum value of -0.67 per formula unit. In addition, certain octahedral positions (Figure 2.14b) will be vacant. These octahedral defects make up 1/9 of the total octahedral positions. Additional

Figure 2.15 - The reaction mechanism between the magnesium octahedra along the edges of talc ribbons after the n-glide operations.

magnesium to fill these positions can be supplied only by a decomposition of some of the sepiolite in the system. Such a decomposition would also generate free silica. The x-ray spectra in Table 2.4b indicate the additional magnesium in the smectite structure. Free silica precipitates as spherules shown in Figure 2.8. Additional magnesium in stevensite (i.e., when Mg is greater than 2.67 in the formula) decreases its layer charge. As these vacant octahedral positions fill with magnesium, talc domains form within the stevensite structure, and may be randomly mixed with smectite domains within a layer. Also, the talc domains may be randomly stacked in successive layers in the form of mixed-layering. This situation continues until all of the vacant octahedral sites are filled and talc is formed.

The smectites shown in Figures 2.6 and 2.7a were probably formed by the proposed n-gliding mechanism. Here, the transition from fibrous morphology to a flaky one is well displayed. The formation of irregularly folded smectite flakes, however, such as those in Figure 2.8, is probably related to a direct precipitation of smectite after the dissolution of the sepiolite. In fact, when the temperature of runs was raised to 600°F, most of the smectite seemed to form by the dissolution-reprecipitation mechanism, independent of additives.

The conversion of fibrous sepiolite with a neutral structure to a flaky (film) or platy smectite with a charged structure is the key factor in understanding the rheological behavior of the sepiolite fluids at high temperature. In the following sections, the effects of hydroxides and chlorides will be systematically examined.

Rheological Properties of the Pure Sepiolite Fluid

The rheological measurements of the pure sepiolite mud are given in Table 2.5 and in Figure 2.16. The latter shows the FANN 50C viscosity in a graphical manner, which reveals a viscosity "hump" at about 300°F of viscometer temperature. The magnitude of this "hump" is much larger for the untreated fluid at 70°F and it decreases with the higher temperatures. In fact, the pure sepiolite muds autoclaved at 700 and 800°F do not show this "hump". This viscosity "hump" is most likely related to the sepiolite-to-smectite conversion described above.

The other rheological data obtained with the FANN 35A viscometer and API and HP-HT filter presses are given in Table 2.5. Values for apparent and plastic viscosity, yield point, and gel strength increase in the temperature range 70 to 500°F. This is most likely related to the transition of fibrous sepiolite into thin films of smectite at these temperatures. These thin smectite films show more resistance to flow (increasing the apparent viscosity) and more surface area (increasing the plastic viscosity). Furthermore the electrostatic charges of these smectite films in contrast to the neutral sepiolite fiber, contribute to the increase in the values of the yield point and gel strengths with the increasing temperature up to 500°F. The newly formed smectites seem also to reduce the fluid loss with this temperature interval. We see however a reduction in viscosity and an increase in the fluid loss when the fluids are autoclaved at and above 600°F. The fluids autoclaved at 700 and 800°F become extremely thin (Figure 2.16). The platy smectite morphology and the formation of the non-swelling minerals such as tremolite and talc seem to be detrimental to the viscosity and the fluid loss

Table 2.5

Rheological measurements of the pure sepiolite fluids autoclaved at high temperatures.

Parameter	70	400	500	600° F
Apparent Viscosity (centipoise)	10.5	21.5	48.5	26
Plastic Viscosity (centipoise)	3	13	26	18
Yield Point (lbs/100 sq ft)	15	17	45	16
Gel Strength (lbs/100 sq ft)	14/17	17/22	31/41	4/9
pH	8.7	7.1	7.0	7.5
API Filtrate (ml/7.5 min.)	68	60	57	56
HP-HT Filtrate (ml/30 min.)*	110/20	80/28	70	64
Cake Thickness (inches)	3/32	15/32	16/32	8/32
HP-HT Cake Thickness (inches)	7/32	34/32	32/32	33/32

*A blow-out occurs after the minutes given following the slash.

Figure 2.16 - The FANN 50C rheograms of the pure sepiolite fluids which were autoclaved at the temperatures marked on the curves.

control of the fluids. The FANN 50C rheograms also indicate that the untreated sepiolite fluid shows the greatest change in viscosity (the so-called "viscosity hump") between 200-400°F after the original temperature thinning of the fluid. The fluids autoclaved at 400 and 500°F show a little more conversion of the sepiolite-to-smectite with the resulting increase in viscosity. In the fluids subjected to 600-800°F temperatures the sepiolite-to-smectite conversion has been completed and their FANN 50C rheograms do not therefore display viscosity humps.

The decrease in the pH values of the fluids in Table 2.5 with the increasing temperature is in agreement with the reaction mechanism of the sepiolite-to-smectite conversion as discussed above.

Changes in Rheology and Morphology of Sepiolite Upon Circulating Through Magcobar's Flow Loop

The Magcobar loop (in Figure 2.17a as designed by Wyant, 1975) consists of series of capillaries that can be heated up to $400 \pm 25^\circ\text{F}$ while circulating a fluid through shear valves. The system is devised to pump about 1.5 pints to 2 gallons of fluid from an atmospheric pressure reservoir through a cycle of heating, intensive high temperature shearing, cooling, low temperature shearing, and final return to the reservoir. Typically, for a two-gallon system the entire mud volume passes through about 6-12 cycles each hour where the individual mud particle goes through each active heating, shearing and cooling cycle in about 30 seconds. Intensive shearing occurs at both high and low temperatures when the mud is forced through spring-loaded back-pressure valves. The usual mud tests can be made on samples taken at the reservoir under atmospheric conditions.

Figure 2.17a - Magcobar high temperature flow loop as designed by Wyant (1975).

Two gallons of sepiolite fluid were circulated through the flow loop for an average of 6 circulations per hour. Any one aliquot of fluid was subjected to the maximum temperature for about 30 seconds for each hour of circulation. Table 2.6 gives the rheological measurements on these aliquots (designated as samples No. 1-18) and on the original sepiolite fluid before treatment (sample No.1). Circulation times and temperatures are also listed in columns 2-3 of Table 2.6. The data in this table indicate that the rheology is first increased by the initial shearing at room temperature. Then the viscosity begins to decrease with circulation time, increasing temperature, and shearing. In fact the viscosity drops from 12 centipoise to 3.5 centipoise. At the same time the fluid loss increases from 54 ml to more than 96 ml. The FANN 50C rheograms of the sepiolite fluids pulled from the flow loop are given in Figure 2.17b.

X-ray diffraction analysis of these aliquots indicates that the sepiolite-to-smectite conversion starts to take place after 12 hours of circulation (sample No. 11) although in very small quantities. The presence of smectite is distinctly visible by its characteristic $17.5\text{\AA}$ reflection (upon glycolation) after 18-1/4 hours of circulation (sample No. 18).

The original sepiolite slurry after being sheared at room temperature consists of well dispersed sepiolite fibers as shown in Figure 2.18. As indicated in Table 2.6, this seems to increase slightly the viscosity and the fluid loss. The rheogram (Figure 2.17b) for the original sepiolite fluid shows a maximum at about 300°F. The sepiolite sample No. 2 which was sheared for two hours in the flow loop has a similar rheogram as the original sample. X-ray diffraction and electron

Table 2.6

Circulation times, temperatures, and rheology of the pure sepiolite fluids pulled from Magcobar's Flow Loop.

Sample No.	hours circulated	average temp- erature (°F) during circu- lation	Apparent Viscosity	Plastic Viscosity	Yield Point	API fluid loss
1	none	n.a.	10.5	3	15	54 ml
2	2	72	12	2	20	55
6	7.5	370	10	3	14	96
11	12	380	7.5	3	9	96
14	15.5	425	6.5	4	5	n.d.
15	16	425	6	4	5	n.d.
18	18.5	435	3.5	3	3	96+

Figure 2.17b - The FANN 50C rheograms of the sepiolite samples pulled from Magcobar's flow loop. Sample No.'s correspond to those in Table 2.6.

microscopic examination (Figure 2.18) do not show any conversion of sepiolite to smectite. However, sepiolite fibers coagulate during low shearing in FANN 50C into large spherical flocks (Figure 2.19).

Sample No. 6 was taken from the flow loop after 7-1/2 hours of circulation and subjected to temperature of 370°F. No conversion of sepiolite to smectite was observed during this circulation. Sepiolite particles occur in smaller aggregates (Figure 2.20) and the individual fibers seem to disappear. This fluid had somewhat lower rheology (Table 2.6) and with FANN 50C measurements gave a different rheogram (curve No. 6 in Figure 2.17b). We now get a viscosity maximum at about 400°F. After the sample was subjected to 500°F in FANN 50C viscometer the conversion of sepiolite to smectite takes place, as indicated by the x-ray diffraction data. The particles in the fluid again aggregate into large floccules during testing with FANN 50C viscometer. These floccules seem to consist of sepiolite fibers with the thin smectite films acting like a gelating agent between the fibers. Conversion of sepiolite to smectite occurs in small amounts in the flow loop circulations above 400°F and the smectite content slightly increases with time, i.e., from sample No. 14 to sample No. 18 in Table 2.6. The fine sepiolite fibers disappear and bundles of sepiolite fibers predominate. More smectites form as thin films around the sepiolite fibers during testing at 500°F in FANN 50C (Figure 2.21). These thin films seem to coagulate with sepiolite fibers into large flocks. The pretreatment of the fluid in flow loop seems to promote the sepiolite-to-smectite in FANN 50C viscometer at 500°F. This conversion is probably responsible for the shifting of the viscosity maximum to higher temperatures in the rheograms for the fluids No. 14, No. 15, and No. 18 in Figure 2.17b.

Figure 2.18 - Dispersed sepiolite fibers in the slurry after being sheared at room temperature for 2 hours.

Figure 2.19 - Aggregation of sepiolite fibers into spherical flocks during testing in FANN 50C viscometer.

