REACTIONS OF ATTAPULGITE AND SEPIOLITE
IN HIGH-TEMPERATURE DRILLING FLUIDS

Necip Guven, Leroy L. Carney, and Li-Jein Lee

Texas Tech University

United States

ABSTRACT

The fibrous clay minerals attapulgite and sepiolite have been sub-
jected to hydrothermal reactions between 149°C (300°F) and 427°C
(800°F). A 4% suspension of each of these clays was autoclaved for 16
to 24 hours with and without the addition of salts of NaCl and KCl at
1% concentration. These fibrous clay minerals start to convert at
204°C (400°F) to a smectite with a lamellar morphology. In fact,
attapulgite converts more readily than sepiolite, and the attapulgite-
to-smectite transformation is fully completed at 316°C (600°F), where-
as 20% to 50% of the sepiolite remains intact at this temperature.
The conversion of the fibrous double- and triple-chain silicates of
attapulgite and sepiolite to a layered silicate, such as smectite,
favorably affects the rheology of the drilling fluids based on these
clays. The mechanism of the conversion is, however, different for
these fibrous clays. Attapulgite dissolves first and then smectite
precipitates whereas this mechanism takes place for sepiolite at 316°C
(600°F). Both attapulgite and sepiolite, and their reaction products,
have been examined with an analytical electron microscope (JEM-100CX)
in TEM, STEM, SEM, and SAD modes. The intensities of the characteris-
tic X-ray spectra for the elements Mg, Al, Si, Fe, Ca, and K are
measured. These observations indicate that (1) significant chemical
differences exist between the fibrous clays and the smectites formed
from them and (2) morphological features of the smectites vary with
the temperature and with the presence of the salts in the system.

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INTRODUCTION

The hydrothermal reactions of fibrous clay minerals attapulgite and sepiolite have been examined within the temperature range 300-800°F and under the pressures up to 16,000 psi. The purpose of these experiments was to understand the rheological behaviour of the drilling fluids based on these clays. The fluids under investigation contained the mineral attapulgite or sepiolite as the basic ingredient. Chlorides of Na and K have been added to the system since these salts may often be present in the geothermal reservoirs.

Hydrothermal reactions of sepiolite up to 600°F were previously described [1, 2]. In this report we cover the reactions at 700 and 800°F in the sepiolite/water system in order to examine the behaviour of sepiolite fluids at very high temperatures. In addition, changes in sepiolite caused by shearing in a flow loop at 400°F and by low shearing in a FANN 50C viscometer at 500°F have also been examined.

An actual geothermal drilling fluid containing sepiolite, Wyoming bentonite and polymers, has been also autoclaved at 800°F in order to find the temperature stability of this mud.

Results of the above studies are reported below following the descriptions of the methods of investigation.

METHODS OF INVESTIGATIONS

Clay-based drilling fluids have been prepared at 4% concentrations below 500°F and at 5% concentrations above this temperature. These suspensions have been autoclaved for 24 hours below 500°F and for 9 hours above this temperature under the appropriate confining pressures. The fluid has then been removed from the autoclave and a portion of it has been transferred to FANN 50C viscometer for rheology measurements. The specifics of these experiments are briefly described in the following.

High-Temperature and High-Pressure Autoclave

The autoclave was manufactured by Autoclave Engineers, Erie, Pennsylvania. It is equipped with a pressure pump, metal seals, and heating coils. A 500 ml Autoclave cell was used for static heating at high temperatures (300-800°F) under the confining pressures up to 16,000 psi. The temperature and pressure are monitored and recorded automatically. The muds were prepared using a Hamilton Beach mixer and then transferred into the autoclave cell. The unit is heated up at a rate of 250°F/hr to the desired temperature and held at that temperature for 6 hours and subsequently cooled in air for about 14 hours. The mud was then removed for testing its rheology with FANN 50C viscometer and for examining with x-ray diffraction and electron microscopy.

FANN 50C Viscometer

The FANN 50C is a rotational viscometer capable of shear rates from 0 to 600 rpm or 0 to 1022 sec^{-1}. The fluid can be heated up to 500°F under the pressures up to 1000 psi. The fluid to be measured is placed in the sample cup and fastened to the rotor. The shear rate, temperature, and pressure can be selected and the

viscosity and temperature are automatically recorded. The viscosity can be correlated with the FANN 35A viscometer measurements at ambient temperature and atmospheric pressure.

Flow Loop

The Magcobar's loop [3] consists of a series of capillaries that can be heated to 400±25°F while circulating a fluid through shear valves. The system is devised to pump about 1.5 pints to 2 gallons of fluid from an atmospheric pressure reservoir. Typically, for a two gallon system the entire mud volume passed through about 6-12 cycles each hour where the individual mud particle goes through each active heating, shearing and cooling cycles in about 30 seconds. Intensive shearing occurs at both high and low temperatures when the mud is forced through spring-loaded back-pressure valves. The usual mud tests can be made on samples taken at the reservoir under atmospheric conditions.

Analytical Electron Microscopy

The solids of the fluids have been examined before and after hydrothermal treatments with x-ray diffraction and with analytical electron microscopy. The x-ray diffraction method does not need further explanation but a brief description of the analytical electron microscopy is included.

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

-transmitted electrons
-secondary electrons
-characteristic x-rays

Transmitted electrons form high-resolution (2-4Å) images of the thin particles like clay crystallites. These images are referred to as "TEM" images. If the incident electrons are scanned and the transmitted electrons are collected for image formation, this mode of transmitted electron imaging is referred to at "STEM" mode. In this mode electrons have higher penetrating power which can reveal the internal structure of solids. The STEM image has a resolution of about 15 Å. Secondary electrons form the image of the surface topography of a solid with a resolution of 30-100Å. These SEM images are formed by the electrons originating from a few 100Å top layer. Characteristic x-rays are produced by inelastic collision of primary electrons with the inner shell electrons of the atoms. These x-ray spectra are used for microanalysis of elements in the particles. The excitation volume (R_x) of x-rays and the penetration depth (R_e) of primary electrons determine the resolution of the detection of the characteristic x-rays. The product of the density (ρ) of a solid with the x-ray excitation volume (R_x) is known as the x-ray mass range. The penetration depth (R_e) of primary electrons are listed in Table 1 for some clay minerals of relevance to this work. Similarly the x-ray mass ranges for the K lines of the relevant elements (Si, Mg, Al, Na, K, Ca, and Fe) are given in Table 2. Considering these data in Table 2, it become obvious that the x-ray

excitation volumes are at least about one micron at 10 kev. Therefore a large discrepancy may exist between the SEM images and the corresponding x-ray spectra. In order to obtain a closer relationship between the electron image and the x-ray spectra, particles need to be extremely thin. Since silicon is a major element all these minerals, all the x-ray spectra are normalized with reference to Si-K line. Furthermore x-ray spectra are obtained in two modes:

    a) the "area" mode in which a selected area is scanned with the electron probe and the x-rays generated from this area are measured.

    b) the "spot" mode in which the electron probe has been hold stationary on a given spot and x-rays generated from this spot are measured.

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

HYROTHERMAL REACTIONS OF ATTAPULGITE

Starting Material

The attapulgite was obtained from International Minerals and Chemicals. It is the commercially available sample from the deposits in Georgia and Florida and carries the trade name "Floridian attapulgite 150". The chemical compositions of the bulk samples of attapulgite and sepiolite are given in Table 3. The x-ray diffraction analysis of the original sample indicates the presence of considerable amounts of impurities. There are 15-20% smectite, 5% illite, and 5% calcite in the clay fractions (-2 microns) of the sample. In addition, quartz occurs as a major impurity in the coarser fractions of the sample.

