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Factors Affecting the Behavior of Bentonite Fluids and Their In-Situ Conversion Into Cement

Final Report

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by

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ABSTRACT

Bentonite is the common viscosifier and fluid loss control additive in water base drilling fluids. Bentonite, however, creates its own problem due to gelation at high temperatures while drilling, completing, or cementing deep oil and gas wells or geothermal wells. Furthermore mud contamination from the formation solids and formation fluids may also affect the performance of bentonite muds. It is therefore rather important to develop a basic understanding of the effects of common salts, hydroxides, and other mud additives on the rheology and other functions of bentonite fluids. For this purpose, bentonite fluids containing these additives were autoclaved at the temperature range 70 to 600°F, and under a pressure of 17,000 psi. Subsequently, the high-temperature rheology of the fluids was measured with a FANN 50C viscometer. Other fluid properties such as plastic viscosity, gel strength, yield point, pH, CEC, and fluid losses were also determined before and after autoclaving of the fluids. The high-temperature reactions occurring in these fluids were studied with x-ray diffraction and electron microscopy.

A pure Na-bentonite fluid becomes highly viscous in the temperature range 250-450°F, leading to the gelation of the fluid when bentonite concentration reaches about 4% in the fluid. The addition of low molecular weight polymers seems to control the viscosity only in the limited temperature range 300-400°F, but not at higher temperatures. NaCl or NaOH at 1% concentration in the fluid tremendously increases the "osmotic" swelling of the bentonite and hence increases the fluid viscosity to undesirably high values. Potassium salts and hydroxide effectively control the fluid gelation at high temperatures by promoting the conversion of (swelling) smectite in the fluid to a (less-swelling) phase of illite/smectite mixed-

- layers. Salts and hydroxide of calcium depress the fluid viscosity at all temperatures.

Another costly problem in drilling technology is related to the poor cement bonding of the casing to the formation. As a solution to this troublesome situation, the in-situ conversion of bentonite fluids into cement has been studied. This conversion has been successfully achieved by the addition of lime to bentonite fluids at and above 300°F.

The addition of lime increases the fluid pH and promotes the high-temperature reaction between lime and smectite. Consequently, tobermorite, which is a cement mineral, precipitates in the fluid. The addition of free silica to the bentonite/lime fluid does not increase the rate of tobermorite precipitation. The addition of CaCl_2 , however, to the bentonite/lime fluid enhances the in-situ formation of cement minerals in bentonite fluid. The addition of magnesia proves to be detrimental both to the cement conversion and to the rheology of the fluid but it provides a buffer for maintaining high pH in the fluid. Lignosulfonates do not seem to cause any noticeable retardation of the cement reactions in bentonite/lime fluids.

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EXECUTIVE SUMMARY

The behavior of bentonite fluids has been systematically studied under high temperatures and high pressures similar to the down-hole conditions in deep wells or in geothermal wells. The effects of various salts, hydroxides and other mud additives have been examined on the properties of the bentonite fluids under the above conditions. The in-situ conversion of bentonite fluids into cement has been studied in order to improve the displacement of drilling fluids by cement slurries.

The purpose of these investigations was to ascertain a full understanding of the viscosity changes (including gelation) in bentonite based fluids under down-hole conditions with temperature, pressure, and time. The down-hole conditions were simulated by an autoclave in the laboratory. Since the problems with drilling fluids usually arise near the bottom of the borehole during static conditions, the autoclaving process was a static one without the agitation. The static autoclave had also the advantages of safety and economy. The bentonite fluids have been autoclaved at temperatures ranging from 300°F to 600°F under the appropriate confining pressures up to 16,000 psi. Subsequently, the fluids were prepared in the presence of salts and hydroxides of Na, K, Ca, and Mg, and other mud additives. The properties of the fluids such as apparent and plastic viscosity, gel strength, yield point, pH, CEC, and fluid losses were determined before and after autoclaving. The changes in the nature of smectites (its hydration state, morphology, and mode of aggregation) and other mineral reactions in these fluids have been studied with x-ray diffraction and electron microscopy. The results revealed a close relationship between the properties of the fluids and the mineral reactions in them. These reactions occur

between smectite particles of the bentonites and the additives in the fluids. These reactions involve:

- a) changes in the morphology of clay particles (smectite),
- b) changes in the state of hydration of smectites,
- c) dissolution of smectites, and
- e) precipitation of new mineral phases that are either detrimental or inert to the rheology of the fluid.

Our investigations have shown that the above reactions involving smectite in bentonite were the causes of the problems that have been experienced over the years while drilling deep and hot wells with the bentonite fluids. A pure bentonite fluid with a Na-smectite as the main constituent becomes gelated (highly viscous) in the temperature range 250-450°F. The low molecular polymer additive (a Cypan-type sodium polyacrylate with a molecular weight of 940-1,400) is found to control the gelatin in the temperature range of 300-400°F but not at higher temperatures. On the other hand, high molecular weight polymers (a sodium polyacrylate with a molecular weight in the range of 750,000 to one million) are found to control the gelation of the bentonite at temperatures as high as 600°F. Thus, by carefully selecting the relative amounts of low molecular and high molecular polymers, a bentonite fluid can be designed to give satisfactory performance at low and high temperatures.

Interlayer cations of the smectites can be easily exchanged by other cations which may predominate the fluid due to mixing with formation brines or solids, or due to the mud additives. The rheological behavior of the bentonite fluids is found to be extremely sensitive to the exchangeable cations in the fluid. Sodium hydroxides, especially NaCl, at 1% concentration in the fluid causes the gelation of the fluid up to 500°F since

the Na-ion increases the "osmotic" swelling of the smectite particles. The presence of free silica (1%) in the fluid greatly depresses the viscosity due to the precipitation of silicates such as analcime and albite. These silicate precipitations may cause permeability damage in the formation. Salts and hydroxides of potassium are found to be very effective in controlling the gelation of bentonite at high temperatures. This is related to the conversion of smectite to illite/smectite mixed-layers at and above 400°F.

The viscosity of the bentonite fluids is greatly reduced by Ca-ions that enter into the smectite interlayers by an ion-exchange reaction. Salts and hydroxides of calcium, therefore, depress the fluid viscosity to unacceptably low levels at all temperatures. For instance, the high-temperature viscosity of a 6% bentonite/1% lime fluid is extremely low even before the autoclaving as shown in Figure I.1. The viscosity of the fluid was raised to an acceptable level only after increasing the bentonite concentration to 10%.

Another costly problem in drilling geothermal and deep wells involves the displacement of the mud by a cement slurry after the casing is placed. It is again the characteristics of bentonite that cause channeling of cement slurries and the difficulty in displacement of the mud. To eliminate these problems, the in-situ conversion of bentonite fluids has been attempted by the addition of lime. The presence of lime is found to increase the fluid pH which dissolves the smectite and subsequently leads to a reaction between lime and silica. Tobermorite, a common cement mineral, forms as the reaction product at and above 300°F. The addition of free silica to the bentonite/lime fluid does not increase the rate of this cement reaction. However, the presence of CaCl_2 in the bentonite/lime

Figure I.1 - The FANN 50C rheograms of the bentonite/1% lime fluids at various bentonite concentrations before the autoclaving.

fluid enhances the in-situ formation of cement minerals. Lignosulfonates do not retard the cement reaction in the bentonite/lime fluids. No cement minerals form when magnesia is added to the bentonite/lime fluid.

INTRODUCTION

While Wyoming bentonite has been used for many years to obtain viscosity and thixotropy of drilling fluids, the intricate reaction mechanisms of bentonite have not been studied in detail until now. Thousands of wells have been drilled using bentonite fluids and a number of bentonite-related problems has been experienced during the drilling, cementing, completion, or production of these wells. These problems may become a major obstacle while drilling geothermal wells or while drilling in deeper formations with high temperatures and under high pressures. Two of these problems are found to be rather common and costly: a) high temperature gelation of bentonite-based muds, b) poor cement jobs behind casing after the borehole has been drilled and casing has been cemented in the well-bore.

The gelation of the mud creates problems with regard to circulation, running logging tools, casing, and to the displacement of mud by completion fluids and cement slurries. Various attempts were made to improve the efficiency of displacement of drilling fluids by cement slurries. But no success has been achieved in increasing the efficiency or in even obtaining a good bond between the casing and the formation.

The investigations under the Sandia contracts #68-4752 and 32-2331 were therefore designed to obtain basic data on the bentonite fluids with the above problems in mind. Specifically, the objectives of the projects were:

1. To understand the conditions leading to high-temperature gelation of bentonite muds.
2. To find remedies to control high-temperature gelation so that a desirable drilling and cement job can be done.

3. To study the following factors which either promote or retard the formations of cement minerals in bentonite/lime fluids:

- * Lime/silica concentrations
- * Temperature
- * pH
- * Lignosulfonate
- * Gypsum
- * MgO

In order to develop a basic understanding of the above troubles with bentonite fluids and with related cement setting, the following fluid systems were studied:

- A. Bentonite fluids containing salts and hydroxides of sodium and potassium or polymers.
- B. Bentonite fluids containing lime and silica for the purpose of understanding the in-situ conversion of the bentonitic fluids into cement.
- C. Effects of additives on cement reaction in bentonitic drilling fluids:
 - a) Bentonite/lime/ CaCl_2 fluid
 - b) Bentonite/lime/gypsum fluid
 - c) Bentonite/lime/lignosulfonate fluid
 - d) Bentonite/lime/MgO fluid.

The above bentonite-based fluid systems have been autoclaved at temperatures ranging from 300°F to 600°F. The properties of these fluids have been measured before and after autoclaving. The high temperature mineral reactions in these fluid systems have been studied with x-ray diffraction

and analytical electron microscopy. The results are described in this report.

Methods of Investigations

Bentonite fluids were autoclaved at the temperature range 300-600°F. The autoclave with a cell of 500 ml capacity was manufactured by Autoclave Engineers, Erie, Pennsylvania. The cell was statically heated at a rate of 150°F/hour to the desired temperature and the pressure was initially produced by a Haskel air-driven liquid pump. Temperature and pressure were monitored and automatically recorded. The autoclave was cooled in air for 14 hours. The fluid, after autoclaving, was transferred from the cell into a plastic bottle for subsequent testing with various viscometers (FANN 50C, FANN 35A, and SANDIA) and a Baroid standard filter press. The temperature was maintained for 6 hours by a temperature controller with the Barber-Colman analog and digital set point controller.

The high-temperature viscosity of the fluids was usually measured with a FANN 50C viscometer and a few occasional tests were run with SANDIA viscometer. The FANN 50C viscometer is equipped with a standard rotor cup with a sample capacity of 50 ml and rotor cup speed of 0-600 RPM. 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 were maintained at 650 psi using nitrogen gas. The viscosity/temperature variations are given in the form of rheograms for each fluid. Other fluid properties such as plastic viscosity, gel strength, and yield point were measured at room temperature and atmospheric pressure with a FANN 35A viscometer. This instrument is a direct reading viscometer that gives the plastic viscosity and yield point directly from the two dial readings at 300 RPM and at 600 RPM. Similarly, gel strengths were determined by dial readings at 3 RPM first after a run for 10 seconds then the second reading after 10 minutes. The gel strengths are reported in pounds per 100 square feet.

The fluid loss properties of the samples were measured by a Baroid Standard Filter Press when the bentonite concentrations were high enough for a meaningful measurement. The Baroid Filter Press consists of a fluid cup, a filtering medium, a pressurized nitrogen gas cylinder and regulator. The filter test was run for 30 minutes under a pressure of 100 psi or until blow-out occurred, at which time the test was stopped and the filtrate was measured.