Figure 2.20 - Small bundles of sepiolite fibers developed during 70 1/2 hours circulation in flow loop at 370°F.

Figure 2.21 - Aggregates of thin smectite films and original sepiolite fibers formed during testing at 500°F with FANN 50C viscometer.

2. SEPIOLITE/CHLORIDE FLUIDS

Chlorides of Na, K, Ca, and Mg have been added at 1% concentrations to the sepiolite fluids. The hydrothermal reactions of sepiolite in the presence of these salts have been examined within the temperature range of 300 to 600°F. One of these fluids (sepiolite/CaCl₂) has also been autoclaved at 700 and 800°F. The effects of the above chlorides on the rheological behavior of these fluids have been also studied. The results are described systematically in the following.

Sepiolite/NaCl Fluid

Appreciable amounts of smectite form in the sepiolite/NaCl fluid autoclaved at 400°F and 500°F indicating that the addition of NaCl enhances the sepiolite-to-smectite conversion (Table 2.7). Morphological features of these smectites are similar to those described for the pure sepiolite fluid. Sepiolite fibers do not undergo any visible changes during the autoclaving of the fluid at 300°F as shown in Figure 2.22. Figures 2.23 and 2.24 display how the thin smectite films grow around the sepiolite fibers at 400°F and 500°F. Smectites formed at 600°F (Figure 2.25) consist of aggregates of crumbled films with platy smectites growing at their edges. Furthermore, amorphous silica spheres are also found in appreciable number in the fluid which was autoclaved at 600°F (Figure 2.25).

Rheological Features of the Sepiolite/NaCl Fluid

The rheological data on the sepiolite/NaCl fluid are given in Table

Table 2.7

High-temperature reaction products of the sepiolite/NaCl fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	-	-
400	Smectite (60%)	thin films
500	Smectite (70%)	thin films
600	Smectite (80%)	platelets + thin films

Table 2.8

Rheological data obtained with a FANN 35A viscometer on the sepiolite NaCl fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	7.5	23	27.5	38
Plastic Viscosity (centipoise)	3	16	15	17
Yield Point (lbs/100 sq ft)	9	14	25	42
Gel Strength (lbs/100 sq ft)	7/13	14/21	17/23	50/106
pH	8.5	7.0	7.0	6.8
API Filtrate (ml/7.5 min.)	106	108	70	48
HP-HT Filtrate (ml/30 min.)*	130/17	96/23	70/24	n.d.
Cake Thickness (inches)	4/32	17/32	20/32	14/32
HP-HT Cake Thickness (inches)	6/32	14/32	34/32	n.d.

*A blow-out occurs after the minutes given following the slash.

Figure 2.22 - Sepiolite fibers after the autoclaving of the sepiolite/NaCl fluid at 300°F.

Figure 2.23 - Conversion of the sepiolite fibers into smectite at 400°F in the sepiolite/NaCl fluid.

Figure 2.24 - Formation of smectites from the sepiolite fibers at 500°F in the sepiolite/NaCl fluid.

Figure 2.25 - Aggregates of crumbled smectite films and smectite platelets at the edges formed at 600°F in the sepiolite/NaCl fluid.

2.8 and in Figure 2.26. The addition of NaCl decreases significantly the viscosity of the sepiolite fluid at 70°F. The fluid regains rather high viscosities after being autoclaved at temperatures 400 through 600°F as shown by the FANN 50C rheograms in Figure 2.26. The autoclaved fluids display again viscosity "humps" between 300°F and 400°F. The increases in the apparent and plastic viscosities, and in the yield point seem to be related to the conversion rates of the sepiolite to smectite. Similarly the API filtrate and the HP-HT filtrate losses decrease significantly with the higher temperatures (Table 2.8). The pH of these fluids steadily decreases with the increasing temperature.

Sepiolite/KCl Fluid

The addition of KCl seems to enhance the conversion rate from sepiolite to smectite as indicated by the x-ray diffraction data in Table 2.9. In fact all the sepiolite dissolves during the autoclaving of the fluid at 600°F. Morphological features of these smectites are similar to those described in the pure sepiolite fluid and in the sepiolite/NaCl fluid. They consist of thin films which are grown around the sepiolite fibers below 500°F. The smectites formed at 600°F develop aggregates of crumbled films (without the sepiolite fibers at their cores) and platelets of smectite.

Rheological Features of the Sepiolite/KCl Fluid

The addition of KCl to the sepiolite fluid at room temperature causes loss of viscosity as indicated by the rheograms in Figure 2.27. When the fluid has been autoclaved, it displays much higher viscosities

Figure 2.26 - The FANN 50C rheograms of the sepiolite/NaCl fluids which were autoclaved at the temperatures marked on the curves.

Table 2.9

High-temperature reaction products of the sepiolite/KCl fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (50%)	thin films
500	Smectite (70%)	thin films
600	Smectite (90%)	thin films + platelets

Table 2.10

Rheological measurements (FANN 35A) of the sepiolite/KCl fluids autoclaved at high-temperatures.

Parameter	70	400	500	600° F
Apparent Viscosity (centipoise)	6.2	27.5	24	27.5
Plastic Viscosity (centipoise)	2.5	18	12	22
Yield Point (lbs/100 sq ft)	8.5	22	24	14
Gel Strength (lbs/100 sq ft)	5/9	19/34	17/28	39/55
pH	8.7	7.0	7.1	7.0
API Filtrate (ml/7.5 min.)	138	84	70	79
HP-HT Filtrate (ml/30 min.)*	110/6.5	85/20	52/9	72/21
Cake Thickness (inches)	6/32	22/32	21/32	15/32
HP-HT Cake Thickness (inches)	6/32	35/32	38/32	26/32

*A blow-out occurs after the minutes given following the slash.

Figure 2.27 - The FANN 50C rheograms of the sepiolite/KCl fluids which were autoclaved at the temperatures marked on the curves.

than the pure sepiolite fluid. The viscosity "hump" becomes well developed at about 300°F. Thus KCl enhances the sepiolite-to-smectite conversion, and the new smectite in the fluid seems to give a high viscosity to it. The filtrate losses at room temperature (API filtrate) and at higher temperatures (HP-HT filtrate) decrease significantly with the higher temperature (Table 2.10). Similarly the pH values of the fluids steadily decrease with increasing temperatures. The gel strengths of the sepiolite/KCl fluids are higher than those of the pure sepiolite fluids or the sepiolite/NaCl fluids.

Sepiolite/CaCl₂ Fluid

The sepiolite/CaCl₂ fluid has been autoclaved from 300°F up to 800°F. Smectite forms below 300°F in this fluid although in very small quantities (5%) as indicated by the x-ray diffraction data in Table 2.11a. The conversion rate of the sepiolite to smectite at higher temperatures in this fluid is similar to that of the pure sepiolite fluid. Similarly silica spheres develop at 600°F. Both tremolite and talc are formed at 700°F and 800°F as described in the pure sepiolite fluid. Morphological features of the smectites are also similar to those described in the pure sepiolite system. Figure 2.28 shows the coalescing sepiolite fibers which may be the onset of the smectite development at 300°F. Smectites formed at 400 and 500°F are closely associated with the original sepiolite fibers as indicated by Figures 2.29 and 2.30. The latter figure strongly suggests a direct transition from the sepiolite fibers to thin smectite films. During the autoclaving of the fluid at 600°F, all the sepiolite dissolves and smectite precipitates along with

Table 2.11a

High-temperature reaction products of the sepiolite/CaCl₂ fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	-	-
400	Smectite (20%)	thin films
500	Smectite (50%)	thin films
600	Smectite (80%) + silica spheres	thin films + platelets
700	Smectite (80%) + tremolite, talc	platelets
800	Smectite (70%) + tremolite, talc	platelets

Table 2.11b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the sepiolite/CaCl₂ fluid.

Particle designation	Elements				
	Al	Mg	Si	Fe	Ca
Talc/700°F	.06 ± .01	.35 ± .01	1.00	.03 ± .01	-
Talc/800°F	.06 ± .01	.34 ± .02	1.00	-	.03 ± .01
Tremolite/800°F	.03 ± .01	.21 ± .03	1.00	.02 ± .01	.26 ± .01
Smectite/800°F	.03 ± .01	.29 ± .01	1.00	.03 ± .01	.01 ± .01

Figure 2.28 - Typical sepiolite fibers in the sepiolite/ CaCl_2 fluid at 300°F/10,000 psi.

Figure 2.29 - Growth of smectite films around the sepiolite fibers at 500°F in the sepiolite/ CaCl_2 fluid.

Figure 2.30 - Transition from sepiolite fibers to smectite films at 500°F in the sepiolite/ CaCl_2 fluid.

Figure 2.31 - Typical smectite aggregates and silica spheres formed at 600°F in the sepiolite/ CaCl_2 fluid.

the silica spheres. Figure 2.31 shows that these smectite aggregates consist of crumbled thin films and some minute platelets. Talc and smectites develop as platy crystals with pseudo-hexagonal outlines at 700°F (Figure 2.32) and at 800°F (Figure 2.33). Tremolite laths which form at 700 and 800°F are shown in Figures 2.34 and 2.35. The x-ray spectra in Table 2.11b are obtained from these high-temperature reaction products and they confirm the above identifications of the phases.

Rheological Properties of the Sepiolite/CaCl₂ Fluid

The addition of CaCl₂ to the sepiolite fluid at 70°F causes a significant decrease in the viscosity of the fluid. The fluids showed higher viscosities when they were autoclaved at temperatures 400°F to 600°F as shown by their rheograms in Figure 2.36. They become extremely thin when the temperatures were raised to 700°F and 800°F (Figure 2.36). The other rheological measurements on the sepiolite/CaCl₂ fluid are given in Table 2.12. Accordingly the API filtrate loss remains relatively high and unaffected by the higher temperatures. This may be due to the flocculation effect of calcium ion on the smectite. The HP-HT filtrate of the fluids improves significantly dropping from 120 ml/9 min at 70°F to 70 ml/30 min at 600°F. Similarly the pH of the fluid evolves from slightly alkaline to neutral with the increasing temperatures.