Electron microscopic examination of the original sample shows that attapulgite occurs as fibers or as aggregates of these fibers. Individual fibers are shown in Figure 1. These fibers have a length less than one micron and a width ranging from 300 to 500 Å. An electron micro-diffraction pattern of a fiber (from the spot marked in Figure 1) gives the following cell dimensions: a = 5.16 ±. 0.01 Å and b = 17.97 ± 0.01 Å. A typical aggregate of the attapulgite fiber is given in Figure 2. As shown in this figure, these aggregates contain small rhombs of calcite and small platelets of illite. X-ray spectra obtained from original attapulgite particles (fibers or bundles of them) are listed in Table 4. Thick attapulgite aggregates look rather fluffy and possess an irregular morphology as shown by the SEM image in Figure 3a. The latter gives a three-dimensional surface topography of the attapulgite aggregate. Figure 3b is the x-ray spectra obtained from this aggregate. The Mg, Al, Si, K, Ca, and Fe are elements present in this spectra. The chemistry of these thick aggregates often contains a little more aluminum. This higher aluminum content may well be related to the tiny mica particles entrapped in these aggregates. To summarize, attapulgite occurs in 3 forms:

    a) individual fibers and parallel sets of them. (Figure 1),

    b) clusters of fibers often with radial arrangement of fibers. (Figure 2), and

    c) thick and fluffy aggregates similar to those of smectites (Figure 3a)

Impurities in the Original Floridian Attapulgite

Smectite occurs as fluffy ill-defined aggregates with a cloudy appearance as shown in Figure 4. The x-ray spectral data in Table 4 indicates a significantly large amount of aluminum and very small amounts of magnesium. Furthermore selected area electron diffraction (SAD) data on these aggregates give the following cell dimensions: $\underline{a}$ = 5.29 Å and $\underline{b}$ = 9.16 Å.

Illite occurs in illite flakes as shown in Figure 5. The x-ray spectra of this flake in Table 4 indicate aluminum as the major octahedral cation. The SAD_o data give the following cell dimensions: $\underline{a}$ = 5.27 ± 0.01 Å and $\underline{b}$ = 9.10 ± 0.02 Å.

Calcite occurs often as small rhombs and rectangles as shown in Figure 2.

Hydrothermal Reactions in Attapulgite/Water System

Hydrothermal runs at the temperature range 300-800°F showed that attapulgite converts already to smectite at 400°F. The pertinent x-ray diffraction data are presented in Figure 6 up to 700°F. The results of the 800°F run are very similar to those at 700°F, therefore, the x-ray diffraction pattern for 800°F has not been included into Figure 6. The dark shaded reflections in this figure represents smectite's first basal reflection upon glycolation. The basal spacings of the smectites are marked before and after glycolation. In order to evaluate the rate of conversion of attapulgite to smectite, synthetic mixtures of a smectite (from Cheto, Arizona) with the Floridian attapulgite have been prepared at 10% intervals. The x-ray patterns of these synthetic mixtures have been compared with those of the patterns obtained after the hydrothermal runs. For this purpose the intensity of the 17 Å smectite reflection (dark-shaded in Figure 6) has been compared with the 10.5 Å attapulgite reflection. The results showed that about 20% of attapulgite converts to smectite at 400°F in the distilled water system. The amount of smectite increases to 60% after 500°F run and no attapulgite survives the experiment at 600°F. Similar results are obtained when 1% NaCl was added to the system. In the presence of 1% KCl the amount of smectite is rather small after the 400°F run but at higher temperatures the rate of conversion is similar. It is also important to remind that the original attapulgite sample contains about 15-20% smectite which is a montmorillonite. The basal spacings of smectites formed in the experiments range between 15.8 - 14.5 Å in the distilled water system, and 15.1 to 15.8 Å in the NaCl system, and 14.7 to 15.5 Å in the KCl system. These basal spacings are unusual for Na or K - saturated smectites (which are usually about 12 Å).

Smectites formed in the above systems have been examined with the JEM-100CX analytical electron microscope and the results are described in the following. Smectite particles formed at 400°F and 500°F consist of extremely thin films which are often grown around the original attapulgite fibers as shown in Figure 7. At 600°F all the attapulgite fibers disappear. Smectites formed in this system consist of aggregates of thin and folded films (Figure 8). These smectite aggregates often contain a large number of dense particles in the form of rectangles, rhombs, and spherules. The average intensities of the x-ray spectral lines for Mg, Al, Si, Fe, and Ca are given in Table 4. The intensities of the x-ray spectra show that Mg/Si and Al/Si ratios are higher in these smectites than in the original attapulgite but the Mg/Al ratio remains similar to that of the original attapulgite Thus Mg and Al concentrations seem to increase in smectite compared to those in the original attapulgite. The natural smectites do not contain high Mg together

with high Al in their structures. Thus the smectite obtained in these hydrothermal runs does not have a natural analog.

The x-ray spectra obtained from spherical particles (Figure 8) consist mainly of silicon indicating that these are silica spheres. The x-ray spectra from rectangular particles count of Ca, Si, and P, suggesting a mixture of silica with calcium phosphate. Calcium is obtained as the only spectra from the rhombohedral particles, indicating that they are calcite rhombs.

Smectites formed at 700°F display different morphological features. These smectites occur as small platelets as shown in Figure 9. Platy smectites are more clearly developed in the presence of NaCl or KCl. Figure 10 shows these smectites platelets and their edge-to-edge aggregations in the form of a mosaic. The chemical composition of these smectite platelets are indicated by the x-ray spectra in Table 4. The chemistry of these smectites is again unusual with regard to their high Mg and Al contents.

A considerable number of silica spherules are also observed to form at 700°F. Figure 11 shows the typical features of these spheres. Smectites formed from attapulgite at 800°F temperature consist mainly of platy forms and their mosaics as shown in Figure 12. Again large number of silica spheres are also precipitated at this temperature. It is noteworthy to point out that the original montromillonite remains in the system. These smectite flakes seem to be extremely rolled and curled. The shearing with FANN 50C does not cause any changes in aggregations of these particles.

HYDROTHERMAL REACTIONS OF SEPIOLITE AT HIGH TEMPERATURES

After the hydrothermal treatments at 700° and 800°F for 6 hours under a pressure of 16,000 psi all the sepiolite disappears from the system. Thus sepiolite seems to dissolve completely. New minerals such as smectite, tremolite, and talc are found to form in the mud. Smectite makes up about 60% of the solids after the run at 700°F and about 40% after the run at 800°F. Tremolite content of the sample seems to increase at 800°F. All these minerals (smectite, tremolite, and talc) often occur together as shown in Figure 13 where tremolite fibers, talc platelets, and smectite films are aggregated. Tremolite fibers occur as bundles or as individuals (Figures 14 a and b). These fibers have a length of 2 to 6 microns. Sometimes these fibers join each other along their fiber edges. The selected area electron diffraction pattern of the tremolite fiber in Figure 14b is given in Figure 14c. The b and c unit-cell parameters obtained from this pattern are $c = 5.27 \pm 0.03$ Å and $b = 18.12 \pm 0.03$ Å.

The chemistry of these fibers is indicated by the x-ray spectral data in Table 5. Thus the chemistry, unit-cell parameters, morphological features confirm the identification of this phase as tremolite. The latter is a fibrous amphibole (an asbestos mineral) with the formal chemical composition: $Ca_2Mg_5Si_8O_{22}(OH)_2$ where part of magnesium can be substituted by divalent iron.

Talc occurs in well-developed platy forms as shown in figures 15a and 15c. The selected area electron diffraction pattern of the talc in figure 15a is given in Figure 15b. The following unit cell parameters are obtained from this pattern: $a = 5.32 \pm 0.2$ Å and $b = 9.08 \pm 0.02$ Å. The x-ray spectra obtained from the talc platelets are given in Table 5. These data agree with the formal composition of talc: $Mg_3Si_4O_{10}(OH)_2$.