The mineral phases in the fluids were examined, before and after autoclaving, with x-ray diffraction and analytical electron microscopy. For the x-ray diffraction, oriented clay films were prepared on glass slides from the fluids. The excess salts, hydroxides, and other soluble additives were washed off by centrifugation of an aliquot of each fluid. The oriented clay films were x-rayed upon air-drying and subsequently upon saturation with ethylene glycol. A Phillips x-ray diffractometer equipped with a graphite monochromator and adjustable divergence slit was used for this purpose.

After identification of high-temperature mineral reactions in the autoclaved fluids with x-ray diffraction, the characteristic features of individual solid particles were examined with a JEM-100 CX Analytical Electron Microscope. This instrument allowed us to use the following signals, generated by the interaction of electrons with solid particles:

- transmitted electrons which form transmission electron (TEM) images and selected area diffraction (SAD) patterns,
- secondary electrons which form SEM images of the surface features of the solid particles, and
- characteristic x-rays which give us the elemental spectral data related to the chemistry of the individual particles. Details of

the energy-dispersive spectral analysis were given in our previous Sandia Report (SAND 82-7032). The intensities of x-ray spectra were counted for 100 seconds in the "area" mode in which a selected area was scanned with the electron probe. The intensity data were collected and processed by an EG&G ORTEC EEDS II analyzer. Since silicon is a major element in most of the mineral particles, all the intensity data for the x-ray spectra were normalized with reference to the intensity of Si-K line. The Cu- and Au-lines in the graphs of the x-ray spectra are related to the sample holder and to the sample coating metal respectively.

I. BEHAVIOR OF THE BENTONITE-BASED FLUIDS AT HIGH TEMPERATURES

1. Pure Bentonite Fluid

The bentonite component of the water-base muds is the main viscosifier and fluid loss control additive in these muds. In order to understand the fundamental role of bentonite on the fluid rheology and its other properties, we first examined purified bentonite fluids. Bentonite fluids were usually prepared by using the raw bentonite, which contains other minerals, such as mica, quartz, feldspars, calcite and gypsum, in addition to the major component of a smectite. It is, of course, the latter clay mineral that generates the desirable properties of the fluid regarding its rheology and fluid loss control. In order to follow directly the contributions of the smectite component, we prepared a purified Wyoming bentonite with 98% smectite, which is a Na-montmorillonite variety in this bentonite. The purified Wyoming bentonite was obtained from the Baroid Division of NL Industries (Houston). It was noted that the viscosity of the purified bentonite becomes high with increasing temperatures and turns the mud into a gel even at a 4% bentonite concentration of the initial mud. We, therefore, reduced the clay concentration to 2% in order to keep them in a fluid state at high temperatures.

The high temperature viscosities and the other properties of the 2% purified Na-bentonite fluids before and after autoclaving in the 300-600°F range are given in Figure 1.1a and in Tables 1.1a and 1.1b. The untreated fluid under the constant 650 psi pressure of FANN 50C shows a significant thickening at 100°F. It reaches a maximum at about 400°F, and thins gradually up to 500°F. The viscosity profile of the untreated 2% bentonite fluid is found to be rather different under higher pressures. Figure 1.1b

Figure 1.1a - The FANN 50C rheograms of the pure 2% bentonite fluids after autoclaving at the temperatures marked on the curves.

TABLE 1.1a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% PURIFIED BENTONITE

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	6.2	7.7	11.8	21.8	28.9
100	3.9	6.4	8.7	16.4	25.6
150	3.1	4.1	5.8	12.5	19.3
200	3.0	2.7	4.5	9.5	15.4
250	4.3	1.9	3.7	7.7	14.95
300	6.9	2.0	4.2	7.7	18.7
350	9.8	3.1	4.5	7.4	20.4
400	10.4	3.0	2.9	4.4	18.9
450	8.2	2.6	3.3	2.7	15.5
500	7.7	2.7	10.0	6.2	10.8

TABLE 1.1b
 PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 2% PURIFIED BENTONITE

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	6	10	20	38	49
Plastic Viscosity (centipoise)	4	8	13	20	19
Yield Point (lb/100 sq ft)	3	4	14	36	50
Gel Strength (lb/100 sq ft)**	1/7	2/2	3/3	9/10	14/15
API Filtrate (ml/30 min.)*					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	8.2	7.6	7.4	7.2	6.8
CEC (milliequivalents/100 gms)	125	125	125	100	25

*Due to the low clay content (2%) of the fluid, the measurements of API filtrate, cake thickness, and HP-HT filtrate were not feasible. These entries are left blank in this and the other tables. Gel Strengths were determined as explained in the text.

**The first number before the slash refers to the gel strength after 10 seconds and the second number (following the slash) to the gel strength after 10 minutes.

shows the viscosity changes of the 2% purified bentonite fluids under the pressures up to 12,000 psi as obtained with the SANDIA viscometer. The fluid viscosity is, in general, increased by high pressure, whereas the high temperature causes a thinning of the fluid. The untreated (70°F) bentonite fluid shows steadily higher viscosity with increasing temperatures and pressures in Figure 1.1b as compared with its viscosity curve in Figure 1.1a under a constant pressure of 650 psi. The viscosity hump is drastically reduced with the pressures above 4,000 psi. The bentonite fluids which were autoclaved at 300 and 400°F show a drastic thinning up to 375°F and 5000 psi, but they all show a similar increase in viscosity with increasing pressures and temperatures (Figure 1.1b).

The above results clearly indicate that the pure Na-bentonite swells tremendously above 200°F and develops a viscosity hump in the temperature range 250 to 450°F when the pressures are kept low. This viscosity hump has been demonstrated with the increase of clay concentration to a more realistic value such as 6%. Figure 1.1c shows this viscosity hump for a 6% purified bentonite fluid whose initial pH was adjusted to 6.5 with formic acid. At this concentration the viscosity of the fluid is about 90 centipoise at 70°F and it rises to about 300 cp at 250°F. In the range 250-400°F it becomes a thick gel for which we could not measure the viscosity. The viscosity drastically decreases from 300 cp at 400°F to about 40 cp at 500°F. For the 2% bentonite fluids which were autoclaved at 300, 400, and 500°F, this viscosity "hump" is relatively depressed as indicated by the viscosity data in Figure 1.1a and in Tables 1.1a and 1.1b. The viscosity "hump" becomes again very distinct after the fluid was autoclaved at 600°F (Figure 1.1a).

Figure 1.1b - The rheograms of the pure 2% bentonite fluids after autoclaving at the temperatures marked on them.

Figure 1.1c - The FANN 50C rheogram of a 6% bentonite fluid with an initial pH = 6.5.

The other properties of the 2% purified bentonite fluids are given in Table 1.1b. Due to the extreme low concentration, there is not enough clay to form a measurable filter cake. Therefore, no meaningful fluid loss values can be obtained. Plastic viscosity and yield point of the fluid show a large increase with the high-temperature treatments (Table 1.1b). The gel strength shows a major jump from 70 to 300°F; and it remains almost unchanged thereafter. The pH and CEC values show a significant decrease with the higher temperatures.

X-ray Diffraction Analysis

The purified NL bentonite consists of a Na-smectite (montmorillonite) with a 11.3 Å basal spacing in air-dried state. It fully expands to 17 Å upon glycol saturation. No changes in the basal spacing of smectite were observed upon autoclaving at the temperature range 300-600°F in distilled water.

Electron Microscopic Data

The original smectite particles consist of well-dispersed thin films or aggregates of such folded films. Those morphological features remain unchanged after autoclaving the fluid at 300 and 400°F as illustrated in Figures 1.2 through 1.4. The thin smectite films seem to disintegrate into smaller pieces after autoclaving the fluid at 500°F as displayed in Figure 1.5. Lath-like particles are also found in small quantities at this temperature (Figure 1.6a-1.6b). The lath-shaped particles become the predominant components of the fluid after autoclaving at 600°F. In addition, there are small amounts of thin smectite films. Figures 1.7 through 1.10 display common forms of the lath-shaped smectite particles in the fluid. The x-ray spectra obtained from the laths show very little Mg and

Figure #: 1.2

Fluid: Bentonite/H₂O/300°F

Magnification: 17,000 X

Film #: 3178

Description:

A typical smectite aggregate consisting of curled thin films in the autoclaved fluid. The x-ray spectra obtained from the smectite film are listed below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Mg	223	.03
Al	2556	.30
Si	8521	1.00
Fe	541	.06

Figure #: 1.3

Fluid: Bentonite/H₂O/400°F

Magnification: 35,000 X

Film #: 3182

Description:

A close view of the smectite thin films in the bentonite fluid after autoclaving at 400°F.

Figure #: 1.4

Fluid: Bentonite/H₂O/400°F

Magnification: 17,000 X

Film #: 3181

Description:

Typical smectite particles showing fluffy morphology and thin films in the fluid which was autoclaved at 400°F.

Figure #: 1.5

Fluid: Bentonite/H₂O/500°F

Magnification: 14,000 X

Film #: 3185

Description:

Commonly observed smectite particles consisting of thin films. Some of the films are broken into smaller pieces after the reaction.

Figure 1.6a

Fluid: Bentonite/H₂O/500°F

Magnification: 27,000 X

Film #: 3187

Description:

A fluffy smectite aggregate showing lath-like extensions developed in the autoclaved fluid.

Figure #: 1.6b

Fluid: Bentonite/H₂O/500°F

Magnification: 27,000 X

Film #: 3188

Description:

Another smectite aggregate showing three sets of laths.

Figure #: 1.6c

Fluid: Bentonite/H₂O/500°F

Magnification: SAD

Film #: 3189

Description:

The selected area electron diffraction pattern obtained from the lath shown in Figure 1.6b. The following unit-cell parameters are obtained from the pattern:

$$\underline{a} = 5.22 \text{ \AA}$$

$$\underline{b} = 8.97 \text{ \AA}$$

Figure #: 1.7

Fluid: Bentonite/H₂O/600°F

Magnification: 27,000 X

Film #: 3192

Description:

Sets of laths which are developed in the fluid auto-claved at 600°F. The minute hexagonal crystals contain Fe, Al, and Si in their composition.

Figure #: 1.8

Fluid: Bentonite/H₂O/600°F

Magnification: 14,000 X

Film #: 3195

Description:

Commonly observed smectite laths and thin smectite films. The laths develop in two sets which are 120° apart.

Figure #: 1.9

Fluid: Bentonite/H₂O/600°F

Magnification: 36,000 X

Film #: 3196

Description:

A magnified view of the smectite laths from the above micrograph. The x-ray spectra of these laths are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Mg	60	.01
Al	2570	.40
Si	6468	1.00
Fe	346	.05
Na	145	.04
Ca	143	.02

Figure #: 1.10a

Fluid: Bentonite/H₂O/600°F

Magnification: 45,000 X

Film #: 3198

Description:

Image of an elongated smectite platelet which has formed in the fluid during the autoclaving process.

Figure #: 1.10b

Fluid: Bentonite/H₂O/600°F

Magnification: SAD

Film #: 3197

Description:

The selected area electron diffraction pattern from the smectite particle shown above. The following unit-cell parameters are obtained from the pattern:

$$\underline{a} = 5.21 \text{ \AA}$$

$$\underline{b} = 8.98 \text{ \AA}$$

K, indicating a beidellite-like composition. Furthermore, the selected area electron diffraction data in Figures 1.6c and 1.10b indicate a 1M polymorph for these beidellite laths.