Sepiolite/MgCl₂ Fluid

The sepiolite/MgCl₂ fluid has also been autoclaved from 70°F up to 600°F. The conversion rate of sepiolite to smectite is smaller in this fluid than in the presence of other chlorides. Only 5% of smectite de-

Figure 2.32 - Platy talc and smectite particles formed at 700°F in the sepiolite/CaCl₂ fluid.

Figure 2.33 - Talc platelets with pseudo-hexagonal morphology developed at 800°F in the sepiolite/CaCl₂.

Figure 2.34 - SEM image of tremolite laths, and aggregates of talc and smectite platelets formed at 800°F in the sepiolite/CaCl₂ fluid.

Figure 2.35 - TEM image of the individual tremolite laths formed at 800°F in the sepiolite/CaCl₂ fluid.

Figure 2.36 - The FANN 50C rheograms of the sepiolite/CaCl₂ fluids which were autoclaved at the temperatures marked on the curves.

Table 2.12

Rheological measurements (FANN 35A) of the sepiolite/CaCl₂ fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	6	13	22	12.5
Plastic Viscosity (centipoise)	3	8	11	5
Yield Point (lbs/100 sq ft)	6	10	22	15
Gel Strength (lbs/100 sq ft)	5/25	8/26	26/28	14/16
pH	8	6.6	6.8	6.9
API Filtrate (ml/7.5 min.)	130	145	120	130
HP-HT Filtrate (ml/30 min.)*	120/9	98/20	65/25	70
Cake Thickness (inches)	6/32	8/32	12/32	13/32
HP-HT Cake Thickness (inches)	4/32	17/32	36/32	32/32

*A blow-out occurs after the minutes given following the slash.

velops at 400°F and 60% at 600°F (Table 2.13). Sepiolite fibers in Figure 2.37 seem to have been affected very little by the autoclaving process of this fluid at 400°F. Thin smectite films develop at 500°F and in small quantities at 600°F as seen in Figure 2.38. Most of the smectites formed at 600°F consist of aggregates of crumbled films (Figure 2.39) or of minute platelets (Figure 2.40).

Rheological Features of the Sepiolite/MgCl₂ Fluid

The addition of MgCl₂ to the sepiolite fluid does not cause as much damage to the viscosity of the fluid at 70°F as the other chlorides. Furthermore higher temperatures do not affect the rheograms of the fluids (Figure 2.41) as much as in the other systems. The viscosities of these fluids are, however, significantly lower than those of the previous sepiolite-based fluids. This may be related to the low rate of the sepiolite-to-smectite conversion. Thus the sepiolite/MgCl₂ fluid seems to be extremely stable at higher temperatures up to 600°F. Both the API filtrate and the HP-HT filtrate losses are rather high for an acceptable fluid (see Table 2.14), especially the filtrate loss of 196 ml at 400°F. The pH of the fluid evolves from slightly alkaline (7.7) at 70°F to slightly acidic (6.2) at 600°F.

Table 2.13

High-temperature reaction products of the sepiolite/MgCl₂ fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	-	-
400	Smectite (5%)	thin films
500	Smectite (40%)	thin films
600	Smectite (60%)	platelets & thin films

Table 2.14

Rheological measurements (FANN 35A) of the sepiolite/MgCl₂ fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	6.5	9	16.5	14.5
Plastic Viscosity (centipoise)	2.5	7	11	18
Yield Point (lbs/100 sq ft)	8	4	11	13
Gel Strength (lbs/100 sq ft)	5/6	3/10	9/13	8/15
pH	7.7	6.4	5.8	6.2
API Filtrate (ml/7.5 min.)	100	196	100	90
HP-HT Filtrate (ml/30 min.)*	130/15	100/5	95/26	85/19
Cake Thickness (inches)	5/32	27/32	16/32	17/32
HP-HT Cake Thickness (inches)	5/32	28/32	30/32	32/32

*A blow-out occurs after the minutes given following the slash.

Figure 2.37 - Sepiolite fibers in the sepiolite/MgCl₂ fluid autoclaved at 400°F.

Figure 2.38 - Smectite films forming around the sepiolite fibers in the sepiolite/MgCl₂ fluid at 600°F.

Figure 2.39 - Smectite aggregates consisting of crumbled films formed at 600°F in the sepiolite/MgCl₂ fluid.

Figure 2.40 - Minute smectite platelets formed at 600°F in the sepiolite/MgCl₂ fluid.

Figure 2.41 - The FANN 50C rheograms of the sepiolite/MgCl₂ fluids which were autoclaved at the temperatures marked on the curves.

3. SEPIOLITE/HYDROXIDE FLUIDS

Hydroxides of Na, K, Ca, and Mg have been added at 1% concentrations to the sepiolite fluids. Their effects on hydrothermal reactions of sepiolite and on the rheology of the sepiolite fluids have been systematically examined within the temperature range up to 600°F. The results are described in the following.

Sepiolite/NaOH Fluid

In the presence of NaOH no smectite has been detected in the fluid which was autoclaved at 300°F. As indicated in Table 2.15, appreciable quantities (20%) of smectite form however at 400°F. The smectite content increases to about 70% at 500°F and to about 100% at 600°F. Morphological features of these smectites are similar to those formed in the sepiolite/NaCl fluid.

Electron microscopic examination of the fluids shows that smectite forms as thin films at 400°F and at 500°F. Typical smectite films are shown in Figures 2.42 and 2.43.

Rheological Properties of the Sepiolite/NaOH Fluid

The rheological data on the sepiolite/NaOH fluid are given in Table 2.16 and in Figure 2.44. As indicated by the FANN 50C rheograms of these fluids, the initial viscosities vary between 30 to 45 centipoise. The viscosities of these fluids are found between 8 to 20 centipoise at 500°F (Figure 2.44); thus showing a temperature induced thinning. The rheograms do not display the high viscosity hump except for the fluid at 70°F,

Table 2.15

High-temperature reaction products of the sepiolite/NaOH fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
300	-	-
400	Smectite (20%)	thin films
500	Smectite (70%)	thin films
600	Smectite (90%)	thin films

Table 2.16

Rheological data obtained with FANN 35A viscometer on the sepiolite/NaOH fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	23	42.5	43	63
Plastic Viscosity (centipoise)	7	29	16	11
Yield Point (lbs/100 sq ft)	32	27	54	104
Gel Strength (lbs/100 sq ft)	12/24	20/27	23/28	34/40
pH	11.7	10.7	10.4	10.3
API Filtrate (ml/7.5 min.)	62	64	64	80
HP-HT Filtrate (ml/30 min.)*	92/16	47/10	60/20	70/18
Cake Thickness (inches)	6/32	14/32	17/32	5/32
HP-HT Cake Thickness (inches)	15/32	16/32	20/32	33/32

*A blow-out occurs and the time elapsed before the blow-out is given after the slash.

Figure 2.42 - Smectite films at 500°F in the sepiolite/NaOH fluid.

Figure 2.43 - Typical aggregates of crumbled smectites formed at 500°F in the sepiolite/NaOH fluid.

Figure 2.45 - Illites develop both laths and equant platelets at 500°F in the sepiolite/KOH fluid.

Figure 2.46 - A closer look of the equant illite platelets with pseudo-hexagonal morphology formed at 600°F in the sepiolite/KOH fluid.

Figure 2.44 - The FANN 50C rheograms of the sepiolite/NaOH fluids which were autoclaved at the temperatures marked on the curves.

which has not been autoclaved.

In addition to the acceptable rheograms, the sepiolite/NaOH fluid possesses relatively low API, and HP-HT filtrate losses (Table 2.16). The apparent and plastic viscosities, the yield point, and gel strength increase as the amount of the smectite becomes predominant in the fluid. Thus we see the highest viscosities (apparent and plastic) under the alkaline conditions and in the presence of sodium ions.

The pH values of the fluids steadily decrease from 11.7 at 70°F to 10.3 at 600°F.

Sepiolite/KOH Fluid

The high temperature reactions in this fluid are rather different from the reactions in the other fluids. Smectites only form at 400°F and they make up not more than 20% of the clays (Table 2.17). Small amounts of illite also are found in the fluid after it has been autoclaved at 400°F. More illite and illite/smectite mixed-layers form as the reaction products of sepiolite at 500°F. Illite becomes the basic ingredient of the fluid at 600°F and sepiolite is completely destroyed at this temperature. The x-ray spectra obtained from these illites show the following intensity ratios: $\text{Al/Si} = 0.06 \pm 0.01$, $\text{Mg/Si} = 0.24 \pm 0.01$, $\text{K/Si} = 0.27 \pm 0.01$, and $\text{Fe/Si} = 0.05 \pm 0.01$. These data indicate that the chemical composition of these illites is similar to that of a tri-octahedral mica such as phlogopite, $\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$. The illites consist of pseudohexagonal well-developed platelets and laths as shown in Figures 2.45 and 2.46. The basal spacing of the illite is $10.3\text{\AA}$ for the air-dried sample and it shifts to $10.0\text{\AA}$ upon glycolation.

Table 2.17

High-temperature reaction products of the sepiolite/KOH fluid and the morphological features of the smectites formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (20%)	thin films
500	illite, I/S	-
600	illite, I/S	-

Table 2.18

Rheological measurements with FANN 35A viscometer on the sepiolite/KOH fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	18	26	5.5	1.5
Plastic Viscosity (centipoise)	6	13	5	3
Yield Point (lbs/100 sq ft)	24	26	1	0
Gel Strength (lbs/100 sq ft)	24/34	8/12	2/2	.5/1
pH	10.4	10.7	10.0	9.8
API Filtrate (ml/7.5 min.)	70	76	118	134
HP-HT Filtrate (ml/30 min.)*	90/15	82/17	27/29	121/18
Cake Thickness (inches)	9/32	16/32	7/32	10/32
HP-HT Cake Thickness (inches)	9/32	22/32	4/32	3/32

*A blow-out occurs, and the time elapsed before the blow-out is given after the slash.