GEOTHERMAL DRILLING FLUID

A fluid with the composition 20 lbm/bbl sepiolite + 5 lbm/bbl Wyoming bentonite + 2 lbm/bbl polymer A + 1 lbm/bbl polymer B has been hydrothermally treated at 800° F. The bentonite consists of a Na-montmorillonite and it occurs typically in folded thin films as shown in Figure 16. Sepiolite particles consist of fibers or bundles of them Figure 17. Both sepiolite and bentonite contains impurities of quartz, feldspars, mica, calcite, and dolomite as detected by x-ray diffraction.

After autoclaving the fluid at 800°F for 6 hours under a pressure of 16,000 psi all sepiolite disappears from the system. Montmorillonite however remains without any noticeable changes. The main hydrothermal reaction in the system is related to the dissolution of sepiolite and subsequent precipitation of talc, tremolite, and smectite. These reaction products are similar to those described above for the pure sepiolite system at 800°F except tremolite and talc are produced in small quantities.

RHEOLOGICAL PROPERTIES OF THE FLUIDS AFTER
HIGH TEMPERATURE REACTIONS

Untreated sepiolite, sepiolite, attapulgite, and geothermal drilling fluids after the 800°F treatments have been tested with respect to their rheologies with the FANN 50C viscometer from ambient to 500°F temperature. The rheogram of the original sepiolite fluid (5g sepiolite/100cc water) with no pre-treatment is given by the curve No. 1 in Figure 19. This shows a viscosity maxima at about 300°F. The viscosity at 1022 sec^{-1} of shear goes from 6.0 centipoises through a maximum of 14.5 centipoises and then drops to 3.0 centipoises at 500°F. The API fluid loss of the original sepiolite fluid is measured to be 54 cc. Sepiolite fluid after autoclaving at 800°F gives a fairly straight line viscosity (curve No. 2) and it has an API fluid loss of 114cc. Attapulite fluid after autoclaving has a viscosity which is lower than that of sepiolite. Furthermore it has no fluid loss control whatsoever. The geothermal drilling fluid's viscosity has been given by curve No. 4A before the treatment and by curve No. 4B after the autoclaving at 800°F. This fluid has an API fluid loss of 84cc it showed temperature thinning and stable rheology through 500°F. The same fluid before autoclaving showed a maximum viscosity at 480°F as shown by curve No. 4A in Figure 19.

In conclusion, attapulgite when subjected to elevated temperatures converts to a smectite. This smectite has an unusually high Mg and Al content and it consists of small platelets rather than the thin folded films of common smectites. This new type of smectite seems to have very low viscosity and no fluid loss control.

Sepiolite when subjected to elevated temperatures converts first to be smectite and also to other minerals (talc + tremolite) at temperatures above 700°F. Surprisingly the reaction products of sepiolite has a remarkable fluid loss control and some visosity.

Using sepiolite in combination with Wyoming bentonite and polymers, a drilling fluid can be formulated that has a very stable viscosity and fluid loss control even after heating at 800°F.

CHANGES IN RHEOLOGY AND MORPHOLOGY OF SEPIOLITE UPON CIRCULATING THROUGH MAGCOBAR'S FLOW LOOP

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

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

Original sepiolite slurry after being sheared at room temperature consists of well dispersed sepiolite fibers as shown in Figure 18. As indicated in Table 6, this seems to increase slightly the viscosity and the fluid loss. The rheogram (Figure 20) for the original sepiolite fluid shows a maxima at about 300°F. The sepiolite sample No. 2 which was sheared for two hours in the flow loop has a similar rheogram as the original sample. X-ray diffraction and electron microscopic examination does not show any conversion of sepiolite to smectite. However, sepiolite fibers develop coagulations during low shearing in FANN 50C as seen in Figure 21 into large spherical flocks.

Sample No. 6 was taken from the flow loop after 7½ hours of circulation and subjected to temperature of 370°F. No conversion of sepiolite to smectite was observed during this circulation. Sepiolite particles occur in smaller aggregates (Figure 22) and the individual fibers seem to disappear. This fluid had somewhat lower rheology (Table 6) and with FANN 50C measurement gave a different rheogram (curve No. 6 in Figure 20). We now get a viscosity maximum at about 400°F. After the sample was subjected to 500°F in FANN 50C viscometer the conversion of sepiolite to smectite takes place. This is indicated by the x-ray diffraction data. The particles in the fluid again aggregate to large flocules (Figure 23) during testing with FANN 50C viscometer. These flocules seem to consist of sepiolite fibers with the thin smectite films acting like a gelating agent between the fibers. Conversion of sepiolite to smectite occurs in small amounts in the flow loop circulations above 400°F and the smectite content slightly increases with time, i.e. from sample No. 14 to sample No. 18 in Table 6. The fine sepiolite fibers disappear and bundles of sepiolite fibers predominate. More smectites form as thin films around the sepiolite fibers during testing at 500°F in FANN 50C (Figure 24). These thin films seem to coagulate with sepiolite fibers into large flocks. The pretreatment of the fluid in flow loop seems to promote the sepiolite-to-smectite in FANN 50C viscometer at 500°F. This conversion is probably responsible for the shifting of viscosity maxima to higher temperatures in the rheograms for the fluids No. 14, No. 15, and No. 18 in Figure 20.

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[2]Leroy L. Carney and Necip Guven, "Investigation of changes in the structure of clays during hydrothermal study of drilling fluids", Society of Petroleum Engineers Journal, October 1980, pp. 385-390.

[3]Reece Wyant, "A unique system for preparation and evaluation of high-temperature drilling fluids", Society of Petroleum Engineers of AIME SPE Paper No. 5515, SPE Dallas-Texas, September 1975.

ACKNOWLEDGEMENTS

Table 1

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

mineral	10 keV	20 keV	100 keV
sepiolite	1.6	5.1	75.5
attapulgite	1.4	4.8	70.6
saponite	1.3	4.3	62.9
Na-montmorllonite	1.4	4.3	63.4

Table 2

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

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

Table 3

Chemical analysis of the bulk samples of sepiolite and attapulgite 150, (on the ignited sample).

	attapulgite	sepiolite
SiO_2	68.0 wt%	67.1 wt%
MgO	10.5	26.5
Al_2O_3	12.0	2.7
Fe_2O_3	5.0	0.66
CaO	1.7	1.48
K_2O	1.0	0.55
Na_2O	0.7	0.32
P_2O_5	n.d.	n.d.
TiO_2	0.7	n.d.
LiO_2	n.d.	0.11

Table 4

Average intensity ratios and the standard deviations of the x-ray spectra obtained from the particles in the original attapulgite sample and from the smectites formed at high temperatures in the system attapulgite/water.

Particles designation	Electron Mode	Mg	Al	Si	Fe	Ca
original attapulgite fiber	STEM/area	.09 ± .01	.09 ± .01	1.00	.06 ± .02	n.d.
original attapulgite aggregate	STEM/area	.08 ± .01	.13 ± .03	1.00	.06 ± .04	.04 ± .02
smectite/600°F	STEM/area	.16 ± .05	.16 ± .04	1.00	.08 ± .02	.03 ± .02
smectite/700 F	STEM/area	.21 ± .14	.24 ± .03	1.00	.14 ± .01	n.d.
smectite/800 F	STEM/area	.19 ± .04	.22 ± .05	1.00	.11 ± .03	.05 ± .02
impurities in the original attapulgite sample:						
smectite	STEM/area	.03 ± .01	.30 ± .03	1.00	.09 ± .03	.01 ± .01
illite	STEM/area	.03 ± .01	.35 ± .03	1.00	.09 ± .09	.02 n.d.

Table 5

Average intensity ratios and the standard deviations of the x-ray spectra obtained from the original sepiolite and from the minerals formed at high temperatures in the system sepiolite/water.