2. Bentonite/Polymer Fluids

High and low molecular weight sodium polyacrylates (SPA) are common fluid additives mainly for the purpose of fluid loss control. A CYPAN-type SPA with a molecular weight in the range of 750,000 to 1,000,000 was used as the high molecular weight polymer. The low molecular weight SPA had a molecular weight of 940-1,400.

High Molecular Weight Polymer

The fluid consisting of 2% bentonite and 0.25% high molecular weight polymer shows a considerably higher viscosity (Figure 1.11) below 300°F as compared with the pure 2% bentonite fluid. However, when this fluid is autoclaved at or above 300°F, it becomes extremely low in viscosity (Figure 1.11 and Tables 1.2a and 1.2b). Plastic viscosity, yield point, and gel strength of the fluid decrease drastically at and above 300°F. Both pH and CEC values steadily decrease with the increasing temperatures. Thus, the above data clearly indicate that the high molecular weight polymer seems to control the fluid viscosity like a thinner in the fluid at temperatures 300°F and above.

Low Molecular Weight Polymer

Because of the thinning effect of this polymer, we increased the bentonite concentration of the fluid to 6%. In fact, the addition of 0.25% low molecular weight polymer to the 6% bentonite fluid eliminated the gelation of the fluid and kept it in a fluid state although with a

Figure 1.11 - The FANN 50C rheograms of the 2% bentonite/0.25% high molecular weight polymer after autoclaving at temperatures marked on the curves.

TABLE 1.2a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 0.25% HIGH MOL. WEIGHT POLYMER

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	19.8	2.7	2.2	1.9	3.3
100	15.5	2.1	1.5	1.3	2.8
150	15.5	1.7	1.1	0.9	2.4
200	14.0	1.4	0.9	0.8	2.2
250	11.1	1.2	0.8	0.6	2.0
300	8.3	1.1	0.7	0.6	1.9
350	6.2	0.9	0.6	0.6	1.7
400	5.3	0.8	0.6	0.6	1.6
450	4.5	0.9	0.7	0.6	1.5
500	4.1	0.8	0.7	0.6	1.3

TABLE 1.2b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 0.25% HIGH MOLECULAR WEIGHT POLYMER

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	20.0	3.5	3.0	2.5	4.0
Plastic Viscosity (centipoise)	16.0	3.0	3.0	2.0	4.0
Yield Point (lb/100 sq ft)	8.0	1.0	0.0	1.0	0.0
Gel Strength (lb/100 sq ft)	4/4	0.5/2	0.5/1	0.5/1	0.5/1
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	7.7	7.5	7.2	7.4	7.2
CEC (milliequivalents/100 gms)	125	100	75	75	50

rather high viscosity. The viscosity of the sample before autoclaving increases drastically above 250°F and reaches a maximum of 166 cp at about 375°F (Figure 1.12 and Tables 1.3a and 1.3b). The typical viscosity hump is again developed since the viscosity drops steeply from 400 to 500°F (Figure 1.12). When the 6% bentonite fluid with 0.25% low molecular weight polymer was autoclaved at 300°F, the viscosity of the fluid drops into a range of 10-30 cp without a viscosity hump. The other properties of the fluid such as gel strength and pH are also significantly lower at 300°F than those of the untreated fluids. However, all these fluid properties including apparent and plastic viscosities increase greatly in the fluids autoclaved at 400°F and above (Figure 1.12). In fact, the fluids autoclaved at 500 and 600°F become a gel and lose their fluid properties. Thus, the low molecular weight polymer does not seem to control the high viscosity of the bentonite fluid at high temperatures.

Figure 1.12 - The FANN 50C rheograms of the 6% bentonite/0.25% low molecular weight polymer after autoclaving at the temperatures marked on the curves.

TABLE 1.3a

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
6% BENTONITE / 0.25% LOW MOLECULAR WEIGHT POLYMER

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	59.0	29.0	85.5		
Plastic Viscosity (centipoise)	4.0	22.5	44.0		
Yield Point (lb/100 sq ft)	37.5	12.5	83.0		
Gel Strength (lb/100 sq ft)	4/4	3/3	10/11	High Viscosity	High Viscosity
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	8.1	6.9	6.7		
CEC (milliequivalents/100 gms)	100	83	75		

TABLE 1.3b

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
6% BENTONITE / 0.25% LOW MOL. WEIGHT POLYMER

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	35.0	27.8	80.0		
100	25.1	19.5	56.9		
150	21.1	14.3	42.6		
200	19.3	11.2	31.4	Very high viscosity	Very high viscosity
250	30.5	10.0	24.9		
300	127.9	12.5	23.7		
350	162.8	15.8	22.8		
400	161.8	16.9	27.6		
450	103.8	22.8	36.1		
500	23.9	23.3	50.9		

II. EFFECTS OF SODIUM CHLORIDE AND SODIUM HYDROXIDE ON THE BENTONITE FLUIDS

1. Bentonite/NaCl Fluid

A 4% bentonite and 1% NaCl fluid exhibits extremely high viscosities with increasing temperatures as shown by the rheograms in Figure 2.1 and by the data in Tables 2.1a and 2.1b. The untreated mud displays a viscosity increase from 32.6 cp at 70°F to 181 cps at 300°F and it shows a similar decrease from the maximum at 300°F to 11.3 cp at 500°F. After autoclaving the fluid at the temperatures 300-500°F, these viscosities are significantly lower although the viscosity hump is still observed. When autoclaved at 600°F the fluid exhibits again very high viscosities. The other properties of the 4% bentonite/1% NaCl fluids are given in Table 2.1b. The pH and CEC values of the fluids show a steady decrease with higher temperatures.

No new mineral phase was detected on the x-ray diffraction analysis of the fluids subjected to high temperature treatments. The large reduction of CEC at higher temperature suggests a possible decomposition (dissolution) of smectite in salt solution at high temperatures.

The addition of NaCl extremely increases the fluid viscosity. Thus NaCl at 1% concentration level seems to promote the "osmotic" swelling of bentonite particles i.e., a maximum up-take of water by them.

2. Bentonite/NaOH Fluid

The addition of bentonite to a 1% NaOH solution inhibited the swelling of the bentonite initially. Therefore, we needed to increase the bentonite concentration to 8% in order to obtain any appreciable viscosity at room temperature. However, as the temperature is raised, the fluid

Figure 2.1 - The FANN 50C rheograms of the 4% bentonite/1% NaCl fluids after autoclaving at the temperatures marked on the curves.

TABLE 2.1a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
4% BENTONITE / 1% NaCl

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	32.6	42.4	92.0	83.1	158.3
100	35.6	35.9	68.7	57.7	114.2
150	58.2	37.4	65.8	56.7	109.7
200	103.8	49.2	75.2	68.5	120.9
250	159.5	55.4	79.1	76.8	115.5
300	181.3	49.8	76.8	73.7	103.8
350	154.3	24.8	47.8	56.1	83.4
400	56.1	n.d.	7.9	12.9	31.2
450	16.5	n.d.	2.7	7.9	19.5
500	11.3	n.d.	1.0	5.6	13.7

becomes highly viscous and reaches a maximum of 267 cps at 300°F as indicated by the viscosity data in Table 2.2a. The rheograms in Figure 2.2 and the data in Tables 2.2a and 2.2b show that the fluid autoclaved at 300°F displays the highest viscosity among the autoclaved bentonite/NaOH fluids. The viscosity declines steadily for the fluids autoclaved at 400 and 500°F. The fluid autoclaved at 600°F becomes extremely thin. The reduction in viscosity of the fluids autoclaved at and above 400°F seems to be related to the dissolution of bentonite and subsequent precipitation of minerals such as analcime and albite. The amount of these new phases becomes larger as the temperature increases. In fact, the CEC values of the fluids similarly show a drastic decline with the increasing temperatures (Table 2.2b). These reaction products are inert for the rheology of the fluid but they form at the expense of smectite in the fluid. Furthermore, they may cause serious permeability damage if they precipitate in the reservoir.

3. Bentonite/NaOH/Silica Fluid

Free silica was added to the previous bentonite/NaOH fluid in order to study the effect of silica on the fluid. For this purpose a fluid composed of a 2% bentonite/1% NaOH/1% silica has been autoclaved in the temperature range 300-600°F. The properties of the untreated and autoclaved fluids are summarized by the rheograms in Figure 2.3 and by the data in Tables 2.3a and 2.3b. The viscosities of these fluids are extremely low and uniform for the untreated as well as for the autoclaved fluids. Similarly, the yield point and gel strengths of these fluids are low as shown in Table 2.3b. Thus, the addition of free silica seems to be a significant factor in controlling the high temperature gelation of the smectite fluid.

TABLE 2.1b
PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
4% BENTONITE / 1% NaCl

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	35.0	51.0	77.0	75.0	127.0
Plastic viscosity (centipoise)	12.5	20.5	32.0	41.5	38.0
Yield Point (lb/100 sq ft)	45.0	61.0	90.0	67.0	178.0
Gel Strength (lb/100 sq ft)	34/48	47/70	57/72	60/67	104/115
API Filtrate (ml/30 min.)		28	24	30	
Cake Thickness (inches)		4/32	6/32	6/32	
HP-HT Filtrate (ml/30 min.)					
pH	7.7	6.8	6.7	6.8	6.8
CEC (milliequivalents/100 gms)	100	63	50	50	50

Figure 2.2 - The FANN 50C rheograms of the 8% bentonite/1% NaOH fluids after autoclaving at the temperatures marked on the curves.

TABLE 2.2a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% NaOH

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	13.7	55.0	30.3	17.9	3.9
100	22.0	19.1	15.6	9.1	2.5
150	51.9	18.7	11.0	6.2	1.9
200	110.9	24.7	9.1	4.7	1.7
250	184.8	43.6	11.0	4.4	1.3
300	267.1	252.5	13.7	5.6	1.2
350	267.1	252.5	16.6	7.3	1.2
400	186.0	62.3	16.4	6.9	1.3
450	45.7	13.3	8.2	2.9	1.4
500	17.4	2.1	5.0	1.3	1.2

TABLE 2.2b
 PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 8% BENTONITE / 1% NaOH

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	4.5	69.5	41	53	4.5
Plastic Viscosity (centipoise)	2.5	37.5	32	34	3.0
Yield Point (lb/100 sq ft)	3.0	63.5	18	38	2.0
Gel Strength (lb/100 sq ft)	3/4	47/64	4/5	6/7	1/2
API Filtrate (ml/30 min.)		16	40	50	
Cake Thickness (inches)		4/32	4/32	5/32	
HP-HT Filtrate (ml/30 min.)					
pH	12.3	12.2	10.2	7.5	7.3
CEC (milliequivalents/100 gms)	100	88	56	25	12.5

Figure 2.3 - The FANN 50C rheograms of the 2% bentonite/1% NaOH/1% silica fluids after autoclaving at the temperatures marked on the curves.

TABLE 2.3a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FAN 50C VISCOMETER FOR THE
 UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 2% BENTONITE / 1% NaOH / 1% SILICA

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	2.5	2.7	1.9	2.0	3.9
100	1.8	1.7	1.1	1.6	2.8
150	1.7	1.4	0.9	1.3	2.5
200	1.4	1.3	0.8	1.1	2.3
250	1.3	1.3	0.9	1.2	2.1
300	1.0	1.2	1.3	1.2	2.0
350	0.9	1.3	1.5	1.2	2.4
400	0.8	1.2	2.2	1.1	2.7
450	0.5	1.3	3.1	0.9	3.1
500	1.2	4.8	0.4	1.0	8.1

TABLE 2.3b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING
OF 2% BENTONITE / 1% NaOH / 1% SILICA

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	1.75	3.25	3.0	2.75	3.75
Plastic Viscosity (centipoise)	1.50	2.50	2.50	2.50	2.50
Yield Point (lb/100 sq ft)	0.50	1.50	1.0	0.50	2.50
Gel Strength (lb/100 sq ft)	0.5/1	1/2	0.5/1	1/4	1/2
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	12.2	12.2	12.1	11.8	11.7
CEC (milliequivalents/100 gms)	125	100	75	25	25

The pH of the fluid evolves from highly alkaline (11.8) at 70°F to alkaline (9.2) at 600°F. This alkaline solution seems to dissolve most of the bentonite since the CEC values are highly reduced after autoclaving at 500 and 600°F.