Rheological Properties of the Sepiolite/KOH Fluids

The rheological characteristics of the sepiolite/KOH fluids are given in Table 2.18 and in Figure 2.47. The FANN 50C rheograms of these fluids have viscosities ranging from about 12-15 centipoise at 70°C to 5-7 centipoise at 500°F for the fluids before and after being autoclaved at 400°F. The viscosity hump is well developed for the autoclaved fluid which is probably related to the sepiolite-to-smectite conversion at 400°F. The API filtrate loss and the HT-HP filtrate loss for the sepiolite/KOH fluids are significantly lower up to 400°F than at higher temperatures (Table 2.18). The fluids autoclaved at 500°F and 600°F become extremely thin as shown in Figure 2.47. This may be directly related to the fact that illite and illite/smectite mixed-layers become the basic ingredients of these fluids at higher temperatures. Thus the sepiolite/KOH fluids become practically useless at temperatures 500°F and above. The pH values of the fluids show a slight decrease with the higher temperatures.

Sepiolite/Ca(OH)₂ Fluid

The addition of Ca(OH)₂ seems to impede the conversion of the sepiolite to smectite. As shown in Table 2.19a, only 10% smectite is developed at 400°F in this fluid. The smectite has a basal spacing of 14.5Å and it occurs as thin films which are epitaxially grown on sepiolite fibers as shown in Figure 2.48. In addition to smectite, a hydrated calcium silicate is also formed in this fluid at 400°F. This mineral has a strong 11.3Å reflection which is characteristic for a tobermorite. The latter phase occurs in long laths and ribbons (Figure 2.49). Smectites make up about 30% of the solids in the fluid at 500°F. They occur again as fluffy

Figure 2.47 - The FANN 50C rheograms of the sepiolite/KOH fluids which were autoclaved at the temperatures marked on the curves.

Table 2.19a

High-temperature reaction products of the sepiolite/ $\text{Ca}(\text{OH})_2$ fluid and the morphological features of the smectites formed in them.

Temperature ($^{\circ}\text{F}$)	reaction products	morphology of smectite
400	Smectite (10%) CSH*	thin films
500	Smectite (30%) CSH	thin films
600	Smectite (95%) CSH	thin films + platelets

*: hydrated calcium silicates (tobermorite)

Table 2.19b

Average intensities of x-ray spectra obtained in STEM/area mode from the high-temperature reaction products of the sepiolite/ $\text{Ca}(\text{OH})_2$ fluid.

Particle designation	Elements			
	Al	Mg	Si	Ca
CSH/600 $^{\circ}\text{F}$	.05 $\pm$.01	-	1.00	.95 $\pm$.01
CSH/600 $^{\circ}\text{F}$	.05 $\pm$.01	.02 $\pm$.01	1.00	1.00 $\pm$.01
Smectite/600 $^{\circ}\text{F}$	.05 $\pm$.01	.24 $\pm$.01	1.00	-

Figure 2.48 - Smectite films and long laths of tobermorite crystals formed at 400°F in the sepiolite/Ca(OH)₂ fluid.

Figure 2.49 - Growth of thin smectite films around the sepiolite fibers at 500°F in the sepiolite/Ca(OH)₂ fluid.

Figure 2.50 - Typical tobermorite crystals formed at 600°F in the sepiolite/Ca(OH)₂ fluid.

Figure 2.51 - Smectite films and mosaic of smectite platelets formed at 600°F in the sepiolite/Ca(OH)₂ fluid.

aggregates of thin films. Smectites formed at 600°F are composed of small platelets and thin films (Figure 2.51). The hydrated calcium silicates (cement minerals) are also a common constituent of the fluids when they are autoclaved at 500°F and 600°F. Typical hydrated calcium silicates (tobermorite) formed at 600°F consist of elongated crystals as shown in Figure 2.50. The x-ray spectra in Table 2.19b are obtained from these minerals and they show only calcium and silicon in them.

Rheological Features of the Sepiolite/Ca(OH)₂ Fluid

The rheological properties of the sepiolite/Ca(OH)₂ fluid are summarized in Table 2.20 and in Figure 2.52. The rheograms of these fluids in Figure 2.52 show rather low viscosities for these fluids in general. A distinct viscosity "hump" only develops for the fluid autoclaved at 400°F. Thus the addition of Ca(OH)₂ seems to be rather detrimental to the viscosity of the sepiolite fluid. Furthermore, API filtrate and HP-HT filtrate losses are extremely high for these fluids as shown in Table 2.20. The pH of the initial fluid is highly alkaline (11.8 at 70°F) and it drops to 9.4 at 600°F. The viscosity data indicate that any smectite formed would be flocculated by the presence of calcium and thus have a lower rheology and higher fluid loss than the sodium analog of the same smectite. Some complications may also arise due to the formation of cement crystals.

Sepiolite/Mg(OH)₂ Fluid

Only small amounts (10%) of smectite develop in this fluid at a temperature of 400°F. The smectite content increases to about 40% at

Table 2.20

Rheological measurements with a FANN 35A viscometer on the sepiolite Ca(OH)_2 fluids autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	9	5.5	9.5	5.75
Plastic Viscosity (centipoise)	5	5	8	2
Yield Point (lbs/100 sq ft)	8	1	3	7.5
Gel Strength (lbs/100 sq ft)	4/4	1/2	2/4	1/1
pH	11.8	9.6	9.3	9.4
API Filtrate (ml/7.5 min.)	410	340	240	120
HP-HT Filtrate (ml/30 min.)*	102/2	107/2	95/4	93/13
Cake Thickness (inches)	19/32	18/32	20/32	10/32
HP-HT Cake Thickness (inches)	9/32	9/32	20/32	24/32

*A blow-out occurs after the minutes given following the slash.

Figure 2.52 - The FANN 50C rheograms of the sepiolite/Ca(OH)₂ fluids which were autoclaved at the temperatures marked on the curves.

500°F and to 90% at 600°F (Table 2.21). Smectites formed at 600°F show higher crystallinity with a symmetrical 12.6° reflection which expands to 17° upon glycolation. Smectite films start forming at 400°F and 500°F epitaxially around the sepiolite fibers as shown in Figures 2.53 and 2.55. Thin smectite films without sepiolite associations (Figure 2.53) are also observed to develop at these temperatures. Smectite aggregates of crumbled films and minute platelets (Figure 2.56) form during the autoclaving of the fluid at 600°F.

Rheological Features of the Sepiolite/Mg(OH)₂ Fluid

The rheological properties of the sepiolite/Mg(OH)₂ fluid are given in Table 2.22 and in Figure 2.57. The addition of Mg(OH)₂ increases significantly the viscosity especially for the fluid autoclaved at 400°F. A steady thinning of the fluids with the higher temperature is also clearly seen on these rheograms. It is interesting to note that the fluid autoclaved at 600°F shows the largest viscosity "hump" at about 400°F. The API and the HP-HT filtrate losses are also relatively lower in this system.

Table 2.21

High-temperature reaction products of the sepiolite/Mg(OH)₂ fluid and the morphological features of the smectite formed in them.

Temperature (°F)	reaction products	morphology of smectite
400	Smectite (10%)	thin films
500	Smectite (40%)	thin films
600	Smectite (90%)	thin films + platelets

Table 2.22

Rheological measurements with FANN 35A viscometer on the sepiolite/Mg(OH)₂ fluid autoclaved at high temperatures.

Parameter	70	400	500	600°F
Apparent Viscosity (centipoise)	22	36.5	21	13.5
Plastic Viscosity (centipoise)	4	15	14	12
Yield Point (lbs/100 sq ft)	36	43	14	3
Gel Strength (lbs/100 sq ft)	20/40	37/41	13/26	2/5
pH	8.0	7.7	7.4	7.0
API Filtrate (ml/7.5 min.)	88	60	100	40
HP-HT Filtrate (ml/30 min.)*	85/7	75/28	58/15	75
Cake Thickness (inches)	10/32	9/32	12/32	13/32
HP-HT Cake Thickness (inches)	10/32	29/32	24/32	25/32

*A blow-out occurs after the minutes following the slash.

Figure 2.53 - Thin smectite films grown around the sepiolite fibers at 400°F in the sepiolite/MgCl₂ fluid.

Figure 2.54 - Thin smectite films formed at 400°F in the sepiolite/MgCl₂ fluid.

Figure 2.55 - Smectite films formed around the sepiolite fibers at 500°F in the sepiolite/Mg(OH)₂ fluid.

Figure 2.56 - Typical smectite aggregates of crumbled films and minute platelets (in the background) formed at 600°F in the sepiolite/Mg(OH)₂ fluid.

SEPIOLITE/Mg(OH)₂

Figure 2.57 - The FANN 50C rheograms of the sepiolite/Mg(OH)₂ fluids which were autoclaved at the temperatures marked on the curves.