Particle designation	Electron Mode	Mg	Al	Si	Fe	Ca
sepiolite fibers (original	STEM/area	.23 ± .04	.02 ± .01	1.00	.02 ± .01	-
smectite/600°F	STEM/area	.29 ± .05	.01 ± .01	1.00	.01 ± .01	-
tremolite/700°F	STEM/spot	.16 ± .04	.02 ± .01	1.00	.03 ± .01	.19 ± .05
tremolite/800°F	STEM/spot	.16 ± .04	.02 ± .01	1.00	.03 ± .02	.16 ± .04
talc/800°F	STEM/area	.33 ± .04	.04 ± .03	1.00	.03 ± .03	-

Table 6

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

Sample No.	hours circulated	average temperature (F°) during circulation	A.V.	rheology obtained from measurements with FANN 35A visiometer				
				600 rpm	300 rpm	PV	YP	API fluid loss
1	none	n.a	10.5	21	18	3	15	54 cc
2	2	72	12	24	22	2	20	55
6	7½	370	10	20	17	3	14	96
11	12	380	7.5	15	12	3	9	96
14	15½	425	6.5	13	9	4	5	n.d.
15	16	425	6	12	8	4	4	n.d.
18	18½	435	3.5	7	6	3	3	96[+]
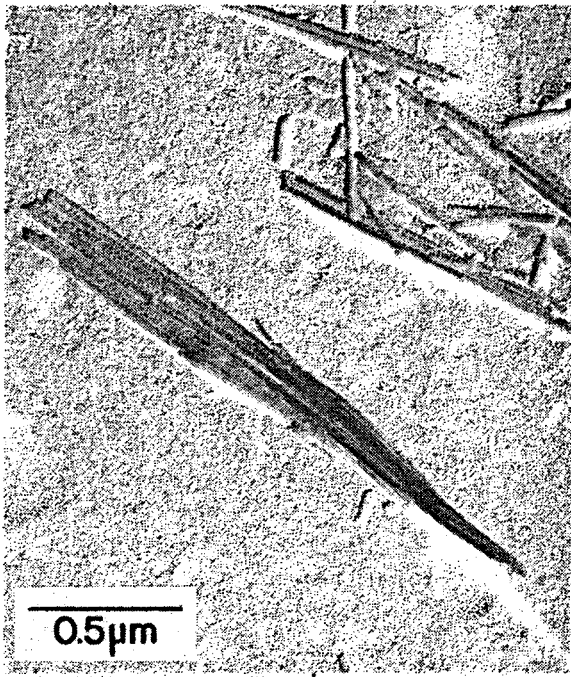
Figure 1. Attapulgite fibers