X-ray Diffraction Data

The main reaction products in this fluid are analcime and albite (Na-feldspar). Analcime ($\text{Na Al Si}_2 \text{O}_6 \cdot \text{H}_2\text{O}$) starts already to form at 300°F in small quantities (10%) but it becomes the major component of the fluid at 400 and 500°F. About 80% of the fluid solids consists of analcime after autoclaving the fluid at 500°F. Albite (Na-feldspar) forms in small quantities (10%) at 500°F but it makes up about 80% of the sample at 600°F. No smectite remains in the fluid after autoclaving at 600°F. Thus, smectite readily dissolves at higher temperature in high alkaline solution and it reacts with free silica with the above reaction products.

4. Electron Microscopic Examination of Mineral Reactions

Smectite particles mainly occur as extremely thin films in the presence of NaOH and silica at temperatures up to 300°F. Figures 2.4 through 2.7 display the typical morphological features of smectite films after autoclaving at various temperatures. At 400°F and 500°F smectite films exhibit minor changes which consist of folds and curled edges. Smectites occur very scarcely after autoclaving the fluid at 600°F. As shown in Figure 2.7, those that survived the treatment consist of thicker flakes which survive the extensive dissolution of smectite at higher temperatures.

Analcime forms as the first reaction product between Na-smectite and silica in sodium-rich solution (NaOH). The amorphous silica in the bentonite seems to be the main source of silica since analcime forms with or

Figure #: 2.4

Fluid: Bentonite/NaOH/SiO₂/300°F

Magnification: 21,000 X

Film #: 3152

Typical smectite thin films in the fluid after autoclaving at 300°F.

Figure #: 2.5

Fluid: Bentonite/NaOH/SiO₂/400°F

Magnification: 21,000 X

Film #: 3155

Description:

Typical thin smectite films showing small foldings in the fluid which was autoclaved at 400°F.

Figure #: 2.6

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 27,000 X

Film #: 3161

Description:

Smectite films whose broken edges may be caused by the dissolution in the fluid autoclaved at 500°F.

Figure #: 2.7

Fluid: Bentonite/NaOH/SiO₂/600°F

Magnification: 35,000 X

Film #: 3169

Description:

Smectite flakes remaining unaltered after the reaction.

without the addition of quartz to the fluid. Typical analcime particles are displayed in Figures 2.8 through 2.9. Albite becomes, however, the predominant reaction product in the fluid at and above 500°F. Albite occurs mostly as laths and rarely as tabular forms. The typical albite particles are shown in Figures 2.10 through 2.13 and they range in length from 5 to 10 microns.

Figure #: 2.8

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 500 X

Film #: a 0000

Description:

A general view of the fluid solids prepared directly on the Cu-boat. The spheres are analcime aggregates and the fibers are albite crystals.

Figure #: 2.9

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 3,000 X

Film #: a 0000

Description:

A magnified view of the analcime crystal displaying well developed faces. The x-ray spectra obtained from the crystal are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Na	711	.04
Al	3475	.21
Si	16171	1.00
Fe	794	.05

Figure #: 2.10

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 6,500 X

Film #: 3160

Description:

Commonly observed aggregates of smectite and newly formed albite laths.

Figure #: 2.11

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 9,000 X

Film #: 3159

Description:

A close view of an albite lath and broken smectite films. The x-ray spectra of the lath are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	7621	.19
Si	40546	1.00
Na	2664	.07
Fe	892	.02

Figure #: 2.12

Fluid: Bentonite/NaOH/SiO₂/600°F

Magnification: 3,000 X

Film #: a0005

Description:

A general view of the commonly observed feldspar crystals. Only a few analcime crystals were found in the system.

Figure #: 2.13

Fluid: Bentonite/NaOH/SiO₂/500°F

Magnification: 4,000 X

Film #: a0004

Description:

A magnified view of the albite crystals which display elongated forms.

III. EFFECTS OF SALTS AND HYDROXIDES OF POTASSIUM ON BENTONITE FLUIDS

1. Bentonite/KCl Fluid

The viscosity of a 4% bentonite and 1% KCl fluid shows a sharp increase from 18 cp at 75°F to a maximum of 238 cp at 360°F (Figure 3.1 and Tables 3.1a and 3.1b). However the viscosities of the autoclaved fluids are drastically reduced. Thus, KCl seems to control the viscosity of the fluid at high temperatures. This is also important to remember when trying to minimize formation damage effects of the drilling fluid.

2. Bentonite/K₂CO₃ Fluid

The untreated fluid containing 8% bentonite and 1% K₂CO₃ becomes practically a gel with very high viscosities beyond our measurement capabilities as displayed by the data in Figure 3.2 and Tables 3.2a and 3.2b. The fluid autoclaved at 300°F shows rather high viscosities with a maximum of 110 cp at 300°F. It develops a typical viscosity "hump" within the temperature range 250-450°F. At and above the temperature of 400°F, the viscosities of the fluids become rather acceptable (ranging from 10 to 30 cp). The pH of the fluid evolves gradually from 9.0 to 7.0 during the temperature range 300 to 600°F. The CEC values, on the other hand, show large reductions from 125 meq/100g at 70°F to 38 meq/100g at 400°F and to 31 meq/100g at 600°F. These reductions in CEC values and also in viscosities at higher temperatures are consistent with the mineral reactions in these fluids. Because of the higher pH, the conversion of the smectite to illite/smectite mixed-layers takes place already at 400°F as compared to 600°F in the bentonite/KCl fluid. Furthermore, at and above 500°F, K-feldspars also form in the bentonite/K₂CO₃ fluid.

Figure 3.1 - The FANN 50C rheograms of the 4% bentonite/1% KCl fluids after autoclaving at the temperatures marked on the curves.

TABLE 3.1a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
4% BENTONITE / 1% KCl

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	18.3	15.4	9.4	3.9	7.8
100	27.7	12.5	5.8	2.8	5.0
150	63.1	12.5	5.4	2.5	3.9
200	110.1	13.3	5.1	2.1	3.4
250	181.7	11.5	4.6	1.7	2.9
300	229.3	7.5	3.9	1.4	3.2
350	237.6	5.1	3.1	1.3	3.3
400	237.6	4.1	2.3	1.2	3.3
450	229.3	3.3	2.0	1.2	3.0
500	177.8	2.5	1.8	1.0	2.6

TABLE 3.1b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
4% BENTONITE / 1% KCl

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	31.0	19.0	14.0	6.0	8.0
Plastic Viscosity (centipoise)	6.0	9.5	10.0	4.0	7.0
Yield Point (lb/100 sq ft)	49.5	19.0	7.5	4.0	3.0
Gel Strength (lb/100 sq ft)	34/40	15/26	6/8	3/4	2/2
API Filtrate (ml/30 min.)		38	40	92	
Cake Thickness (inches)		5/32	4/32	7/32	
HP-HT Filtrate (ml/30 min.)					
pH	7.8	6.9	6.2	5.6	4.2
CEC (milliequivalents/100 gms)	100	75	63	63	50

Figure 3.2 - The FANN 50C rheograms of the 8% bentonite/1% K₂CO₃ fluid after autoclaving at the temperatures marked on the curves.

TABLE 3.2a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% K_2CO_3

Fann 50C Temperature °F	70	Autoclaved at temperature (°F)			
		300	400	500	600
75	untreated sample had a very high viscosity	83.1	40.4	20.0	15.4
100		35.1	18.3	11.3	8.6
150		25.1	12.2	8.7	6.6
200		24.1	10.2	9.3	6.6
250		35.1	9.8	11.0	7.5
300		110.1	11.0	12.8	7.0
350		107.6	14.5	12.5	6.5
400		?	20.8	11.6	6.0
450		29.1	30.3	10.4	6.7
500		20.8	13.7	11.8	5.0

TABLE 3.2b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% K_2CO_3

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)		106.0	38.5	19.0	14.0
Plastic Viscosity (centipoise)		58.5	29.0	17.0	11.5
Yield Point (lb/100 sq ft)	High Viscosity	95.5	19.0	4.0	5.5
Gel Strength (lb/100 sq ft)		19/89	2/4	2/4	2/2
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH		9.0	7.8	7.4	7.0
CEC (milliequivalents/100 gms)		81	38	38	31

3. Bentonite/KOH Fluid

The properties of an 8% bentonite and 1% KOH fluid proved to be rather useful for the control of the high-temperature gelation of bentonite. The initial viscosity of the fluid at room temperature was so low that we needed to increase bentonite concentration to 8%. The viscosity of the untreated 8% bentonite/1% KOH fluid was extremely low as compared with the high viscosities of the untreated bentonite/KCl and bentonite/ K_2CO_3 fluids. As shown by the data in Figure 3.3 and Tables 3.3a and 3.3b, the viscosity enhancement is rather small when the fluid was autoclaved at 300°F and above. The pH of the fluid evolves from 12.3 at 70°F to 7.2 at 600°F. The CEC values show a significant reduction with increasing temperatures. These reductions in CEC and pH are consistent with the mineral reactions at higher temperatures. Smectite seems to dissolve in the alkaline conditions at lower temperature and illite/smectite mixed-layer and K-feldspar precipitate already at 400°F. These reaction products become larger in quantity at temperatures 500 and 600°F. The decrease in smectite content of the fluid and the nature of the reaction products cause, however, an increase in fluid loss while they depress favorably the viscosity of the fluids.

Thus, the inclusion of K^+ -ion in the mud system as KOH is more favorable in controlling the viscosity enhancement of the bentonite fluids. At the same time, the permeability damage from swelling smectites in the formation can be also reduced by the K^+ -ion in the drilling fluid.

4. Mineralogical Reactions in Bentonite Fluids Containing

Salts and Hydroxides of Potassium

4% Bentonite and 1% KCl Fluid: The x-ray diffraction data indicated a slight but steady decrease of the basal reflection of K-smectite from

Figure 3.3 - The FANN 50C rheograms of the 8% bentonite/1% KOH fluids after autoclaving at the temperatures marked on the curves.

TABLE 3.3a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% KOH

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	1.6	6.6	4.6	7.9	3.7
100	1.8	5.3	3.1	4.8	2.7
150	3.1	5.0	2.5	4.0	2.2
200	3.7	4.7	2.1	3.8	2.0
250	4.4	4.4	2.0	4.1	1.8
300	4.6	4.2	2.3	5.1	1.8
350	3.8	3.9	3.3	6.5	2.0
400	3.8	3.9	4.1	6.4	2.0
450	3.7	3.7	4.4	5.0	2.0
500	3.6	3.8	4.8	4.4	1.9

TABLE 3.3b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% KOH

Fluid Property	Autoclaved at temperatures (°F)				
	70	300	400	500	600
Apparent Viscosity (centipoise)	2.0	7.5	6.0	8.0	5.5
Plastic Viscosity (centipoise)	2.0	5.0	5.0	7.5	5.0
Yield Point (lb/100 sq ft)	0.5	5.0	2.0	1.0	1.0
Gel Strength (lb/100 sq ft)	0.5/1	3.5	0.5/1	1/1	1/1
API Filtrate (ml/30 min.)		60	48	50	
Cake Thickness (inches)		6/32	4/32	3/32	
HP-HT Filtrate (ml/30 min.)					
pH	12.3	12.0	9.5	9.0	7.2
CEC (milliequivalents/100 gms)	100	75	44	31	25

12.0 Å at room temperature to 11.3 Å after the autoclaving at 500°F. This suggests the development of illite/smectite mixed-layers in small amounts. Large quantities of illite/smectite mixed-layers with the predominance of non-swelling illite component form at 600°F and they display a basal spacing of 10.9 Å.