—

lignosulfonates (Unical, and Spersene), Quebracho, and lignites (XP-20):

Fluid A: Base Mud = 20 lbs/bbl Wyoming bentonite
20 lbs/bbl Texas bentonite

Fluid B: Base Mud + 4 lbs/bbl Quebracho
.25 lbs/bbl NaOH

Fluid C: Base Mud + 4 lbs/bbl Unical
 .25 lbs/bbl NaOH

Fluid D: Base Mud + 4 lbs/bbl Spersene
 2 lbs/bbl of XP-20
 .25 lbs/bbl NaOH

These fluids were prepared by hydrating 20 lbs/bbl of Wyoming bentonite and 20 lbs/bbl of Texas (southern) bentonite in water. The clay slurry was mixed thoroughly and allowed to hydrate for 24 hours. Following the rehydration, samples of the clay slurry were treated with various mud additives listed above and mixed for 10 minutes before measuring the FANN 35A data. The samples were then placed in an oven and heated for 16 hours at 150°F. The samples were then cooled and remixed for 5 minutes before measuring with FANN 35A. The rheological measurements on these fluids are given in Table 3.1. The high-temperature viscosities of these fluids are shown in Figures 3.1 and 3.2. As can be observed from the viscosity curves (plotting apparent viscosity vs temperature), the conventional systems show temperature thinning up through the 121°C (250°F) range. Above 149°C (300°F), the conventional fluids begin to have an increase in viscosity and by 204°C (400°F), they start to undergo high temperature gellation. This causes the fluids to be inoperative from the rheological standpoint and, thus, the fluid loss is not important on these fluids. While the oil industry has relied on the use of oil muds for high temperature drilling, it is advantageous to use water-base systems for geothermal wells. The conventional bentonite-base drilling fluids when subjected to temperature show a viscosity hump in the temperature range of 350°F and above. Even though these simple clay slurries have no drilled solids nor weighting material in them, they still show the viscosity increase with temperature. Any additional solids would amplify this viscosity increase and thus the clay-base systems become inoperative. Any contaminations of these systems by such things as calcium, salt, or carbonate ions cause more viscosity increases with or

Table 3.1

Rheological measurements with FANN 35A viscometer on the conventional base muds.

Fluid		Apparent Viscosity	Plastic Viscosity	Yield Point	HT-HP Fluid Loss (ml) 400°F/500 PSI
Fluid A	Initial	26.5	21	11	NC
	150°F	32.5	26	13	
Fluid B	Initial	37	31	12	22
	150°F	26	21	11	
Fluid C	Initial	28	27	2	22
	150°F	21	17	8	
Fluid D	Initial	23	14	18	19
	150°F	42	26	32

Figure 3.1 - The FANN 50C rheograms showing the high-temperature viscosity of the base muds with various additives.

Figure 3.2 - The FANN 50C rheogram showing the high-temperature viscosity of the base mud containing Spersene, XP-20, and NaOH.

without temperature. Therefore, the combined viscosity increase from both temperature and contamination leads very quickly to inoperative and unacceptable systems. The base clay slurry (Fluid A in Figure 3.1) shows the characteristic viscosity increase starting at about 325°F. The viscosity is lowered somewhat by treatment of the clay slurry with Quebracho (Fluid B); however, the viscosity still increases with temperature and, therefore, high temperature gellation will occur with Quebracho type fluids. More recently designed systems such as Fluid C (Figure 3.1) and Fluid D (Figure 3.2) lower the viscosity of clay base muds even more at lower temperature ranges. However, this does not eliminate the high temperature gellation. By using heavy treatments of lignosulfonates, the viscosity can be controlled to some extent, however, the high temperature gels are inevitable and, thus, there is a temperature limitation of about 400°F on these conventional base muds.

2. ADDITION OF POLYMERS TO ATTAPULGITE AND SEPIOLITE FLUIDS

Our studies on attapulgite- and sepiolite-based muds point out that most of these fluids have unacceptably high fluid losses. To remedy this problem, we added polymers to these fluids. A large number of polymers are currently used but much confusion exists in their applications since the reaction mechanism between polymers and clay minerals is not well understood. Polymers currently used for drilling, completion, gravel packing, and workover fluids may be roughly divided into the following categories (Carney, 1975):

1. Natural gums, starches, and extracts.

2. Cellulose-based polymers.
3. Nitrile compounds.
4. Polyacrylates (homo, co-polymer, and ter-polymers).
5. Sulfonated co-polymers.

It is generally known that in the case of sodium polyacrylates (SPA), the relationship between viscosity of clay slurries, molecular weight, and concentration of polymer can be expressed by a family of curves given in Figure 3.3. The fluid loss of a clay slurry with low salinity and low hardness can be expressed generally by another set of curves in Figure 3.4. However, the fluid loss values will increase as salinity increases for any given molecular weight (Figure 3.5).

Both high and low molecular weight sodium-polyacrylates have been added to the sepiolite and attapulgite fluids with the following formulations:

Fluid E: 25 lbs/bbl sepiolite
4 lbs/bbl SPA high mol. weight
1 lbs/bbl SPA low mol. weight

Fluid F: 25 lbs/bbl attapulgite
4 lbs/bbl SPA high mol. weight
1 lbs/bbl SPA low mol. weight

CYPAN-type sodium-polyacrylates with a molecular weight in the range of 750,000 to 1,000 were used for the high molecular weight SPA, and the low molecular weight SPA had a molecular weight of 940-1,400. These fluids were prepared by mixing the clays in water and allowing them to yield overnight. Then the SPA's were added into the clay slurries and mixed on a Hamilton Beach mixer for 10 minutes. The initial rheology was measured with a FANN 35A viscometer. Each fluid was then heated overnight at 150°F and then remixed and rheology was measured again with FANN 35A

Figure 3.3 - The relationship between the viscosity of the clay fluid vs. concentration of polymers with different molecular weights.

Figure 3.4 - The relationship between the fluid loss (API) of the clay fluid vs. the concentration of the polymer with various molecular weights.

Figure 3.5 - The relationship between the fluid loss (API) of the clay fluid and its polymer concentration in the presence of salts.

viscometer. Subsequently, the fluid was transferred to FANN 50C viscometer and its rheology was measured up to 500°F. The fluid losses were again measured on the samples at 400°F and 500 psi. These rheological measurements are given in Table 3.2 and in Figure 3.6. These data clearly show that the addition of the polymers to the fluids improves drastically the fluid loss and also increases the viscosity of the sepiolite and attapulgite fluids. In fact, the high temperature rheology of the sepiolite/polymers is rather good up to 500°F. By selecting various acrylate polymers either viscosity (with high mol. SPA) or thinning (with low mol. SPA) can be controlled. With the addition of these polymers we can thus control both the rheology and fluid loss of the sepiolite- or attapulgite-based fluids. The sepiolite/polymers fluid has much better viscosity and fluid loss control than the attapulgite/polymers fluid.

3. SEPIOLITE/ENGLISH MICA/SPA FLUIDS

A set of fluids was prepared by adding English Mica and SPA's to the sepiolite fluids to give the compositions below.

Fluid G:	15 lbs/bbl sepiolite 10 lbs/bbl English Mica 4 lbs/bbl SPA high mol. weight 1 lbs/bbl SPA low mol. weight
Fluid H:	15 lbs/bbl sepiolite 20 lbs/bbl English Mica
Fluid I:	15 lbs/bbl sepiolite 20 lbs/bbl English Mica 4 lbs/bbl SPA high mol. weight
Fluid J:	15 lbs/bbl sepiolite 20 lbs/bbl English Mica 1 lbs/bbl SPA low mol. weight

English Mica is a pure fine-grained mica under the trade name Micro Mica

Table 3.2

Rheological measurements with FANN 35A viscometer on the sepiolite and attapulgite fluids after the addition of sodium polyacrylates.

Fluid	Apparent Viscosity	Plastic Viscosity	Yield Point	HT-HP fluid loss (ml) at 400°F/500 PSI
Fluid E				
initial	23.5	23	1	
150°F	30	29	10	21
Fluid F				
initial	2	1	2	
150°F	2	1	2	25

Figure 3.6 - The FANN 50C rheograms of the sepiolite and attapulgite fluids after the addition of sodium polyacrylates.

C-1000 and it was obtained from English Mica Company. This mica is described further in the next section.

The rheological measurements with a FANN 35A viscometer on these fluids are given in Table 3.3. The FANN 50C rheograms of these fluids are displayed in Figure 3.7. The sepiolite/English Mica fluids (H-J) without the high molecular weight sodium polyacrylate are extremely thin and they are practically useless before the conversion of sepiolite to smectite by temperature. The addition of the high molecular weight polymer to the sepiolite/English Mica fluid increases the viscosity of the fluid (I in Figure 3.7) at temperatures below 200°F. The fluid "G" containing sepiolite/English Mica/high and low molecular weight SPA's gives a remarkable rheology as shown in Figure 3.7. The apparent and plastic viscosities and the yield point values of this fluid (Table 3.3) are also rather satisfactory for a good drilling fluid.

4. SEPIOLITE/BENTONITE/SPA Fluids

After studying the data from all the previous fluids and the effects of the various additives on them, we have formulated two fluids for geothermal drilling. These new fluid formulations are designated as "GDF-1" and "GDF-2". Both of these fluids contain sepiolite and bentonite as their basic ingredients. Sepiolite was selected because it has shown better performance than attapulgite at elevated temperatures. Bentonite was used in low concentrations provide fluid loss control at the lower temperature ranges. The amount of bentonite can be varied in practice and even entirely deleted as the temperature increases since smectite formed

Table 3.3

Rheological measurements with FANN 35A viscometer on the sepiolite English Mica/SPA fluids.

Fluid	Apparent Viscosity	Plastic Viscosity	Yield Point
Fluid G			
initial	29.5	25	9
150°F	26.5	22	9
Fluid H			
initial	2.5	2	1
150°F	2.5	2	1
Fluid I			
initial	23.5	23	1
150°F	30	25	10
Fluid J			
initial	2	1	2
150°F	2	1	2

Figure 3.7 - The FANN 50C rheograms showing the high-temperature viscosity of sepiolite-based muds with the addition of English Mica and polymers.

from sepiolite would eliminate the need for the bentonite. The high molecular weight Na-polyacrylate was chosen for its contribution to viscosity and to the fluid loss control. The data in the previous section showed that this polymer remains stable at elevated temperatures especially in association with clays. The low molecular weight Na-polyacrylate was added because of its excellent dispersion characteristics on clay slurries and because of its temperature stability. A drilling fluid for geothermal use with sepiolite and bentonite was earlier formulated by Carney (1976) and Remont (1977) under the designation of "HTM-1". The high temperature rheology of these fluids has been examined and the results are separately described below for each fluid.