Figure 2. An aggregate of attapulgite fibers

Figure 3a. SEM image of a thick and fluffy attapulgite aggregate
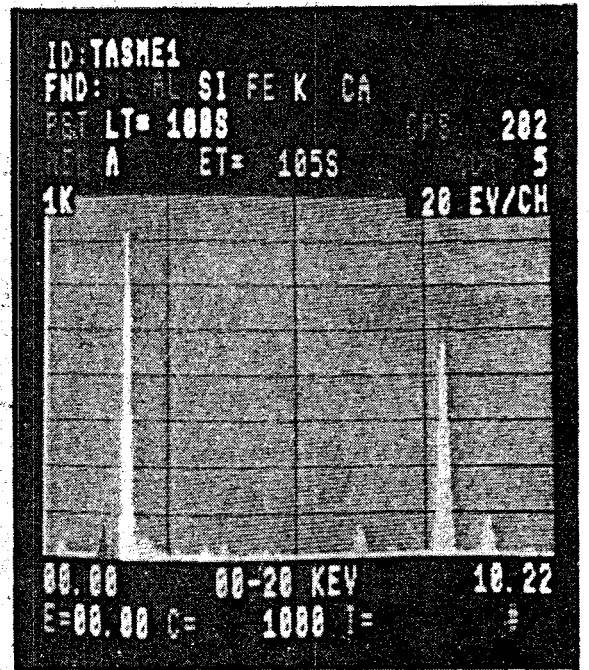
Figure 3b. The x-ray spectra obtained from the attapulgite aggregate in Fig. 3a.
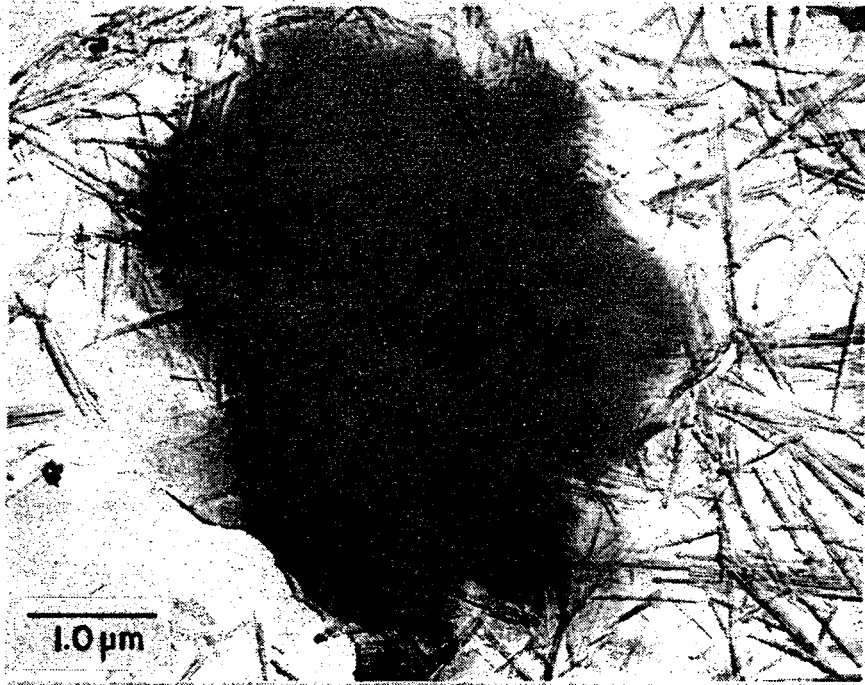
Figure 4. Smectite aggregate in attapulgite sample.
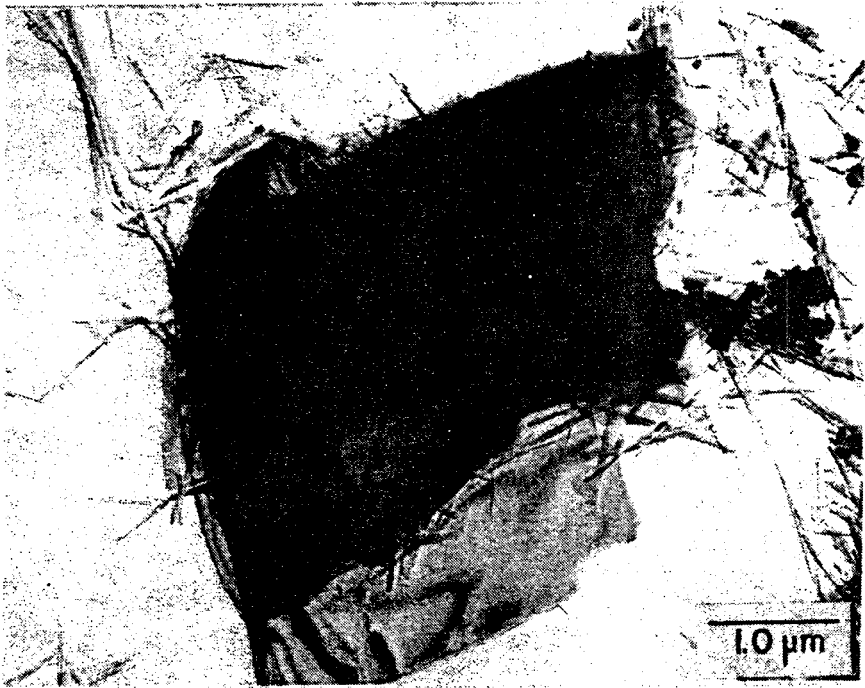
Figure 5. A typical illite particle in attapulgite sample.
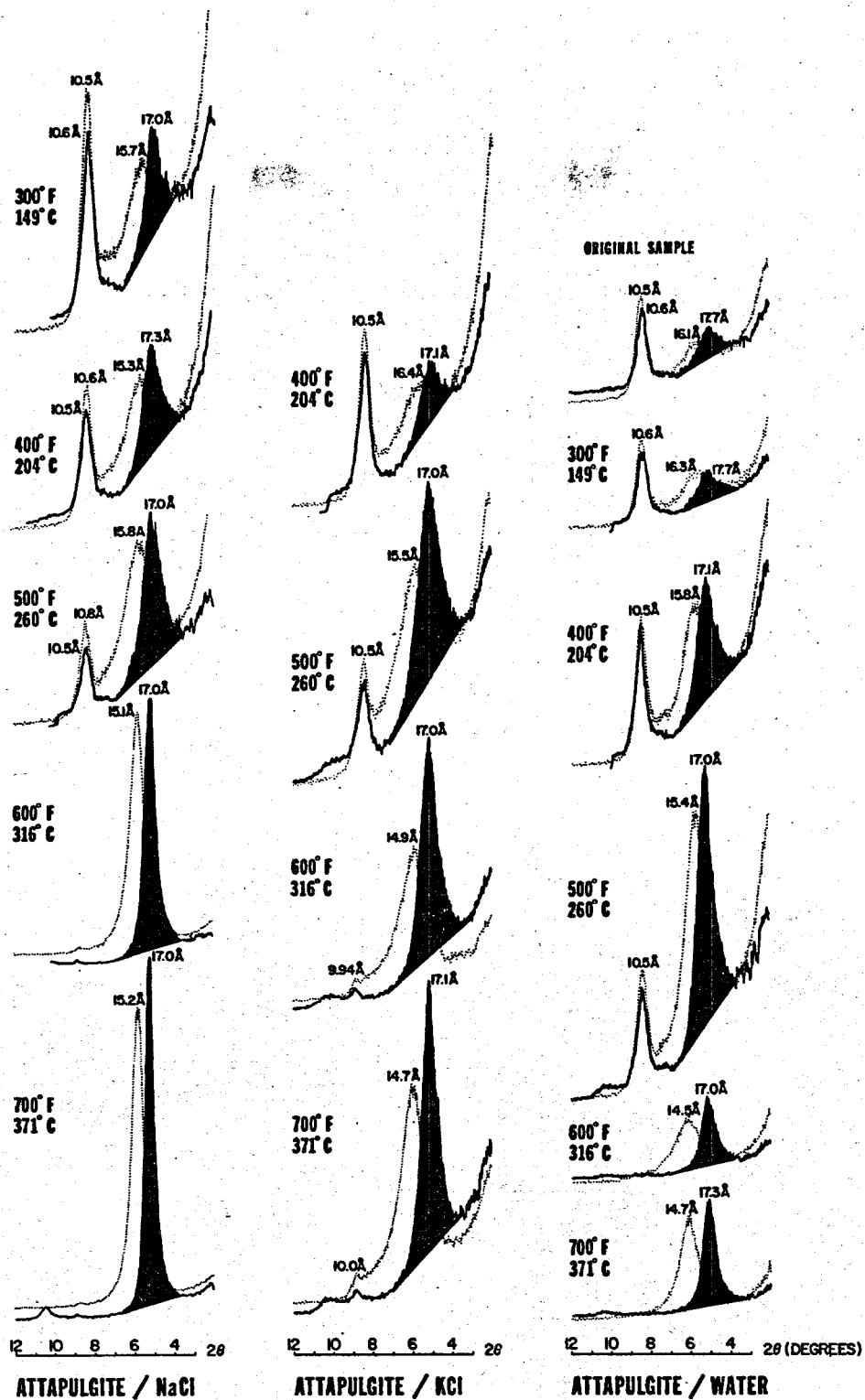
Figure 6. X-ray diffraction patterns of attapulgite after various
hydrothermal treatments (dotted lines before the glycolation and
solid lines after the glycolation).
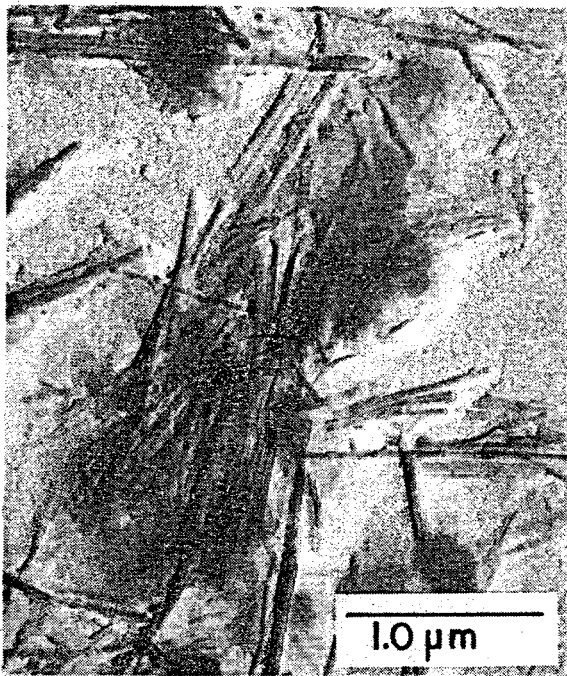
Figure 7.   Smectite films grown around the attapulgite fibers at 500°F in the attapulgite/water system.
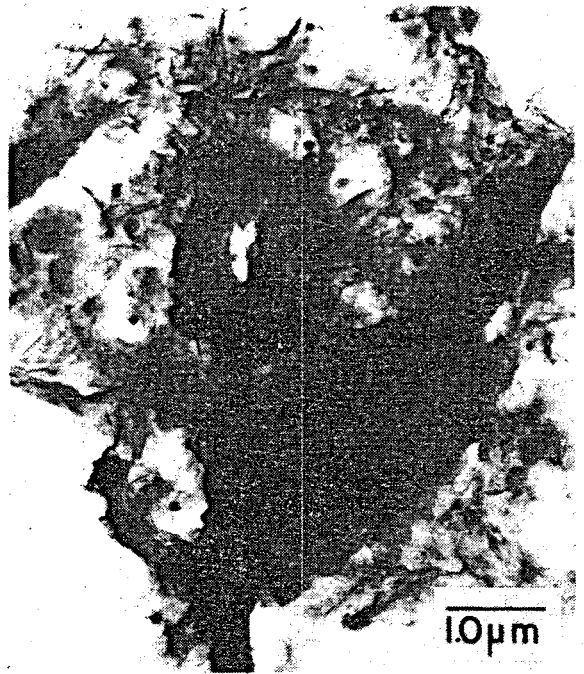
Figure 8.   Smectites formed at 600°F in the attapulgite/water system (note the dense impurities).