The newly developed illite/smectite mixed-layers display morphological features which are very different from those of original smectite particles. Thin platelets of illite/smectite mixed-layers or aggregates with a mosaic of such thin platelets are observed during the electron microscopic examination of the fluid autoclaved at 500°F (Figures 3.4a and 3.5). Most of the smectite still maintains its typical fluffy morphology with thin folded films as in Figure 3.4a. Thin platelets of illite/smectite mixed-layers become the predominant particles in the fluid after autoclaving at 600°F. Figures 3.6a and 3.7a give close views of these thin illite/smectite platelets. The selected area diffraction pattern in Figure 3.6b gives the unit-cell dimensions of $\underline{a} = 5.17 \text{ Å}$ and $\underline{b} = 9.06 \text{ Å}$ as expected from a dioctahedral mica-type layers. The x-ray spectra in Figure 3.7b indicate significantly larger K than was found in Figure 3.4b for the original smectite.

8% bentonite + 1% KOH and 8% bentonite + 1% K₂CO₃ Fluids: Illite/smectite mixed-layers with predominantly non-swelling illite components develop in large quantities already at 400°F in these fluids. The K-saturated smectite gives a basal spacing of 11.8 Å at 70°F and it remains unchanged after autoclaving at 300°F in these fluids. This basal reflection shifts to 20.8 Å in the presence of KOH at and above 400°F. It shows, however, a steady decrease from 10.9 Å at 400°F to 10.5 Å at 600°F. The original smectite particles consist of aggregates of thin and

Figure #: 3.4a

Fluid: Bentonite/KC1/500°F

Magnification: 13,000 X

Film #: 3678

Description:

The commonly observed smectite particles in the sample. The smectite occurs as fluffy aggregate with folded edges, however, small and thin film-like platelets are also developed in the system.

Figure #: 3.5

Fluid: Bentonite/KC1/500°F

Magnification: 44,000 X

Film #: 3699

Description:

A close view of the thin film-like platelets as magnified from the above micrograph. The thickness of the platelets is approximately about several hundreds of Angstroms. These platelets are probably the I/S mixed-layers formed from the smectite.

Intensity
counts/100 sec.

Figure 3.4b

X-ray spectra obtained from the smectite
aggregate in Figure 3.4a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Al	1320	.24
Si	5475	1.00
Fe	362	.07
K	688	.13

Figure #: 3.6a

Fluid: Bentonite/KCl/600°F

Magnification: 88,000 X

Film #: 3697

Description:

Image of an isolated thin
platelet of I/S mixed-layer.

Figure #: 3.6b

Fluid: Bentonite/KCl/600°F

Magnification: SAD

Film #: 3696

Description:

The selected area electron diffraction pattern obtained from the thin platelets shown in the above micrograph. The extra points resulted from another layer of I/S mixed-layer. The cell parameters calculated from the pattern are:

$$\underline{a} = 5.167\text{\AA}$$

$$\underline{b} = 8.956\text{\AA}$$

Figure #: 3.7a

Fluid: Bentonite/KCl/600°F

Magnification: 65,000 X

Film #: 3695

Description:

A close view of the thin platelets from the above micrograph. The edges of the platelets are curled up because of dehydration under vacuum.

Figure #: 3.8a

Fluid: Bentonite/KOH/300°F

Magnification: 13,000 X

Film #: 3711

Description:

The commonly observed particles in the autoclaved fluid. Smectite occurs as thin films and does not show significant changes in morphology, though a small amount of thin platelets has also been observed.

Intensity
counts/100 sec.

Figure 3.7b

X-ray spectra obtained from the thin
platelets in Figure 3.7a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Mg	55	.01
Al	1779	.28
Si	6438	1.00
Fe	533	.08
K	2486	.39

Intensity
counts/100 sec.

Figure 3.8b

X-ray spectra obtained from the
smectite aggregate in Figure 3.8a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Al	594	.29
Si	2035	1.00
K	151	.07
Fe	238	.12
Mg	100	.05

folded films which do not undergo any significant changes in morphology after autoclaving at 300°F. Common smectite particles in the fluid are displayed in Figures 3.8a and 3.9. However, a small number of platelets with a submicron particle-size is also developed in the fluid at 300°F. The typical thin platelets of illite/smectite mixed-layers develop in the fluid at and above 400°F. Such platelets have irregular outlines and a sub-micron size as shown in Figure 3.10a. The selected area electron diffraction pattern in Figure 3.10b indicates a domain micro-structure leading to the equally strong 6 inner spots in the pattern. The x-ray spectra in Figure 3.10c show the K-content of the platelet is larger than that in the original smectite. In the fluid autoclaved at 500°F, the illite/smectite platelets become larger and better in crystalline forms. Figure 3.11a shows such thin platelets of illite/smectite mixed-layers. Its SAD pattern in Figure 3.11b indicates a 1M-stacking sequence. Both the K-content and the crystallinity of these illite/smectite platelets are enhanced at 600°F as displayed in Figure 3.12a. The SAD pattern in Figure 3.12b indicates a stacking sequence of 1M illite polymorph. At 600°F there are also a few extremely well-crystallized mica (muscovite) platelets developed in the fluid. Figure 3.13a illustrates such a muscovite along with its SAD pattern in Figure 3.13b. The latter shows again a 1M polymorph of muscovite. The x-ray spectra in Figure 3.13c indicate that the K- and Al-content of the muscovite are significantly larger than those in illite/smectite mixed-layers. Thus, the smectite in the original bentonite dissolves in increasing amounts in 1% KOH solution at and above 300°F. Large amounts of illite/smectite mixed-layers with thin platy morphology precipitates in the fluids autoclaved at and above 400°F. This conversion of smectite to a mixed-layered phase with predominantly (non-swelling) illite

Figure #: 3.9

Fluid: Bentonite/KOH/300°F

Magnification: 45,000 X

Film #: 3712

Description:

A close view of a smectite aggregate showing typical thin film-like morphology.

Figure #: 3.10a

Fluid: Bentonite/KOH/400°F

Magnification: 66,000 X

Film #: 3710

Description:

A close view of an I/S mixed-layer occurring as an isolated thin platelet.

Intensity
counts/100 sec.

Figure 3.10c

X-ray spectra obtained from the thin
illite platelet in Figure 3.10a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Al	555	.30
Si	1829	1.00
K	253	.14
Fe	315	.17
Mg	106	.06

Figure #: 3.10b

Fluid: Bentonite/KOH/400°F

Magnification: SAD

Film #: 3709

Description:

The selected area electron diffraction pattern obtained from the I/S platelet in the above micrograph. The calculated cell parameters are:

$$\underline{a} = 5.17 \pm .01 \text{ \AA}$$

$$\underline{b} = 8.88 \pm .01 \text{ \AA}$$

Figure #: 3.11a

Fluid: Bentonite/KOH/500°F

Magnification: 88,000 X

Film #: 3454

Description:

A magnified view of an I/S mixed-layer occurring as thin platelet.

Figure #: 3.11b

Fluid: Bentonite/KOH/500°F

Magnification: SAD

Film #: 3453

Description:

The selected area electron diffraction pattern obtained from the above thin platelet. The following unit-cell parameters are obtained:

$$\underline{a} = 5.19 \pm 0.01 \text{ \AA}$$

$$\underline{b} = 8.93 \pm 0.01 \text{ \AA}$$

Figure #: 3.12a

Fluid: Bentonite/KOH/600°F

Magnification: 66,000 X

Film #: 3446

Description:

An isolated illite platelet. The selected area electron diffraction pattern indicates that the illite possesses a 1 M type structure.

Figure #: 3.12b

Fluid: Bentonite/KOH/600°F

Magnification: SAD

Film #: 3445

Description:

The selected area electron diffraction pattern obtained from the illite platelet shown in the above micrograph. The calculated cell parameters are:

$$\underline{a} = 5.22 \text{ \AA}$$

$$\underline{b} = 8.99 \pm .03 \text{ \AA}$$

Figure #: 3.13a

Fluid: Bentonite/KOH/600°F

Magnification: 35,000 X

Film #: 3702

Description:

A close view of a well-crystallized muscovite platelet. The x-ray spectral data in Figure 3.13c from the muscovite indicate a higher amount of K and Al as compared with the composition of I/S mixed-layers.

component seems to be directly related to the rheological behavior of the bentonite/KOH described above.

K-feldspar also develops as another reaction product in smaller quantities in the fluids autoclaved at and above 400°F. Figure 3.14a displays such a K-feldspar crystal with a length of about 2 microns. The feldspar laths display a distinct growth mosaic. The x-ray spectra in Figure 3.14a from the particle show a typical K-feldspar composition.

In summary, the mineral reaction in the fluids at and above 400°F can be given as:

Figure #: 3.13b

Fluid: Bentonite/KOH/600°F

Magnification: SAD

Film #: 3703

Description:

The selected area electron diffraction pattern obtained from the mica platelet in the above figure. The unit-cell parameters are calculated to be:

$$\underline{a} = 5.17 \pm 0.01 \text{ \AA}$$

$$\underline{b} = 9.07 \pm 0.01 \text{ \AA}$$

Figure #: 3.14a

Fluid: Bentonite/KOH/600°F

Magnification: 44,000 X

Film #: 3704

Description:

A close view of a K-feldspar crystal with a mosaic of pseudo-hexagonal platelet.

Intensity
counts/100 sec.

Figure 3.13c

X-ray spectra obtained from the mica
platelet in Figure 3.13a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Al	1051	.43
Si	2458	1.00
K	591	.24
Fe	263	.11
Mg	56	.02

Intensity
counts/100 sec.

Figure 3.14b

X-ray spectra obtained from the
feldspar in Figure 3.14a:

Elements	Intensity counts/100 sec.	Intensity ratio/Si
Al	649	.24
Si	2695	1.00
K	943	.35

IV. IN-SITU CONVERSION OF BENTONITE FLUIDS INTO CEMENT MINERALS

1. Bentonite/CaCl₂ Fluid

Because of the strong inhibiting effect of calcium ion on the swelling of the smectite, we increased the bentonite concentration in the fluid to 8% in order to have some measurable viscosities. The viscosities of an 8% bentonite/1% CaCl₂ fluid remain extremely low at all temperatures as displayed in Figure 4.1 and Table 4.1a. The pH of the fluid shows a slight decline from 7.7 at 70°F to 7.0 at 600°F. However, the CEC values significantly decrease from 100 meq/100g at 70°F to 50 meq/100g at 600°F (Table 4.1b).

2. Bentonite/Lime Fluid

It is well-known that "spud" muds are prepared from bentonite and lime. The thixotropy obtained from such muds is related to the flocculation of the bentonite at a high concentration. However, such a high viscous bentonite/lime fluid does not have any fluid loss control. A major problem in drilling technology is related to the poor bonding between the cement behind the casing and the filter cake on the borehole wall. The addition of lime to the bentonite fluid may lead to the formation of cement minerals at high temperatures. We therefore examined the effects of lime additive on bentonite muds at both low (2% bentonite/1% lime) and higher concentrations (8% bentonite/1% lime).