HTM-1 FLUID

The HTM-1 fluid has the following composition:

- 15.0 lbs/bbl sepiolite
- 5.0 lbs/bbl Wyoming bentonite
- 20.0 lbs/bbl brown coal
- 2.5 lbs/bbl SPA
- 2.0 lbs/bbl NaOH

The major difference between this fluid and the new geothermal drilling fluids is related to the addition of brown coal and sodium hydroxide. The brown coal was used to improve the filtration properties of the fluid. The sodium hydroxide is used for the purpose of raising the pH and to increase the solubility of lignite (brown coal). The high temperature rheology of the HTM-1 fluid is given in Figure 3.8. The behavior of the HTM-1 fluid is qualitatively similar to that of Fluid "E" consisting of sepiolite and SPA's. The initial viscosity of HTM-1 fluid is 49 centipoise, but the final viscosity at 500°F is very similar to that for the

Figure 3.8 - The FANN 50C rheograms of the geothermal drilling fluids: "GDF-1" (before and after autoclaving at 500°F) and HTM-1 (not autoclaved).

system Fluid "E" (Figure 3.6 vs Figure 3.8). The main difference between the two samples is that the change in viscosity during the hump period is much higher for the HTM-1. The differential hump height in Fluid "E" is 8 centipoise, and in HTM-1 the change is 15 centipoise.

Geothermal Drilling Fluid "GDF-1"

This fluid was prepared by essentially deleting the brown coal and sodium hydroxide from the HTM-1 fluid:

- 20 lbs/bbl sepiolite
- 5 lbs/bbl Wyoming bentonite
- 2 lbs/bbl SPA high mol. weight
- 1 lbs/bbl SPA low mol. weight

This fluid has been autoclaved at 800°F under a pressure of 16,000 psi. All the sepiolite dissolves during the autoclaving but the montmorillonite of the bentonite is found to survive the hydrothermal treatment. The main high temperature reactions in the system are related to the dissolution of sepiolite and subsequent precipitation of talc, tremolite, and smectite. These reaction products are similar to those described above for the pure sepiolite systems at 800°F. The high temperature rheology of the geothermal drilling fluid before and after autoclaving at 800°F is measured with a FANN 50C viscometer and presented in Figure 3.8. These data indicate that the new fluid has a stable viscosity even after autoclaving at 800°F.

Geothermal Drilling Fluid "GDF-2"

This fluid was prepared by adding English Mica and KOH to the previous formula:

12	lbs/bbl	sepiolite
4	lbs/bbl	Wyoming bentonite
3.2	lbs.bbl	SPA high mol. weight
0.8	lbs/bbl	SPA low mol. weight
8	lbs/bbl	English Mica
0.8	lbs/bbl	KOH

English Mica was added in order to simulate drilled solids because it would not alter during the high temperature as compared with the other clays. Furthermore the smectites in the fluids will convert eventually to a mica-like (illite) material with the increasing temperatures. The potassium hydroxide was selected for pH control. Our previous experiments with KOH showed that it decreases viscosity at high temperatures whereas NaOH and Ca(OH)_2 enhance the fluid viscosities. The presence of K^+ also promotes the smectite-to-illite conversion in the fluid. Thus this formula has been put together by considering the results from each phase of this study. Naturally, this basic formula can be varied in order to respond to any given situation. If needed, a high temperature lubricant or a corrosion inhibitor can also be added in order to reduce the costly corrosion problems in geothermal drilling.

The rheological properties and the fluid loss values (Table 3.4) of this fluid are very desirable for good drilling fluid practices. A yield point of 12 lbs/100 sq ft will provide a good hole cleaning capability. The low gel strength of 5-7 lbs/100 sq ft is ideal to support drill cuttings during the static periods and would not require much initial pressure to regain circulation. The fluid loss of 6.0 ml is also in the ideal range and would not form a heavy wall cake. The high temperature viscosity curves obtained by FANN 50C, in Figure 3.9 show an excellent response to the increasing temperatures. The fluid exhibits a gradual reduction in viscosity as the temperature is increased. The

Table 3.4

Rheological measurements with a FANN 35A viscometer on the geothermal drilling fluid "GDF-2".

Parameter	70	300	400	500	600	700	800°F
Apparent Viscosity (centipoise)	27.5	17.0	16.0	61.5	32.5	24.0	5.0
Plastic Viscosity (centipoise)	21.5	16.5	15.0	34.0	19.0	14.0	5.0
Yield Point (lbs/100 sq. ft.)	12.0	0.5	1.0	55.0	27.0	20.0	0.0
Gel Strength (lbs/100 sq. ft.)	5/7	2/2.5	1/16	13/20	6/38	11/24	2.4
pH	10.6	10.0	9.3	8.6	9.0	8.6	8.0
API Filtrate (ml/7.5 min.)	6.0	10.4	12.0	15.8	19.0	46.0	260.0
Cake Thickness (inches)	1/32	1/32	1/32	3/32	5/32	2/32	7/32

Figure 3.9 - The FANN 50C rheograms of the geothermal drilling fluid "GDF-2" which was autoclaved at temperatures up to 800°F.

characteristic "viscosity hump" of around 400°F is minimized and much improved as compared with the behavior of the HTM-1 and "GDF-1" fluids in Figure 3.8.

The "GDF-2" fluid has been autoclaved at the temperatures from 300°F to 800°F. The rheological data on the autoclaved "GDF-2" fluid and its high temperature viscosity curves are given in Table 3.4 and in Figure 3.9 respectively. These data show an excellent rheology through 600°F. The viscosity of the fluids displays a significant increase after autoclaving at 500°F. This is related to the conversion of sepiolite to smectite as observed with the x-ray diffraction analysis. At temperatures 700 and 800°F the fluid loss drastically increases. The x-ray diffraction and electron microscopic examination shows that the smectites are converted to illite in considerable amounts at 700°F and completely at 800°F. Thus the fluid consists mostly of illite and K-feldspar with minor quantities of smectite after autoclaving at 700°F. Only illite and K-feldspar remain in the fluid after autoclaving at 800°F, illite and K-feldspar, explain the low viscosity and high fluid loss of the fluid after autoclaving at 800°F. Since these reaction products are generated by the addition of KOH and English Mica, these components should be deleted at temperatures 700°F and above. Thus the "GDF-1" formula will better function at the temperatures 700°F and above, whereas the "GDF-2" fluid will perform much better at and below 600°F.

IV. EFFECTS OF THE SEPIOLITE-BASED FLUIDS ON THE FORMATION

The question arises whether the fine fibers of sepiolite may penetrate into the pores of the reservoir rocks and cause a formation damage. Dennis et al (1979) designed experiments to test the invasion of the sepiolite-based fluids into the sandstone cores from East Mesa Geothermal Reservoir of Imperial Valley. These cores were saturated with a solution representative of the formation water and the initial permeability measurement was made on samples at simulated borehole condition, including overburden pressure (5,000 psi), pore fluid pressure (2,165 psi), and temperature (390°F). All permeability measurements were made in the direction of backflow. The cores were then subjected to simulated circulation and stagnation of drilling muds. After tests were completed the cores were then measured for permeability change due to the possible invasion of drilling fluids. One test core (2-76) suffered significant permeability impairment after 48 hours stagnation with the HTM-1 drilling fluid at 212°F whereas the other test core (2-64) suffered only negligible permeability loss after 12 hours stagnation at 392°F. The virgin core (1-64) and the two test cores (2-64 and 2-76) were sent to us after these tests.

We analyzed these cores with x-ray diffraction and with SEM/EDS modes of the analytical electron microscope in order to see whether the clays (especially sepiolite) from the HTM-1 mud invaded the test cores. Each core was originally 4 inches long. We divided them into 4 parts, each being one inch long. These sections were designated by the letters A,B,C, and D, with "A" being the core end which was in direct contact

with the mud. These sections were separately examined. The framework mineralogy of these sandstones consist of quartz (65%), feldspar (20%), and calcite (10%). The rest (5%) of the sandstone is made up of clay minerals which coat the framework grains and thus line the pores in the sandstone. In order to properly identify these clay minerals, the <2 micron fractions of the cores have been separated and x-rayed. The results are listed in Table 4.1. The data show that illite/smectite mixed-layers and chlorite are the clay minerals of the sandstone. The SEM/EDS examination reveals both the morphology and the mode of occurrence of these clay minerals. Typical chlorites in the virgin core occur as coatings of sand grains (Figures 4.1a, 4.1b, and 4.1c). These chlorites are authigenic in origin i.e. formed in situ in the sandstone during its diagenesis. As shown in Figure 4.1c, the quartz grains display euhedral faces which are developed as diagenetic overgrowths. Illite/smectite mixed-layers mostly consist of fibrous illites which have grown on the sand grains (Figure 4.1d). Because of these fragile morphological features of illite/smectite mixed-layers and their swelling properties, these clay minerals are well known for their water-sensitivity (i.e. they can migrate and plug the pore throats of the reservoir rocks). As in the virgin core, the test cores contain authigenic illite/smectite mixed-layers and chlorites of similar morphological features. It is important to note that these clays are distinctly different from the clays (bentonite and sepiolite) in the HTM-1 drilling fluids. No bentonite or sepiolite particle has been found in the test cores. Therefore the observed permeability impairment of these test cores must be related to the behavior of the native clays in them but not to the invasion of the HTM-1

Table 4.1

X-ray diffraction data on the clay fractions(<2 microns) of the East Mesa Sandstone Cores.

Core/section	Illite/Smectite		Chlorite	Calcite	Feldspar	Quartz
	Mixed-layer					
1-64A	40%		40%	5%	5%	10%
1-64B	40		40	5	5	10
1-64C	40		40	5	5	10
1-64D	40		45	5	1	10
2-64A	45		45	3	3	3
2-64B	45		45	3	3	3
2-64C	45		50	1	2	2
2-64D	45		50	1	2	2
2-76A	50		50	—	1	1
2-76B	50		45	5	—	—
2-76C	45		40	10	5	—
2-76D	40		40	15	5	—

Figure 4.1a - Coating of sand-grains with clay minerals in the virgin core (1-64). Further magnified in Figure 4.1b.

Figure 4.1b - A closer look at the fragile chlorite rosettes and hairy illite/smectite mixed-layers.