Figure 9.   Platy smectite particles formed at 700°F in the attapulgite/water system.
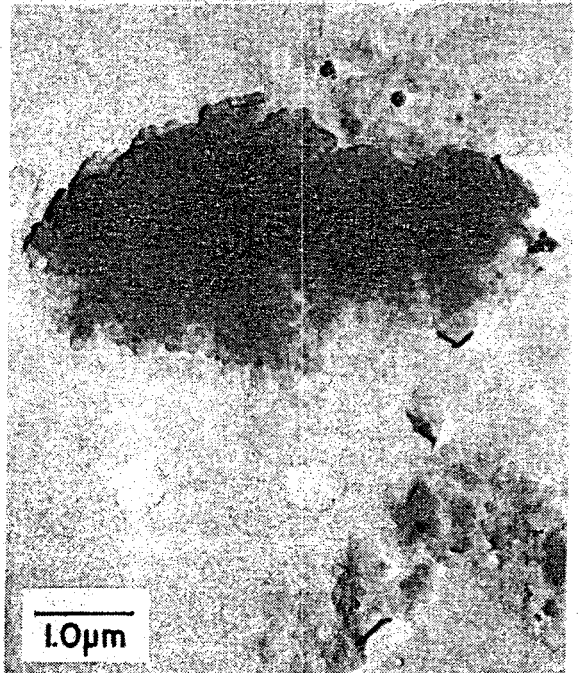
Figure 10.   Mosaics of small smectite particles formed at 700°F in the presence of 1% NaCl in the attapulgite/water system.
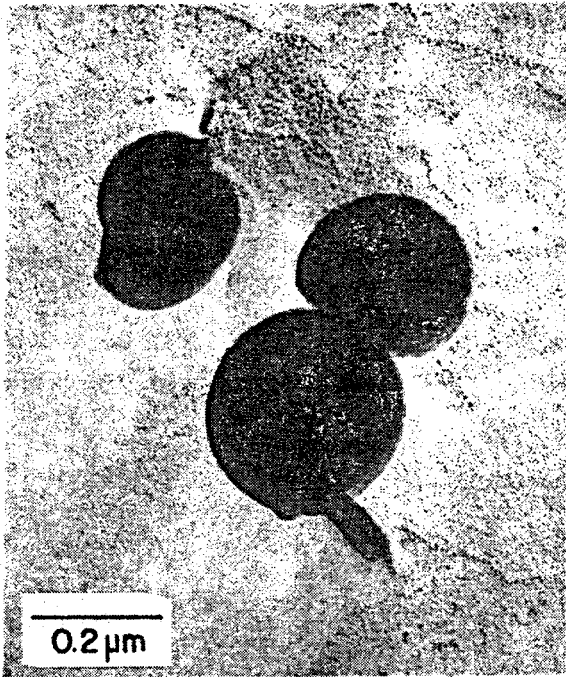
Figure 11. Silica spheres formed at 700°F in the attapulgite/water system.

Figure 12. Platy smectites formed at 800°F in the attapulgite/water system.

Figure 13. Aggregates of tremolite (fibers), talc (platelets) and smectite (thin films) formed at 800°F in the sepiolite/water system.
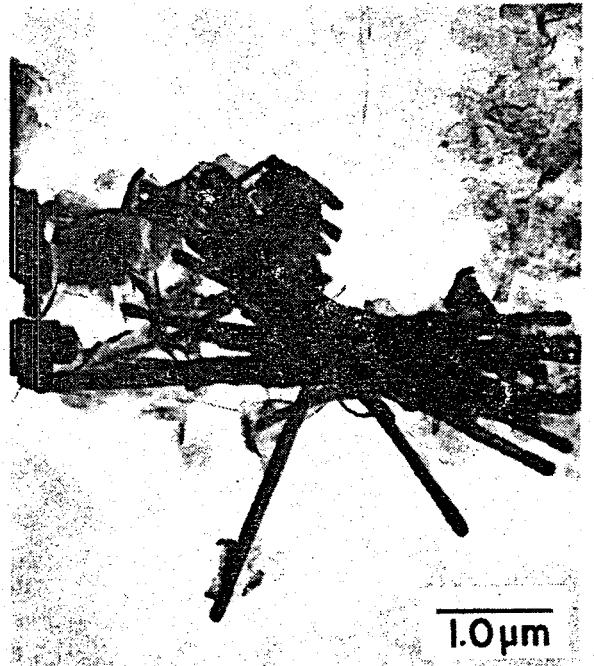
Figure 14a. A bundle of tremolite fibers formed at 800°F in the sepiolite/water system.

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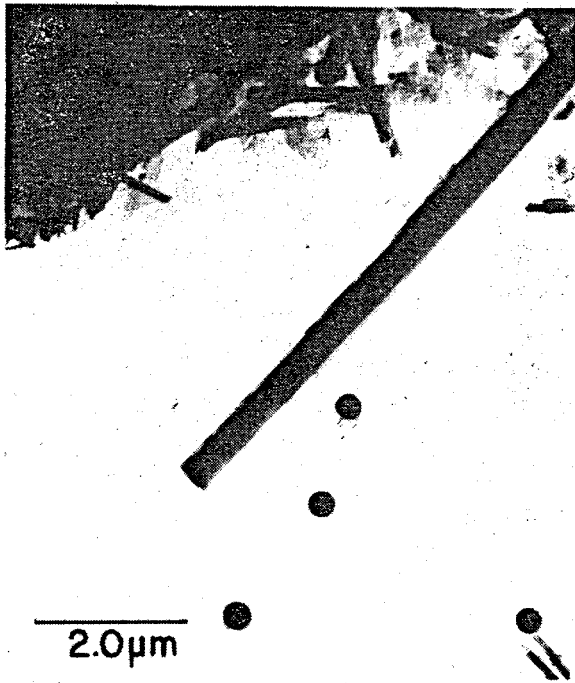
Figure 14b. A tremolite fiber formed at 800°F in the sepiolite/ water system.
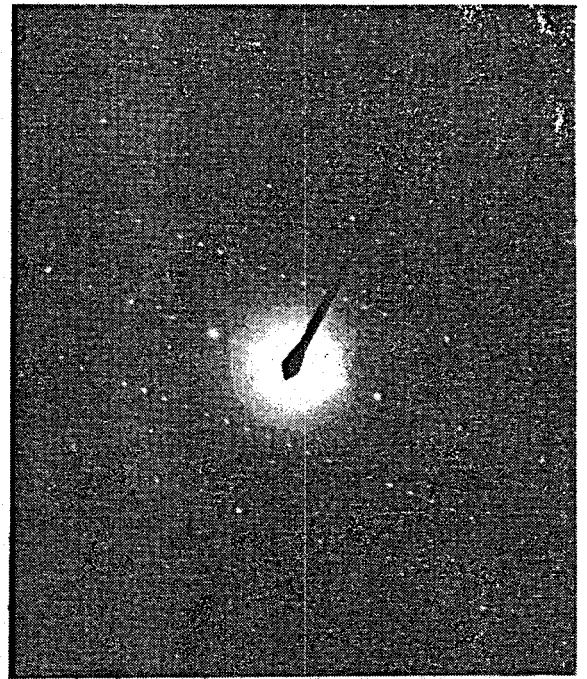
Figure 14c. Selected area electron diffraction pattern of the tremolite fiber in Figure 14b.
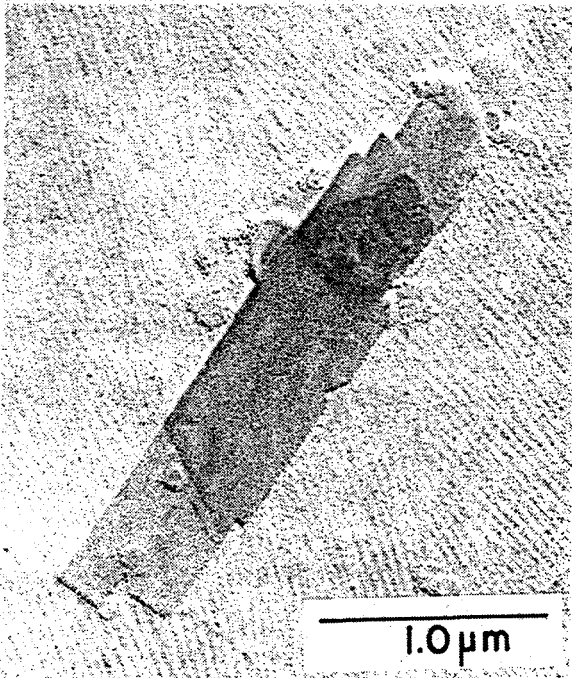
Figure 15a. A talc platelet formed at 800°F in the sepiolite/ water system.
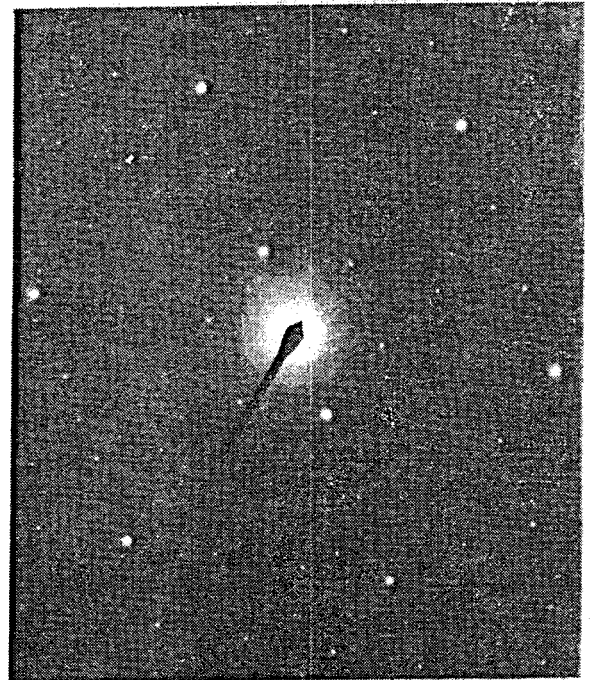
Figure 15b. The selected area electron diffraction pattern of the talc platelet in Figure 15a.
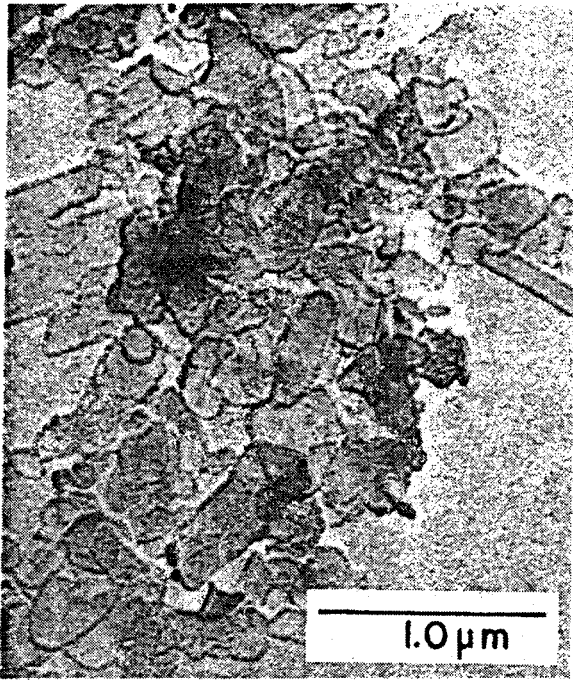
Figure 15c. Talc platelets formed at 800°F in the sepiolite/water system.