The rheological parameters of the 2% bentonite/1% lime fluid are given by the rheograms in Figure 4.2 and by the data in Tables 4.2a and 4.2b. The addition of lime decreases drastically the viscosity of the bentonite fluid at all temperatures from 70 to 600°F, as compared with

Figure 4.1 - The FANN 50C rheograms of the 8% bentonite/1% CaCl₂ fluids which were autoclaved at high temperatures up to 600°F.

TABLE 4.1a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% CaCl_2

fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	3.2	2.3	2.5	2.5	1.7
100	2.8	2.3	2.8	2.4	1.9
150	2.2	1.7	2.5	1.9	1.6
200	1.3	1.4	2.1	1.5	1.3
250	1.1	1.3	2.0	1.3	1.2
300	1.1	1.3	1.9	1.3	1.1
350	1.2	1.3	1.9	1.3	1.0
400	1.2	1.4	1.9	1.3	1.0
450	1.4	1.5	2.1	1.4	1.0
500	1.2	1.3	1.5	1.0	1.0

TABLE 4.1b
 PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 8% BENTONITE / 1% CaCl₂

Fluid Property	Autoclaved at temperatures (°F)				
	70	300	400	500	600
Apparent Viscosity (centipoise)	2.0	2.25	2.75	2.5	2.5
Plastic Viscosity (centipoise)	1.5	2.0	2.0	2.0	2.0
Yield Point (lb/100 sq ft)	1.0	0.5	1.5	1.0	1.0
Gel Strength (lb/100 sq ft)	0.5/2	1/2	1/2	1/1.5	1/1.5
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	7.7	6.8	6.9	7.1	7.0
CEC (milliequivalents/100 gms)	100	69	62.5	56	50

Figure 4.2 - The FANN 50C rheograms of the 2% bentonite/1% lime fluids which were autoclaved at the temperatures marked on the curves.

TABLE 4.2a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN %C VISCOMETER FOR THE
 UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 2% BENTONITE / 1% LIME

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	3.2	2.7	2.3	1.4	1.8
100	3.0	2.3	1.9	1.2	1.6
150	2.7	2.1	1.8	0.9	1.3
200	2.2	1.9	1.7	0.2	1.0
250	2.3	1.7	1.4	0.3	0.9
300	2.1	1.5	1.0	0.4	1.0
350	1.9	1.3	0.9	0.8	1.0
400	1.8	1.2	0.9	0.9	0.9
450	1.9	1.5	1.0	0.4	0.8
500	2.0	1.7	1.1	1.0	0.8

TABLE 4.2b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% $\text{Ca}(\text{OH})_2$

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	1.75	3.5	3.5	2.5	1.25
Plastic Viscosity (centipoise)	1.50	2.0	3.0	2.5	1.0
Yield Point (lb/100 sq ft)	0.50	3.0	1.0	0.0	0.5
Gel Strength (lb/100 sq ft)	0.5/4	2/2	2/2	0/5/0.5	0.5/0.5
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	12	11.6	11	9.2	9.2
CEC (milliequivalents/100 gms)	125	50	50	25	25

the pure 2% bentonite fluid. The pH of the 2% bentonite/1% lime fluid, evolving from 12 at 70°F to 9.2 at 600°F, remains always highly alkaline. The CEC values drastically decrease from 125 meq/100g at 70°F to 25 meq/100g at 600°F. This indicates a substantial dissolution of smectite in alkaline conditions with the subsequent reaction products.

The higher bentonite concentration in 8% bentonite/1% lime fluid gives rise to higher viscosity values for the untreated fluid and for those autoclaved at 300 and 400°F as indicated by the rheograms in Figure 4.3 and by the data in Tables 4.3a and 4.3b. However, at higher temperatures (500-600°F) the fluid viscosities drop drastically. The pH of the fluids reduces from 12 at 70°F to 7.4 at 600°F. Similarly, the CEC values suffer a large decrease from 100 meq/100g at 70°F to 1.25 meq/100g at 600°F.

3. Bentonite/Lime/Silica Fluid

Free silica was added to the bentonite/lime fluid with the expectation to enhance the cement formation since the cement reactions are generally based on the reactions between lime and silica. For this purpose a fluid consisting of 2% bentonite, 1% lime, and 1% silica was autoclaved at temperatures from 300 to 600°F. The rheological properties of this fluid are represented by the data in Figure 4.4 and in Tables 4.4a and 4.4b. The viscosities of this fluid are extremely low at all temperatures as it was the case for the 2% bentonite/1% lime fluid. The pH range of the fluids is also similar to the previous bentonite/lime fluid, evolving from 12.8 at 70°F to 9.2 at 600°F. One unusual parameter of the fluid is its low CEC value (75 meq/100g) at the ambient temperature. The CEC drops however to 25 meq/100g at 600°F, indicating a substantial decomposition of smectite in the alkaline conditions at high temperatures.

Figure 4.3 - The FANN 50C rheograms of the 8% bentonite/1% lime fluids which were autoclaved at the temperatures marked on the curves.

TABLE 4.3a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR THE
 UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 8% BENTONITE / 1% LIME

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	24.1	18.7	37.5	3.4	2.1
100	14.3	11.5	22.0	2.8	2.0
150	11.6	8.4	21.3	2.4	1.7
200	9.6	5.8	21.2	2.3	1.5
250	7.5	3.5	18.7	2.4	1.5
300	7.1	2.5	12.0	2.4	1.5
350	6.8	2.1	5.6	2.1	1.2
400	7.5	1.7	3.0	1.9	1.0
450	9.1	2.9	1.7	2.0	1.5
500	12.9	14.9	18.3	1.9	1.2

TABLE 4.3b
PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
8% BENTONITE / 1% LIME

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	19.5	21.5	35.5	4.0	3.0
Plastic Viscosity (centipoise)	5.0	4.0	24.0	2.5	2.0
Yield Point (lb/100 sq ft)	29.0	25.0	23.0	2.5	0.5
Gel Strength (lb/100 sq ft)	7/8	6/8	7/9	3/4	1/2
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)*	45/1	60/2			
pH	12.0	10.4	10.0	7.8	7.4
CEC (milliequivalents/100 gms)	100	50	56	50	12.5
HP-HT Cake Thickness (inches)		23/32			

*if the filtration time was below 30 minutes, it is indicated following the slash.

Figure 4.4 - The FANN 50C rheograms of the 2% bentonite/1% lime/1% silica fluids which were autoclaved at the temperatures marked on the curves.

TABLE 4.4a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% SILICA

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	1.5	2.9	2.1	2.3	2.4
100	1.4	2.7	1.9	1.9	2.1
150	1.1	2.6	1.6	1.3	1.7
200	0.9	2.5	1.6	1.2	1.5
250	0.8	2.3	1.5	0.9	1.3
300	0.6	2.0	1.3	1.0	1.3
350	0.5	2.0	1.2	1.4	1.2
400	0.5	2.0	1.3	1.3	1.5
450	0.4	2.7	2.0	1.2	1.2
500	0.5	2.0	1.8	1.0	1.0

TABLE 4.4b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% SILICA

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	2.25	3.25	3.0	2.5	2.25
Plastic Viscosity (centipoise)	1.5	2.5	2.5	2.5	2.5
Yield Point (lb/100 sq ft)	1.5	1.5	1.0	1.0	0.5
Gel Strength (lb/100 sq ft)	1/2	1.5/2	1/4	1/1.5	0.5/3
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	11.8	11.2	9.8	9.0	9.2
CEC (milliequivalents/100 gms)	75	75	75	25	25

4. Mineral Reactions In The Autoclaved Fluids Containing Calcium

8% Bentonite/1% CaCl_2 Fluid

The x-ray diffraction data show no new mineral phases formed in the fluid except for halite. The latter is due to the exchange of Na in smectite for calcium in the solution, and halite forms when the chloride solution with Na has been dried at room temperature. The pH of the fluid seems to be too low for the formation of tobermorite, a cement mineral.

2% Bentonite/1% $\text{Ca}(\text{OH})_2$ Fluid

The main reaction products in the 2% bentonite/1% lime fluids are calcite and tobermorite. Calcite is generated by the conversion of lime to calcite even at the ambient temperature when the fluid is exposed to CO_2 in the air. This readily happens during the air-drying of the fluid. Tobermorite is the cement mineral with the formal composition $5 \text{CaO} \cdot 6 \text{SiO}_2 \cdot 5\text{H}_2\text{O}$. Tobermorite forms only in trace quantities at 300°F but in large quantities at 400°F and 500°F . A Ca-feldspar similar to anorthite forms in small amounts at 500°F but in larger quantities at 600°F . Consequently the tobermorite content is reduced to about 20% at 600°F .

Electron Microscopic Observations

Smectite particles are found to have dissolved and disintegrated with increasing temperatures. Typical smectites are shown in Figure 4.5a after autoclaving the fluid at 300°F and in Figure 4.5b after the treatment at 600°F . Tobermorite crystals occur at 300°F as laths which are often aggregated with smectite films. Figures 4.6 and 4.7 display such tobermorite and smectite particles in the fluid. Well-developed tobermorite laths are

Figure #: 4.5a

Fluid: Bentonite/Ca(OH)₂/300°F

Magnification: 26,000 X

Film #: 3129

Description:

Fluffy smectite thin films in the autoclaved fluid. The x-ray spectra obtained from the smectite are given below:

Element	Intensity count/100 sec.	Intensity ratio/Si
Al	859	.20
Si	3032	1.00
Ca	594	.20
Fe	234	.08

Figure #: 4.5b

Fluid: Bentonite/Ca(OH)₂/600°F

Magnification: 20,000 X

Film #: 3147

Description:

Smectite flakes in the autoclaved fluid.

Figure #: 4.6

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /300°F

Magnification: 12,000 X

Film #: 3124

Description:

Commonly observed aggregates of tobermorite and smectite. The x-ray spectra obtained from the aggregate are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	695	.20
Si	3527	1.00
Ca	2451	.69
Fe	119	.03

Figure #: 4.7

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /300°F

Magnification: 35,500 X

Film #: 3125

Description:

A magnified view of the tobermorite laths from the previous micrograph.

found at 400°F as shown in Figure 4.8a along with its SAD pattern in Figure 4.8b. Calcite rhombs and irregular spherules occur also in the fluid after autoclaving at 400°F. Smectite particles decrease in quantity in the fluid at and above 400°F. Tobermorite becomes the predominant component of the fluid after autoclaving at 500°F. These tobermorites consist of laths as shown in Figures 4.9a and 4.9b. Some of these laths display dissolution features. Tobermorite remains as a major component of the fluid after autoclaving at 600°F. A typical tobermorite formed at 600°F is displayed in Figure 4.10a with its SAD pattern in Figure 4.10b.

8% Bentonite/1% Ca (OH)₂ Fluid

X-ray diffraction analysis shows that no tobermorite forms in the system. This may be caused by the lower pH values as well as lower dissolved Ca/Si ratios in these fluids. Calcite is the prominent reaction product at and below 500°F and it may form due to the same reasons as discussed above. A calcium-feldspar forms, however, in small quantities at 500°F and in larger amounts at 600°F. Smectites remain in the system in their Ca-forms with a basal spacing of 15.2⁰Å.

2% Bentonite/1% Lime/1% SiO₂ Fluid

The major reaction products in this fluid are tobermorite, calcite, and Ca-feldspar as in the previous 2% bentonite/1% lime fluid. Calcite readily forms even at the ambient temperature due to the reaction of lime with CO₂, which mostly takes place during the drying of the mud in the air. Tobermorite develops in the fluid in small amounts (5%) during autoclaving at 300°F but in larger amounts (15-30%) at higher temperatures (400-600°F). It is interesting to note that significantly less tobermorite is formed in this fluid (with extra silica) than in the 2% bentonite/1% lime fluid.