Figure 4.1c - Authigenic chlorite rosettes, hairy illite/smectite mixed-layers and quartz overgrowths form the common diagenetic products in this sandstone (core 1-64).

Figure 4.1d - A closer look at fibrous (hairy) illite/smectite mixed-layers in the virgin core (1-64).

mud. The sepiolite-based fluids are not therefore expected to cause formation damage any more than other clay-based fluids.

V. SUMMARY AND CONCLUSIONS

Attapulgite and sepiolite fluids with and without the addition of chlorides or hydroxides of Na, K, Ca, and Mg have been autoclaved in the temperature range 300–800°F. The rheological properties of these autoclaved fluids have been examined. The mineral reactions occurring in these fluids at the high temperatures have been determined by x-ray diffraction and analytical electron microscopy. The changes in the rheological properties have been correlated with the mineralogical reactions in the fluids. New fluids have been formulated for use in geothermal drilling.

Attapulgite-Based Fluids

Attapulgite with a fibrous morphology is observed to convert with the high temperature into a smectite with a thin film or platy morphology. This conversion has a paramount effect on the rheological properties of the fluid. Table 5.1 summarizes the high temperature reactions of the attapulgite fluids. Attapulgite starts to convert to smectite at 300°F, though in very small quantities. Appreciable amounts of smectite develop in the fluid during the autoclaving process at 400 and 500°F. When the chlorides are added at 1% concentrations to the fluids, the promoting effect of the cations on the attapulgite-to-smectite conversion rate seems to be $Mg > Ca > Na > K$ within the intermediate temperature range up to 500°F. When the hydroxides are added at 1% concentrations, the divalent cations (Mg, Ca) show a much higher promoting effect than monovalent cations (Na, K). At and above 600°F all the attapulgite disappears from

Table 5.1

Summary of the x-ray diffraction data on the attapulgite fluids which were autoclaved at various temperatures with the addition of chlorides or hydroxides of Na, Ca, and Mg.

Fluid	autoclaved at temperature & pressures in °F/PSI	°C/bars	% smectite formed during autoclaving	Other minerals formed
ATTAPULGITE/H ₂ O	300/10,000	149/690	+	
	400/10,000	204/690	30	
	500/10,000	260/690	60	
	600/10,000	316/690	80	
	700/16,000	371/1,104	100	Si-SPHERE
	800/16,000	427/1,104	100	Si-SPHERE
ATTAPULGITE/NaCl	300/10,000	149/690	10	
	400/10,000	204/690	40	
	500/10,000	260/690	65	
	600/10,000	316/690	90	
	700/16,000	371/1,104	100	Si-SPHERE, FELD
	800/16,000	427/1,104	100	Si-SPHERE, FELD
ATTAPULGITE/KCl	400/10,000	204/690	20	
	500/10,000	260/690	70	
	600/10,000	316/690	80	I/S ILLITE
	700/16,000	371/1,104	70	ILLITE, I/S
	800/16,000	427/1,104	10	ILLITE, I/S
ATTAPULGITE/MgCl ₂	400/10,000	204/690	45	
	500/10,000	260/690	95	
	600/10,000	316/690	100	
	700/16,000	371/1,104	100	Si-SPHERE
	800/16,000	427/1,104	100	Si-SPHERE
ATTAPULGITE/CaCl ₂	400/10,000	204/690	60	
	500/10,000	260/690	90	
	600/10,000	316/690	100	
	700/16,000	371/1,104	100	Si-SPHERE
	800/16,000	427/1,104	100	Si-SPHERE
ATTAPULGITE/NaOH	400/10,000	204/690	30	FELD
	500/10,000	260/690	30	FELD
	600/10,000	316/690	45	FELD

Table 5.1 -continued-

ATTAPULGITE/KOH	400/10,000	204/690	+	ILLITE
	500/10,000	260/690	-	ILLITE, K-Si-H, I/S
	600/10,000	316/690	-	ILLITE, K-Si-H, I/S
ATTAPULGITE/Mg(OH) ₂	400/10,000	204/69	70	
	500/10,000	260/690	85	
	600/10,000	316/690	90	
ATTAPULGITE/Ca(OH) ₂	400/10,000	204/690	50	CSH
	500/10,000	260/690	60	CSH
	600/10,000	316/690	70	CSH

Si-SPHERE: silica sphere

FELD : feldspars

I/S : illite/smectite mixed-layers

K-Si-H : hydrated potassium silicate

CSH : hydrated calcium silicate (tobermorite)

+: present but below 5% level

the fluids. The newly formed smectites become the main ingredients of the fluids except in the presence of KCl or KOH. In the attapulgite/KOH fluid no smectite forms but an illite with high magnesium and iron content does. In the attapulgite/KCl fluid, smectite develops at and below 500°F, but illite/smectite mixed-layers and illite develop above 600°F. The smectites formed at intermediate temperature (below 600°F) consist of thin films which are often grown around the original attapulgite fibers. The smectites formed at and above 600°F develop a platy morphology and contain large amounts of Mg and Al in their structures. These are rather unusual smectites as compared to the natural smectites. Additional mineral phases that form in the fluid are amorphous silica spheres, and hydrated calcium silicates in the attapulgite/Ca(OH)₂ fluid, and hydrated aluminum silicates in the attapulgite/NaOH fluid.

Rheological Properties of the Attapulgite-Based Fluids

The pure attapulgite fluid which was not autoclaved displays a temperature thinning from a viscosity of about 8.5 centipoise at 70°F to 3.5 centipoise at about 350°F. It then goes through a viscosity maximum between 400 to 500°F, which is probably related to the attapulgite-to-smectite conversion. When the pure attapulgite fluids are autoclaved at high temperatures, the fluids become extremely thin except for the one autoclaved at 500°F. This suggests that most of the attapulgite fibers dissolve with high temperatures and the newly formed platy smectites do not give much viscosity or fluid loss control to these fluids. The pure attapulgite fluids are therefore not desirable for a drilling fluid.

The addition of the chlorides to the 70°F fluids depresses their viscosity tremendously. These fluids regain their viscosities when autoclaved at 400 to 600°F. The favorable effect of the cations on the attapulgite/chloride fluids seems to be: Mg > Ca > Na > K, which is very similar to the promoting effect of these cations on the attapulgite-to-smectite conversion. At very high temperatures, (700-800°F) the attapulgite/chloride fluids become extremely thin. All these fluids regardless of the autoclaving temperature show very little of the fluid loss control desirable for a good drilling fluid.

In the presence of hydroxides, the attapulgite fluids show higher viscosities in the following order: Na > Ca > Mg > K. The fluid losses of the attapulgite/MgCl₂ slurries are significantly lower than those of the other fluids. Therefore, the attapulgite/MgCl₂ fluid is probably the best fluid among the attapulgite-based muds.

Sepiolite-Based Fluids

The major mineral reaction in the sepiolite fluids at high temperatures is related to the breakdown of sepiolite fibers and the subsequent formation of smectites. This conversion from sepiolite to smectite seems to be a key factor affecting the rheology of these fluids at high temperatures. The conversion starts at 300°F in very small quantities. The conversion rates at higher temperature and other reaction products are summarized in Table 5.2. Within the intermediate temperature range (300-500°F), the chlorides of Na, K, Ca, and Mg promote the rate of the sepiolite-to-smectite conversion quite differently--Na-ion in the fluid seems to be most effective and Mg-ion the least effective.

Table 5.2

Summary of the x-ray diffraction data on the sepiolite which were autoclaved at various temperatures with the addition of chlorides or hydroxides of Na, K, Ca, and Mg.

Fluids	Autoclaved at temperatures and pressures in		%smectite formed during autoclaving	Other minerals formed
	°F/psi	°C/bars		
SEPIOLITE/H ₂ O	300/475	149/33	+	
	300/10,000	149/690	5	
	400/500	204/35	20	
	500/1,000	260/69	40	
	600/20,000	316/1,379	80	
	700/16,000	371/1,104	60	TALC, TREMOLITE
	800/16,000	427/1,104	40	TALC, TREMOLITE
SEPIOLITE/NaCl	300/475	149/33	+	
	300/10,000	149/690	+	
	400/1,000	204/69	60	
	500/1,000	260/69	70	
	600/20,000	316/1,379	80	Si-SPHERE
SEPIOLITE/KCl	400/10,000	204/690	50	
	500/10,000	260/690	70	
	600/20,000	316/1,379	90	
SEPIOLITE/MgCl ₂	300/475	149/33	+	
	300/10,000	149/690	+	
	400/1,000	204/69	5	
	500/1,000	260/69	40	
	600/20,000	316/1,379	60	
SEPIOLITE/CaCl ₂	300/475	149/33	+	
	300/10,000	149/690	+	
	400/1,000	204/69	20	
	500/1,000	260/69	50	
	600/20,000	316/1,379	80	
	700/16,000	371/1,104	80	TREMOLITE, TALC
	800/16,000	427/1,104	70	TREMOLITE, TALC

Table 5.2 -continued-

SEPIOLITE/NaOH	300/200	149/14	+	
	400/500	204/35	20	
	500/1,000	260/69	70	
	600/10,000	316/690	90	
SEPIOLITE/KOH	400/10,000	204/690	20	ILLITE, I/S
	500/10,000	260/690	+	ILLITE,
	600/10,000	316/690	+	ILLITE
SEPIOLITE/Mg(OH) ₂	300/200	149/14	+	
	400/500	204/35	10	
	500/1,000	260/69	40	
	600/10,000	316/690	90	
SEPIOLITE/Ca(OH) ₂	300/200	149/14	+	
	400/500	204/35	10	
	500/1,000	260/69	30	
	600/10,000	316/690	95	CSH (Tobermorite)

+: Present but below 5% level.