Figure 16. Typically folded smectite flakes in Wyoming bentonite.
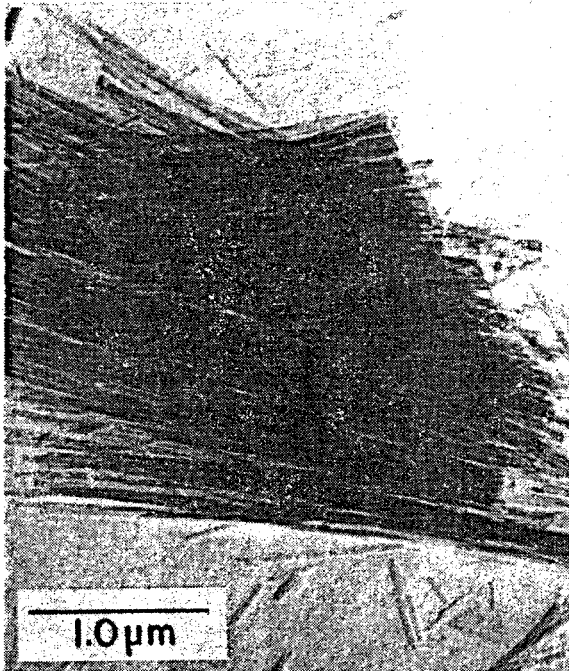
Figure 17. Sepiolite fibers in the original sample before the hydrothermal treatments.