Figure #: 4.8a

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /400°F

Magnification: 9,000 X

Film #: 3134

Description:

Well-developed tobermorite plates in the autoclaved fluid.

Figure #: 4.8b

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /400°F

Magnification: SAD

Film #: 3133

Description:

The selected area electron diffraction pattern of the tobermorite shown above.

Figure #: 4.9a

Fluid: Bentonite/ Ca(OH)_2 /500°F

Magnification: 16,000 X

Film #: 3145

Description:

Image of the tobermorite fibers showing dissolution features.

Figure #: 4.9b

Fluid: Bentonite/ Ca(OH)_2 /500°F

Magnification: 50,000 X

Film #: 3144

Description:

A magnified view of the tobermorite fibers from the above micrograph.

Figure #: 4.10a

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /600°F

Magnification: 26,000 X

Film #: 3149

Description:

Image of a calcium silicate hydrate (CSH) crystal. The x-ray spectra obtained from the crystal are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	536	.11
Si	4850	1.00
Ca	6211	1.28

Figure #: 4.10b

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2$ /600°F

Magnification: SAD

Film #: 3148

Description:

The SAD pattern of the CSH crystal shown above.

Thus the excess silica (fine quartz powder) does not promote the formation of cement minerals in the fluid. The tobermorite seems, therefore, to be a product of the reaction between lime and smectite (perhaps the amorphous silica in the bentonite) but not between lime and silica from the fine quartz powder.

Electron Microscopic Observations

After autoclaving the fluid at 300°F, smectite particles occur as thick aggregates as shown in Figures 4.11 and 4.12. These aggregates often contain dense and sometimes spherical particles of calcite and tobermorite that are entrapped in them (Figure 4.13). Thus, there are no more well-dispersed thin films of smectites in the fluid but larger coagulated particles. Tobermorite crystals appear in the form of thin laths, fibers, or ribbons as displayed in Figures 4.14 and 4.15a. The selected area electron diffraction pattern in Figure 4.15b gives the unit-cell parameter of a tobermorite, for the ribbon-like particle, in Figure 4.15a. Sometimes, these ribbons and laths seem to join each other and form platy particles of tobermorite. Such a platy tobermorite with a mosaic of laths is illustrated in Figure 4.16. The x-ray spectra obtained from the platelet give strong Ca- and Si-lines as expected from a tobermorite.

Tobermorite crystals that precipitate after autoclaving the fluid at 400°F and at 500°F seem to improve its crystalline forms. They consist of longer laths and fibers (Figure 4.17); and some of them display a well-developed tabular morphology as shown in Figure 4.18a. The SAD pattern in Figure 4.18b and the x-ray spectra obtained from the platelet in Figure 4.18a confirm the identity of tobermorite. Tobermorite laths often develop cabbage-like aggregates after autoclaving the fluid at 400 and 500°F. Such a tobermorite aggregate is displayed in Figure 4.19. Calcite occurs as

Figure #: 4.11

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2$ /

Magnification: 5,000 X 300°F

Film #: 3102

Description:

A general view of the smectite aggregates after the reaction. Smectite may retain its fluffy outlines, but most of them are partially fragmented. Calcite rhombs and Ca- and Si-containing spheres are commonly trapped in the aggregates.

Figure #: 4.12

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2$ /

Magnification: 13,000 X 300°F

Film #: 3103

Description:

A magnified view of the smectite aggregate from the above micrograph. A few tobermorite laths are visible together with some calcium-rich spheres on the background.

Figure #: 4.13

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 33,000 X 300°F

Film #: 3104

Description:

Another magnified view of the smectite films from Figure 4.11.

Figure #: 4.14

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 13,000 X 300°F

Film #: 3105

Description:

A general view of the tobermorite laths in the sample, some of them also occur in plates.

Figure #: 4.15a

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 20,000 X 300°F

Film #: 3109

Description:

Another tobermorite aggregate consisting of both platy and lath-shaped individuals.

Figure #: 4.15b

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: SAD 300°F

Film #: 3108

Description:

The SAD pattern of the tobermorite shown above:

$$\underline{b} = 7.25 \text{ \AA}$$

$$\underline{c} = 21.8 \text{ \AA}$$

Figure #: 4.16

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2$

Magnification: 13,000 X 300°F

Film #: 3107

Description:

A platy tobermorite which is composed of laths. The x-ray spectra of this plate are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	167	.13
Si	1333	1.00
Ca	1438	1.08

Figure #: 4.17

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2$

Magnification: 20,000 X 400°F

Film #: 3114

Description:

A closeup of the tobermorite fibers and the smectite remains.

Figure #: 4.18

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/400^\circ\text{F}$

Magnification: 33,000 X

Film #: 3112

Description:

Some of the tobermorite crystals display tabular morphology with distinct faces such as this one, but they are not very common. The x-ray spectra obtained from the plate are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	114	.08
Si	1513	1.00
Ca	1804	1.19

Figure #: 4.18b

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/400^\circ\text{F}$

Magnification: SAD

Film #: 3115

Description:

The SAD pattern of the tobermorite crystal shown above.

$$\underline{b} = 7.29 \text{ \AA}$$

$$\underline{c} = 21.8 \text{ \AA}$$

rhombs but mostly as spherules (Figure 4.20). Tobermorite laths become thicker and larger in size after the fluid was autoclaved at 600°F as typically shown in Figures 4.21 and 4.22. At this temperature a large number of a Ca-feldspar also precipitates in the form of equant and thick crystals. Most of the smectite dissolves and disintegrates as the autoclave temperature is increased from 400 to 600°F.

Figure #: 4.19

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 3,300 X 500°F

Film #: 3115

Description:

The commonly observed tobermorite fibers and their cabbage-like aggregates. The original smectite flakes have been disintegrated into thin films. A few of the calcite rhombs are observed, but most of them occur as spheres. The x-ray spectra of the tobermorite are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	1661	.18
Si	9414	1.00
Ca	3957	.42
Fe	619	.06

Figure #: 4.20

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 20,000X 500°F

Film #: 3116

Description:

A magnified view of the tobermorite and calcium-rich spheres from the previous figure.

Figure #: 4.21

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 14,000X 600°F

Film #: 3118

Description:

A general view of the commonly observed tobermorite in this fluid.

Figure #: 4.22

Fluid: Bentonite/ $\text{Ca}(\text{OH})_2/\text{SiO}_2/$

Magnification: 13,000X 600°F

Film #: 3112

Description:

Aggregates of the tobermorite fibers. The x-ray spectra obtained from the aggregate are given below:

Element	Intensity counts/100 sec.	Intensity ratio/Si
Al	107	.05
Si	2063	1.00
Ca	1702	.83
Fe	111	.05

V. EFFECTS OF VARIOUS ADDITIVES ON CEMENT REACTIONS IN BENTONITE FLUIDS

1. Bentonite/Lime/CaCl₂ Fluid

A fluid composed of 2% bentonite/1% lime/1% CaCl₂ has been autoclaved at high temperatures with the purpose of increasing Ca²⁺-concentration in the fluid with regard to the formation of tobermorite. The characteristics of the fluid are described by the rheograms in Figure 5.1 and by the data in Tables 5.1a and 5.1b. These data show that the viscosities of the fluid are extremely low at all temperatures similar to the other bentonite fluids with high Ca²⁺-concentrations. The fluid pH steadily decreases from 12 at 70°F to 8.9 at 600°F, thus remaining always alkaline. The CEC values drastically decrease from 75 meq/100g at 70°F for the untreated fluid to 12.5 meq/100g for the fluid autoclaved at 600°F. This indicates most of the smectite dissolves in these alkaline solutions at high temperatures.

X-ray Diffraction Analysis

Calcite, halite, tobermorite occur as the main reaction products in this fluid. Calcite readily forms by the carbonatization of lime in the air. Halite crystallizes while the chloride solution has dried. Sodium is supplied from the smectite by the ion exchange reaction between the Ca²⁺ in the solution and Na⁺ in the original clay. Tobermorite, the cement mineral, first appears at 300°F and it becomes a major component of the mud at higher temperatures. A calcium feldspar is also formed while autoclaving the fluid at 600°F.

It is very important to note that smectite entirely disappears from the fluid at 400°F. Thus, the addition of CaCl₂ to the bentonite/lime fluid favors the total replacement of smectite by tobermorite.

Figure 5.1 - The FANN 50C rheograms of the 2% bentonite/1% lime/1% CaCl₂ fluids which were autoclaved at the temperatures marked on the curves.

TABLE 5.1a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR THE
 UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 2% BENTONITE / 1% Ca(OH)₂ / 1% CaCl₂

Fann 50C Temperature °F	Autoclaved at Temperature (°F)				
	70	300	400	500	600
75	1.1	2.2	1.5	1.7	1.4
100	0.7	2.1	1.4	1.8	1.2
150	0.6	2.0	1.2	1.7	1.1
200	0.6	1.9	1.1	1.6	1.1
250	0.6	1.8	1.0	1.5	1.0
300	0.6	1.8	1.0	1.5	1.0
350	0.5	1.8	1.0	1.5	1.0
400	0.6	1.7	1.2	1.5	1.1
450	0.6	1.5	0.8	1.6	1.3
500	0.6	1.8	1.3	1.7	1.6

TABLE 5.1b
 PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
 2% BENTONITE / 1% LIME / 1% CaCl₂

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	1.5	2.5	2.5	2.5	1.5
Plastic Viscosity (centipoise)	1.0	2.0	2.0	2.0	1.0
Yield Point (lb/100 sq ft)	1.0	1.0	1.0	1.0	1.0
Gel Stregth (lb/100 sq ft)	0.5/2	0.5/2	1/1	1/1.5	0.5/1
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	12	11.0	10.6	10.3	8.9
CEC (milliequivalents/100 gms)	100	75	50	12.5	12.5

2. Bentonite/Lime/Gypsum Fluid

With the addition of gypsum a new fluid was prepared with the composition of 2% bentonite/1% lime/1% gypsum. The measured properties of this fluid are given in Figure 5.2 and in Tables 5.2a and 5.2b. This fluid exhibits rather low viscosities as the other bentonite/lime fluids. The fluid pH and CEC values decrease significantly with the higher temperatures.

X-Ray Diffraction Analysis

The main reaction products are calcite, tobermorite, and anhydrite in this fluid. Gypsum seems to convert to anhydrite by simple dehydration during the autoclaving of the fluid at high temperatures of 300-500°F. Tobermorite first forms in small quantities at 300°F but in larger amounts at higher temperatures.

In summary, gypsum does not seem to give any special benefits in bentonite/lime fluids.

3. Bentonite/Lime/Lignosulfonate Fluid

A fluid with the composition of 2% bentonite/1% lime/0.25% lignosulfonate exhibits extremely low viscosities at all temperatures as shown by the data in Figure 5.3 and in Tables 5.3a and 5.3b. The fluid pH evolves from 12.0 at 70°F and to 8.5 at 600°F, similar to other bentonite/lime fluids. Again the CEC values of the fluid show a reduction from 100 meq/100g at 70°F to 14 meq/100g at 600°F.

X-Ray Diffraction Analysis

Tobermorite appears in small quantities at 300°F and in larger amounts at higher temperatures. Calcite forms again due to the

Figure 5.2 - The FANN 50C rheograms of the 2% bentonite/1% lime/1% gypsum fluids after autoclaving at temperatures marked on the curves.