The overall order is $\text{Na} > \text{K} > \text{Ca} > \text{Mg}$. In the sepiolite/hydroxide fluids we observe a different sequence for the promoting effects of the cations on the conversion: $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$. The presence of K in alkaline conditions leads to the formation of illite and illite/smectite mixed-layers. The smectites formed at the intermediate temperature range occur as thin films which often surround the principal sepiolite fibers. At 600°F all the sepiolite in the fluid is practically converted to a smectite. The latter occurs mostly in large aggregates of folded films or in mosaics of platelets. This platy morphology of smectites becomes predominant at very high temperatures (700–800°F). At these very high temperatures talc and tremolite (a fibrous amphibole) also form in the fluid along with the smectites. Other mineral phases that form in the fluid are silica spheres at 600°F in the sepiolite/NaCl fluid and hydrated calcium silicates in the sepiolite/ $\text{Ca}(\text{OH})_2$ fluid.

The effect of high pressure is found to be negligible on the sepiolite-to-smectite conversion as previously explained by Güven and Carney (1979), whereas the high temperature plays the paramount factor on this conversion.

Rheological Properties of the Sepiolite-Based Fluids

The untreated pure sepiolite fluid (70°F) shows a temperature thinning from 70 to 200°F, and it develops a viscosity maximum around 300°F. The pure sepiolite fluids which were autoclaved at 400 and 500°F still show this viscosity "hump" with a smaller magnitude. The fluids autoclaved at and above 600°F show rather low viscosities. The fluid losses of these pure sepiolite slurries are much lower than those of the pure attapulgite slurries.

The fluids prepared with 1% chlorides at room temperatures do not show the viscosity hump. Their overall viscosities become rather low and they uniformly decrease from 70 to 500°F on their FANN 50C rheograms. When these muds were autoclaved at temperatures of 400 to 600°F, the fluids regained their viscosities with cations increasing the viscosity in the following order: $K > Na > Ca > Mg$. The filtrate losses are, however, lower for Na-ion than for K-ion. Thus the sepiolite/NaCl fluid shows rather good rheology for a high temperature drilling fluid. The smectites formed in these fluids seem to give favorable properties to them. At very high temperatures (700 and 800°F) these fluids become extremely thin. The sepiolite/hydroxide fluids show extremely good rheology in the temperature range 70-600°F, except for $Ca(OH)_2$. The favorable effects of the cations on the rheology can be given in the following sequence: $Na > Mg > K > Ca$. The sepiolite/KOH fluid becomes extremely thin when autoclaved at 500 and 600°F. This is related to the formation of illite and illite/smectite mixed-layers instead of smectite at these temperatures. The fluid losses for these slurries are lower for Na- and Mg-ions and extremely high for Ca-ion. Thus the sepiolite/NaOH seems to be the best fluid among the sepiolite-based fluids. The initial apparent viscosities of the sepiolite/NaOH fluids are between 25 and 40 centipoise and they steadily decrease to about 5-10 centipoise at 500°F on their FANN 50C rheograms. In addition to its acceptable rheology, the sepiolite/NaOH fluid possesses low API and HP-HT filtrate losses. Furthermore yield points and gel strengths remain high with the increasing temperatures.

In conclusion the sepiolite-based fluids display significantly better rheologies and fluid loss controls than the corresponding attapulgite-

based fluids. We need, however, to decrease the fluid losses for the sepiolite slurries in order to make them usable for the high temperature drilling. For this purpose new fluids have been formulated by adding polymers, English Mica, and Wyoming bentonite to the sepiolite fluids.

New Fluid Formulations

Low and high molecular weight Na-polyacrylates (SPA'a) have been added to sepiolite and attapulgite fluids. The sepiolite/SPA's fluid displays better high-temperature rheology and fluid loss control than the attapulgite/SPA's fluid. The sepiolite/SPA's is further improved with the addition of English Mica. Two geothermal drilling fluids "GDF-1" and "GDF-2" are formulated by adding Wyoming bentonite to the sepiolite/SPA's fluid. The presence of Wyoming bentonite gives a good substrate for filter cake formation and tightness. This fluid exhibits excellent rheology up to 800°F. The effect of the inert drilled solids on this fluid is tested by adding English Mica to the fluid. Furthermore KOH has been added to control pH and to decrease the viscosity at the elevated temperature. KOH was also found to form new minerals in the fluid, which drastically increases the fluid loss at 700 and 800°F. Thus the fluid "GDF-2" has been recommended as the best geothermal drilling fluid. The rheology and the fluid loss of this fluid can be controlled by Na-polyacrylates and KOH at elevated temperatures through 600°F. If thinning is needed then more of low molecular weight Na-polyacrylates and KOH can be added to the fluid. If more viscosity and lower fluid loss are required, then the amount of high molecular weight Na-polyacrylates in the fluid can be increased. At temperatures of 700°F and above, the additives KOH

and English Mica can be deleted so that the "GDF-1" composition will be used. Another fluid known as HTM-1 contains brown coal and NaOH in addition to sepiolite/Wyoming bentonite/SPA's. With coals and lignites we often experience the evolution of the dangerous gases such as CO_2 and H_2S which may cause serious problems. In addition the rheology of the HTM-1 mud is found to be inferior to the above geothermal drilling fluid.

Possible formation damage caused by sepiolite-based fluids has been examined in cores subjected to circulation and stagnation with the sepiolite fluids. No sepiolite and bentonite particle has been found to invade the cores from the drilling fluid. Thus the sepiolite-based fluids are not therefore expected to cause formation damage any more than other clay-based fluids.

REFERENCES

- Carney, L.L. and Meyer, R.L. (1976) A new approach to high-temperature drilling fluids: SPE Paper No. 6025 presented at the SPE 51st Annual Technical Conference, New Orleans, 1976.
- Carney, L.L. (1975) "Completion Fluids," Chapter IV in Halliburton Institute of Technology Text.
- Carney, L.L. and Güven, N. (1980) Investigation of changes in the structure of clays during hydrothermal study of drilling fluids. SPE Journal October 1980, pp. 385-390.
- Ennis, D. O. Bergosh, J.L., Butters, S.W., and Jones, A.H. (1979) Drilling fluid/formation interaction at simulated in situ geothermal conditions: Final report of Sandia Contract # 13-9407.
- Güven, N. and Carney, L.L. (1979) The hydrothermal transformation of sepiolite to stevensite and the effect of added chlorides and hydroxides: Clays and Clay Minerals Vol. 27, pp. 253-260.
- Remont, L.J. (1977) Maurer Engineering's Geothermal drilling fluids project: in "Conference on Geothermal Drilling Fluids" sponsored by DOE/DGE pages 33-42.
- Savins, J.G. and Roper, W.F. (1954) A direct indication viscometer for drilling fluids, API Drill. Prod. Prac., pp. 7-22.
- Wyant, R. (1975) A unique system for preparation and evaluation of high temperature drilling fluids" , SPE Paper No. 5515, September 1975.

ACKNOWLEDGEMENTS

This work was made possible primarily through the grant 13-5104 by Sandia National Laboratories, Albuquerque, New Mexico. Center for Energy Research of Texas Tech University provided us with some additional funds for support of this project. Special thanks are due to Mr. Reece Wyant of Dresser-Magcobar for making the flow loop runs and to Mr. Bryce King, manager of Fann Instrument Operations, Dresser Magcobar for his personnel attention in setting up the FANN 50C Viscometer at Texas Tech University.

DO NOT MICROFILM

DISTRIBUTION:

TID-4500-R66-UC-66c (507)

Tom Anderson
Venture Innovations
P.O. Box 35845
Houston, Texas 77035

Ed Bingman
Shell Oil Company
Two Shell Plaza
P.O. Box 2099
Houston, Texas 77001

Larry Diamond
Dyna-Drill
P.O. Box C-19576
Irvine, California 92713

Tom Turner
Phillips Petroleum Company
Geothermal Operations
655 East 4500 South
Salt Lake City, Utah 84107

Jim Kingsolver
Geothermal Operations
Smith Tool
P.O. Box C-19511
Irvine, California 92713

John C. Rowley
Los Alamos National Labs
Mail Stop 570
Los Alamos, New Mexico 87545

Ed Martin
Superior Oil
Eastern Division
P.O. Box 51108 OCS
Lafayette, Louisiana 70505

B. J. Livesay
129 Liverpool
Cardiff, California 92007

Gene Polk
NL Baroid
6400 Uptown Blvd. N.E., 365W
Albuquerque, New Mexico 87110

James W. Langford
Security Division
Dresser Industries, Inc.
P.O. Box 24647
Dallas, Texas 75224

John E. Fontenot
NL Petroleum Services
P.O. Box 60087
Houston, Texas 77205

Del E. Pyle
Union Geothermal Division
Union Oil Co. of California
Union Oil Center
Los Angeles, California 90017

William D. Rumbaugh
Research & Development
Otis
P.O. Box 34380
Dallas, Texas 75234

Dwight Smith
Halliburton
Drawer 1431
Duncan, Oklahoma 73533

Tom Warren
Amoco Production Company
Research Center
P.O. Box 591
Tulsa, Oklahoma 74102

H. E. Mallory
P.O. Box 54696
Tulsa, Oklahoma 74155

DISTRIBUTION cont.

Dr. Melvin Friedman
Professor of Geology
Center for Tectonophysics
and Dept. of Geology
Texas A&M University
College Station, Texas 77843

Dr. Necip Guven (10)
Dept. of Geosciences
Texas Tech University
Lubbock, Texas 79409

U.S. Department of Energy (4)
Geothermal Hydropower
Technologies Division
Forrestal Bldg., CE 324
1000 Independence Ave. S.W.
Washington, D.C. 20585
Attn: J. Bresee
D. Clements
R. Toms
D. Allen

W. P. Grace, DOE/ALO
Nuclear & Geosciences Division

3141 L. J. Erickson (5)
3151 W. L. Garner (3)
9000 G. A. Fowler
9700 E. H. Beckner
9730 W. D. Weart
9740 R. K. Traeger
9741 J. R. Kelsey (10)
9741 C. C. Carson (10)
9746 B. Granoff
9747 P. J. Hommert
9750 V. L. Dugan
9760 R. W. Lynch
8214 M. A. Pound