Figure 18. Dispersed sepiolite fibers in the slurry after being sheared at room temperature for 2 hours.
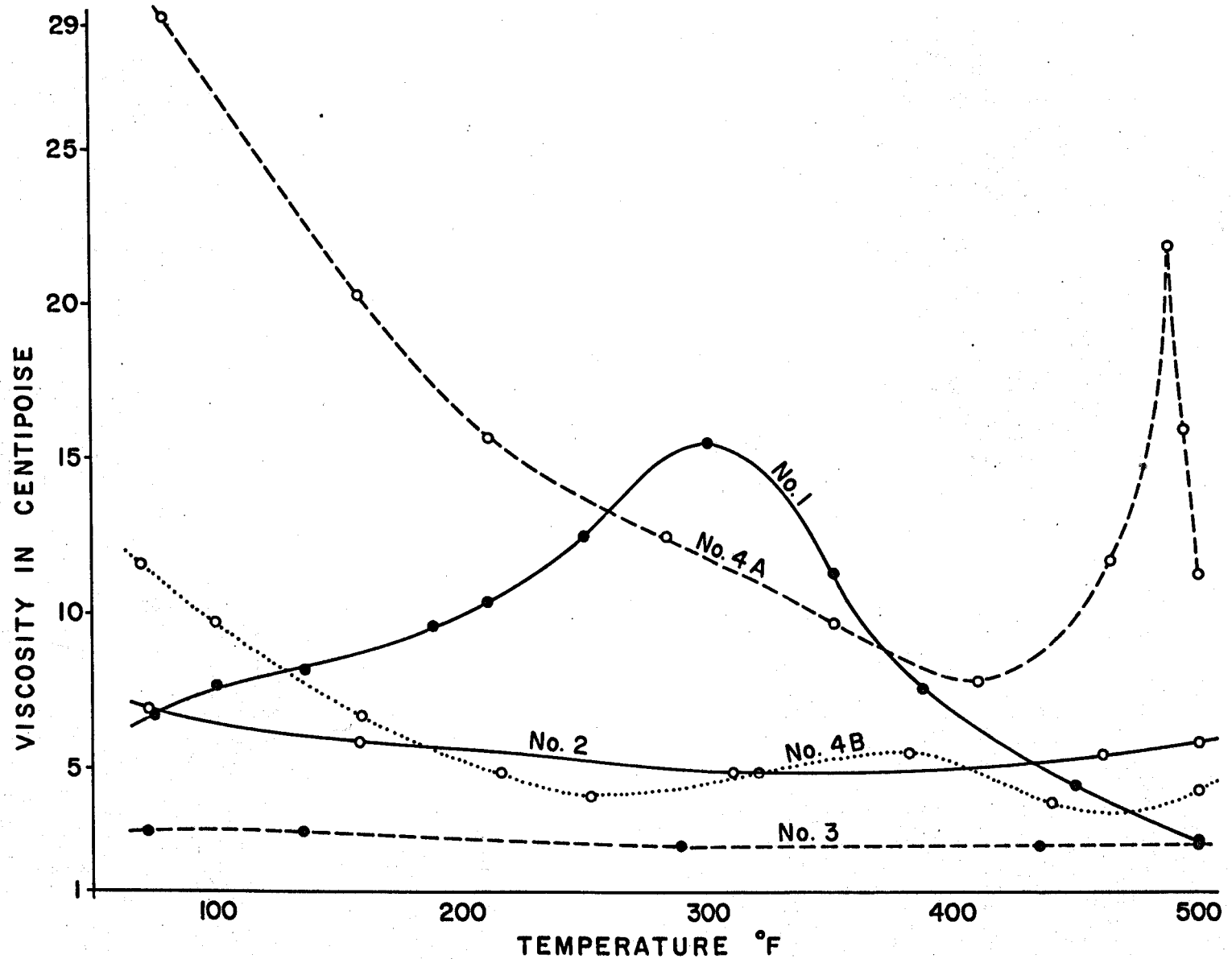
Figure 19.   Rheograms of the various drilling fluids as measured by FANN 50C viscometer.   No. 1: the untreated sepiolite slurry; No. 2:   Sepiolite slurry after autoclaving at 800°; No. 3: attapulgite slurry after autoclaving at 800°F; No. 4A: the untreated geothermal drilling fluid; No. 4B: geothermal drilling fluid after autoclaving at 800°F.
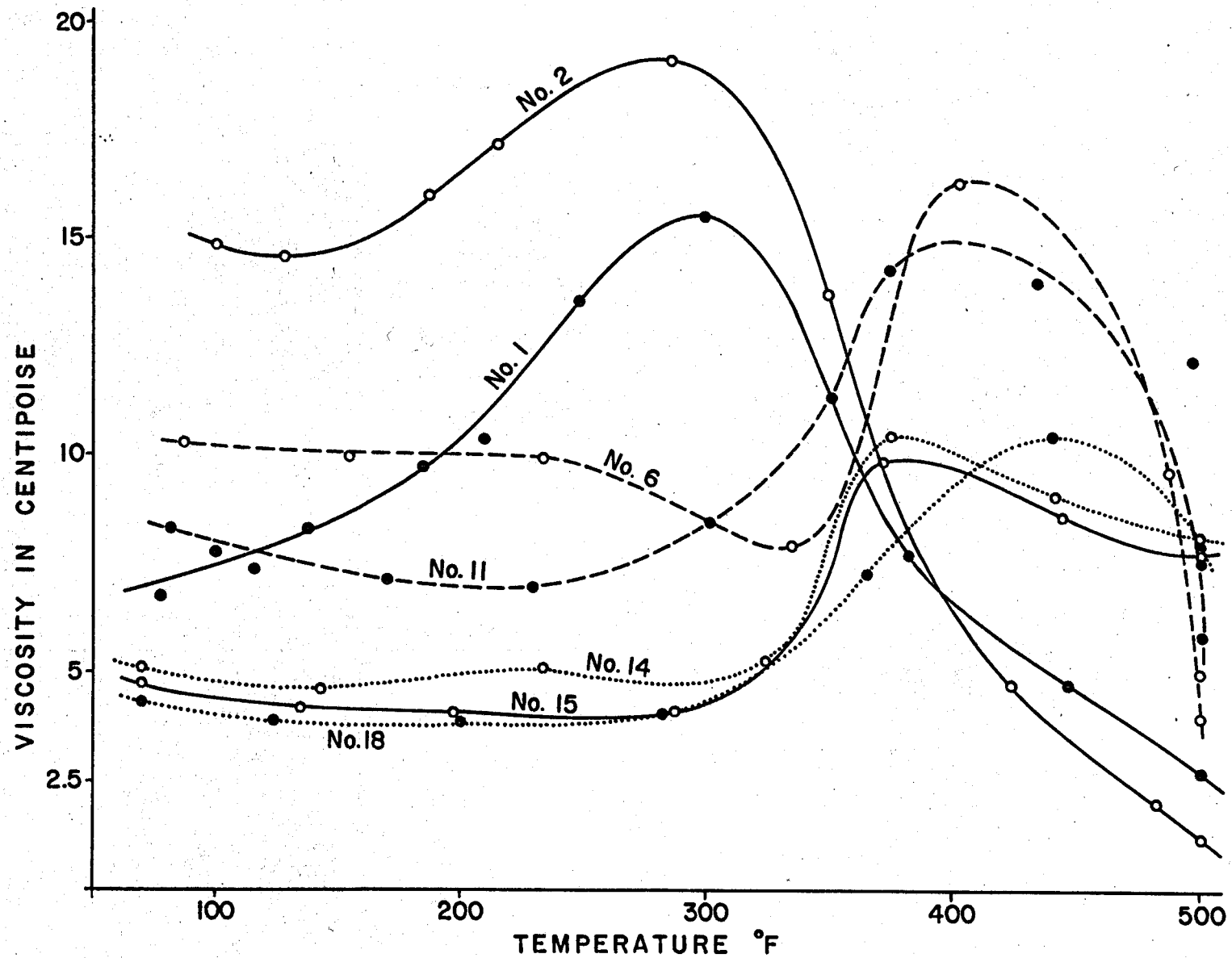
Figure 20. Rheograms of the sepiolite samples pulled from Magcobar's flow loop. Sample No.'s correspond to those in Table 6.

Figure 21. Aggregation of sepiolite fibers into spherical flocks during testing in FANN 50C viscometer.
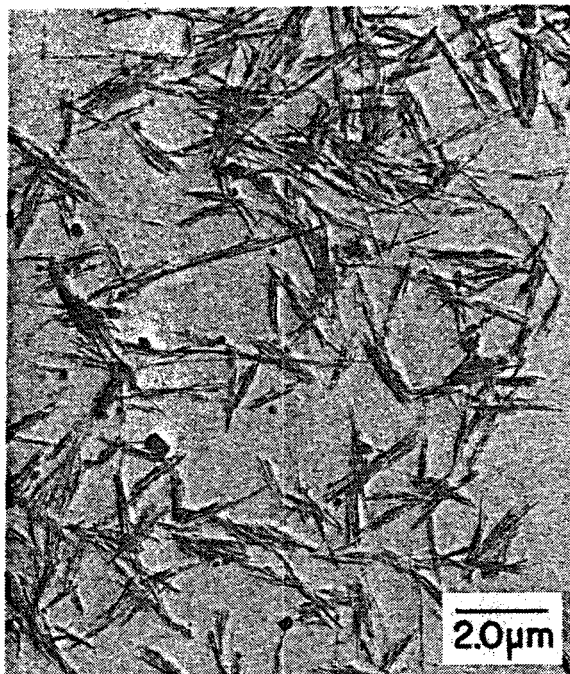

Figure 22. Small bundle of sepiolite fibers developed during 7½ hours circulation in flow loop at 370°F.
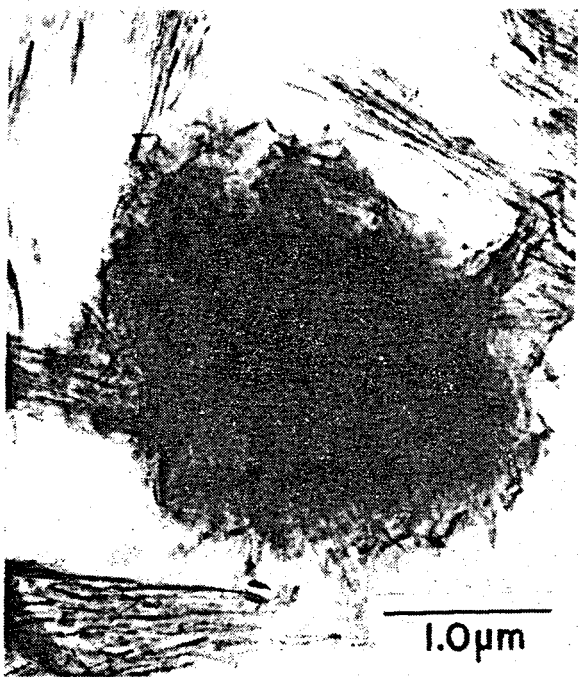

Figure 23. Large fluccules (in the center) of sepiolite and smectite formed during testing with FANN 50C viscometer at 500°F.

Figure 24. Aggregates of thin smectite films and original sepiolite fibers formed during testing at 500°F with FANN 50C viscometer.