TABLE 5.2a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% GYPSUM

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	1.4	3.9	2.2	4.2	1.2
100	1.2	3.3	1.9	3.8	1.0
150	0.8	2.8	1.8	3.7	1.0
200	0.7	2.7	1.8	3.5	1.0
250	0.8	2.6	1.7	3.3	1.0
300	0.8	2.5	1.7	3.1	1.0
350	0.7	2.3	1.7	2.9	1.0
400	0.8	2.2	1.6	2.7	1.0
450	1.0	1.7	1.1	3.9	1.0
500	0.9	1.5	0.8	9.3	1.0

TABLE 5.2b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% GYPSUM

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	2.0	6.0	4.0	7.0	1.5
Plastic Viscosity (centipoise)	1.5	3.0	2.5	3.5	1.5
Yield Point (lb/100 sq ft)	1.5	6.0	2.5	7.5	0.0
Gel Strength (lb/100 sq ft)	1/2	3/4	3/5	4/4	0.5/1.5
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	12.6	11.5	11.6	11.4	9.4
CEC (milliequivalents/100 gms)	100	50	25	25	25

Figure 5.3 - The FANN 50C rheograms of the 2% bentonite/1% lime/0.25% lignosulfonate fluids after autoclaving at the temperatures marked on the curves.

TABLE 5.3a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 0.25% LIGNOSULFONATE

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	1.3	1.0	1.1	1.3	1.8
100	1.1	0.8	0.9	0.8	1.3
150	1.1	0.7	0.8	0.7	1.1
200	1.1	0.7	0.5	0.6	1.1
250	1.1	0.6	0.5	0.6	1.0
300	1.1	0.6	0.4	0.6	1.0
350	1.0	0.6	0.4	0.6	1.0
400	1.0	0.7	0.4	0.5	1.0
450	0.9	0.9	0.3	0.8	1.1
500	0.8	1.0	0.2	0.8	1.3

TABLE 5.3b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 0.25% LIGNOSULFONATE

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	1.5	1.5	2.0	1.5	1.5
Plastic Viscosity (centipoise)	1.0	1.5	1.5	1.0	1.5
Yield Point (lb/100 sq ft)	1.0	0.5	0.5	1.0	0.0
Gel Strength (lb/100 sq ft)	0.5/4	0.5/0.5	0.5/1	0.5/1	0.5/1
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	12.0	11.5	10.8	10.7	8.5
CEC (milliequivalents/100 gms)	100	50	50	25	25

carbonatization of lime in the air. A calcium-feldspar develops at 500° and 600°F in the fluid. Some of the smectite still remains in the fluid even after autoclaving at 600°F, whereas a large portion of smectite has been dissolved in the alkaline solution fluids subjected to high temperatures.

Although lignosulfonates are expected to give a temporary retardation to the formation of cement minerals, we do not see such an effect in the bentonite/lime fluid.

4. Bentonite/Lime/MgO Fluid

A fluid with the composition of 2% bentonite/1% lime/1% MgO showed rather interesting features. The properties of this fluid are summarized in Figure 5.4 and Tables 5.4a and 5.4b. The viscosities of the fluid remain rather low at all temperatures. The fluid pH remains rather low at all temperatures. The fluid pH remains highly alkaline without significant changes at higher temperatures in contrast to the other fluids described above. The CEC values, however, show an unusually low value of 75 meq/100g at 70°F and a decrease to 25 meq/100g at 300°F.

X-Ray Diffraction Analysis

The addition of MgO to the bentonite/lime mud results in unusual reaction products. MgO readily hydrates to brucite, $\text{Mg}(\text{OH})_2$ in the fluid at 70°F, whereas lime similarly reacts with CO_2 in the air to calcite. Both calcite and brucite occur as reaction products at higher temperatures (300-600°F), indicating that the fluid is saturated with respect to Ca^{2+} and Mg^{2+} . At higher temperatures some of the brucite seems to react with CO_2 (in the fluid) and form magnesite (MgCO_3). It is interesting to note that magnesia readily reacts at 300°F with smectite and forms a serpentine

Figure 5.4 - The FANN 50C rheograms of the 2% bentonite/1% lime/1% MgO fluids after autoclaving at the temperatures marked on the curves.

TABLE 5.4a

APPARENT VISCOSITIES (CP) MEASURED WITH THE FANN 50C VISCOMETER FOR
THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% MgO

Fann 50C Temperature °F	Autoclaved at temperature (°F)				
	70	300	400	500	600
75	1.7	2.7	2.5	2.7	1.5
100	1.7	2.6	2.3	2.4	1.2
150	1.5	2.6	2.2	2.3	1.1
200	1.3	2.7	2.3	2.3	1.0
250	1.2	2.8	2.3	2.4	1.0
300	1.3	2.8	2.5	2.5	1.0
350	1.2	2.7	2.6	2.6	1.0
400	1.4	2.7	2.6	2.6	1.0
450	1.0	3.5	3.7	4.4	1.0
500	1.2	4.5	11.5	20.6	1.3

TABLE 5.4b

PROPERTIES OF THE UNTREATED AND AUTOCLAVED FLUIDS CONSISTING OF
2% BENTONITE / 1% LIME / 1% MgO

Fluid Property	70	Autoclaved at temperatures (°F)			
		300	400	500	600
Apparent Viscosity (centipoise)	2.0	3.0	4.0	4.0	2.0
Plastic Viscosity (centipoise)	2.0	2.5	3.0	2.5	1.0
Yield Point (lb/100 sq ft)	0.5	1.5	1.5	2.5	1.5
Gel Strength (lb/100 sq ft)	1/2	1/2	2/2	2/2	1/1
API Filtrate (ml/30 min.)					
Cake Thickness (inches)					
HP-HT Filtrate (ml/30 min.)					
pH	11.6	11.8	11.8	11.6	12.2
CEC (milliequivalents/100 gms)	75	25	25	25	15

mineral (possibly amesite). In fact, all the smectite has been replaced by this serpentine mineral when the fluid was autoclaved at and above 400°F. Thus, no smectite remains in the fluid at and above 400°F. Furthermore, no cement mineral (tobermorite) crystallizes when MgO is added to the fluid, instead, a garnet-like phase has been found. It is also important to remember the addition of MgO maintains the fluid pH at high alkaline values, thus providing a buffering agent for the water-base fluids.

Electron Microscopic Examination

The common reaction product in the fluid after autoclaving at and above 400°F is a serpentine mineral. This phase is not a swelling clay mineral like smectite, and it, therefore, depresses the viscosity of the fluid. At higher temperatures, after autoclaving the fluid at and above 500°F, a garnet-like mineral seems to develop instead of tobermorite. Typical serpentine and garnet particles are shown in Figure 5.5a. Garnets occur as micron-sized spherical crystals whereas the serpentine develops hexagonal platelets with sub-micron dimensions. Close views of these serpentine platelets are displayed in Figures 5.6a and 5.7a. The x-ray spectra in Figure 5.6b give strong spectral lines of Mg, Al, and Si. This suggests an amesite or aluminum lizardite variety of serpentine with the general chemical formula:

The selected area electron diffraction pattern in Figure 5.7b gives a and b unit-cell parameters, which are compatible with the above serpentine species.

Figure #: 5.5a

Fluid: Bentonite/ Lime/MgO/600°F

Magnification: 13,000 X

Film #: 3687

Description:

A general view of the commonly observed reaction products consisting of serpentine and garnet.

Figure #: 5.6a

Fluid: Bentonite/ Lime/MgO/600°F

Magnification: 44,000 X

Film #: 3683

Description:

A close view of the newly formed serpentine platelets showing well-developed hexagonal outlines.

Intensity
counts/100 sec.

Figure #: 5.7a

Fluid: Bentonite/Lime/MgO/600°F

Magnification: 65,000 X

Film #: 3686

Description:

A close view of a clay (serpentine) platelet with hexagonal outlines.

Figure #: 5.7b

Fluid: Bentonite/Lime/MgO/600°F

Magnification: SAD

Film #: 3685

Description:

The selected area electron diffraction pattern obtained from the platelet shown in Figure 5.7a. The cell parameters calculated from the pattern are:

$$\underline{a} = 5.37 \text{ \AA}$$

$$\underline{b} = 9.27 \text{ \AA}$$

In summary, the addition of MgO in the fluid prevents the formation of cement minerals but the new phases (serpentine, garnet, magnesia etc.) do not lend any viscosity to the fluid.

VI. SUMMARY AND CONCLUSIONS

Factors controlling the high-temperature behavior of bentonite fluids and their in-situ conversion into cement have been studied. In order to understand the conditions leading to high-temperature gelation, bentonite fluids have been autoclaved at the temperature range 300-600°F for 16 hours under 16,000 psi with a systematic addition of polymers (low and high molecular weight sodium polyacrylates), sodium chloride, sodium hydroxide, silica, and salts and hydroxides of potassium. Bentonite/lime, bentonite/ CaCl_2 , and bentonite/lime/silica fluids have been examined for the purpose of inducing the in-situ conversion of the mud into cement. Effects of the additives such as CaCl_2 , gypsum, lignosulfonates, and MgO on the conversion rate of mud to cement were evaluated by studying the following fluid systems:

- bentonite/lime/ CaCl_2
- bentonite/lime/gypsum
- bentonite/lime/lignosulfonate
- bentonite/lime/ MgO

The high-temperature rheologies of the above fluids were measured with a FANN 50C viscometer and with the SANDIA viscometer before and after autoclaving. Other properties (plastic viscosity, gel strength, yield point, pH, CEC, fluid loss, filter cake thickness) of the fluids were also measured. The mineral reactions of these autoclaved fluids have been studied with x-ray diffraction and electron microscopy. Changes in the properties of the fluids were correlated with the high temperature mineral reactions in them.

The Major Conclusions of the Investigation

1. Pure Na-bentonite fluid becomes highly viscous (gelation) in the temperature range 250-450°F.
2. Low molecular weight polymer controls the viscosity only in the limited temperature range 300-400°F.
3. High molecular weight polymer increases the fluid viscosity only for the untreated mud. It reverses this function when the fluid is autoclaved at and above 300°F.
4. Sodium hydroxide, especially NaCl, at 1% concentration in the fluid greatly increases the fluid viscosity (gelation) up to 500°F. The addition of 1% silica to the fluid significantly reduces the viscosity but it leads to the precipitation of Na-silicates (analcite and albite) which may cause permeability damage in the formation.
5. Salts and hydroxides of potassium provide excellent controls on the fluid viscosity at high temperatures. This is related to the conversion of smectite to illite/smectite mixed-layers at and above 400°F.
6. Salts and hydroxides of calcium depress the fluid viscosity to very low levels at all temperatures.
7. The addition of lime increases the fluid pH and promotes the high-temperature reaction between bentonite and lime with the precipitation of tobermorite, the common cement mineral.
8. The addition of free silica to the bentonite/lime fluid does not promote the formation of cement minerals in the fluid.
9. The addition of 1% CaCl_2 to the bentonite/lime fluid leads to the total conversion of bentonite (smectite) into the cement mineral

tobermorite. Gypsum, on the other hand, does not give any benefits for the mud-to-cement conversion.

10. Lignosulfonates do not seem to cause any appreciable retardation in the conversion of the bentonitic mud into cement.
11. The addition of MgO to the bentonite/lime fluid prevents the precipitation of cement minerals but instead leads to the formation of a serpentine mineral. The latter phase is a non-swelling layer silicate and it does not lend any viscosity to the fluid. The addition of magnesia becomes detrimental to the fluid viscosity. Magnesia provides, however, a reliable buffer for maintaining a high pH in the fluid at increasing temperatures.

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