# USE OF CLAY IN DRILLING FLUIDS

By Delmar H. Larsen *

## INTRODUCTION

The rotary method of drilling wells for oil and gas is now the most widely used system in point of footage drilled, and is the only presently available method for very great depths. In the rotary system of drilling, a drilling fluid or "drilling mud" is maintained in the hole at all times while the hole is being drilled, and is circulated in such a way that the cuttings produced by the action of the bit are removed from the hole continuously, thus permitting uninterrupted drilling, except for shut-downs occasioned by the necessity for changing bits, adding new lengths of drill pipe, setting casing, and by occasional drilling accidents. The essential mechanical features of a rotary drilling operation can be seen from figure 1; the bit is rotated by means of a hollow drill pipe, down which the drilling fluid is circulated. Holes in the bit allow the mud to emerge at the bottom of the well, from which point the mud travels upward in the cylinder of annular cross section formed by the drill pipe and the walls of the hole. Both rotary and vertical movement of the drill pipe are permitted without interruption of circulation by introducing the mud at the top of the drill pipe through a rubber hose, a swivel joint, and a special top section attached to the drill pipe by means of which the pipe can be rotated. The mud flows out through the bits, emerges from the top of the hole, is screened to remove sand and cuttings, and enters a pit, from which the mud pumps can pick up the mud for recirculation.

In the very early days of drilling wells by circulating fluid methods, water was used as the fluid. The advantages of using a slurry of clay and water, however, soon became apparent, doubtless through clay adventitiously incorporated in the fluid as a result of drilling through argillaceous strata, and in time it became the usual practice to add surface clays deliberately in order to prepare a mud for circulation. The primary function of the circulating mud is, of course, to remove cuttings continuously, and this action is enormously facilitated by providing a thickened slurry as distinguished from a liquid of low viscosity and no shear strength, such as water. Moreover, because subterranean formation fluids are generally and normally under a pressure roughly corresponding to or slightly exceeding that of a column of water of equal depth, the density of 1.1 to 1.2 provided by ordinary clay slurries served to keep the formation fluids confined to their respective formations during the course of drilling. Another operational advantage yielded by a clay-water slurry was that of impeding the loss of the fluid into permeable low pressure strata. Whereas water will flow away into such a stratum, clay will generally form a filter pack on the face of such a formation, thus retaining the mud in the hole.

These benefits imparted by the use of clay are still of prime importance, and most of the progress in drilling-mud technology during the last two or three decades has been directed toward enhancing these advantages, in some cases by careful selection of clays and other materials entering into the muds, and in others by the development and introduction of new materials and processes for accomplishing much the same results.

## FUNCTIONS OF CLAY IN MUDS

### Flow Properties and Density

As has been indicated, the ordinary and common drilling mud consists of water to which clay has been added to an extent sufficient to impart a viscosity several times greater than that of water as well as an appreciable shear strength and, in the majority of cases, thixotropy as well. Such drilling muds are thus plastic fluids in which the degree of plasticity—that is shear strength—increases with time of standing of the mud, but decreases again upon agitation.† An idea of the degree to which these properties are developed, as well as the density increase resulting from the addition of the clay, may be obtained from figure 2. There are shown in figure 2 the shear strength immediately after agitation (dashed line), the shear strength developed by ten minutes quiescence (dot-and-dash), and the so-called Stormer viscosity (solid line) at 600 rpm, for three clays used in drilling muds, as a function of the percent by weight of clay in the mud. The density of the mud also appears on the figure. The clays used were a bentonite (a) from the Black Hills area (Wyoming-type bentonite), a Turner Valley, Alberta, surface clay (B), and a clay (c) from Rogers Dry Lake, California, one of the better-known Mojave Desert playas. The viscosity is shown in centipoises as measured with the regular Stormer viscometer as specified by the American Petroleum Institute (A.P.I.), although even an approximation to absolute measurements can scarcely be made with this instrument. It was deemed preferable to give test results on these slurries made by the standard American Petroleum Institute method rather than to use one of the many modifications of the apparatus which have been proposed because of the wide usage of the former. Shear strengths, or "gel strengths," as they are designated by the A.P.I. Code, are shown in grams Stormer, again the officially adopted unit; but they may be very approximately converted to dynes per square centimeter by multiplying by the factor 2.2. The usual norm of mud viscosity corresponding to good practice is about 15 centipoises.

It will be apparent from figure 2 that some range in density is available by proper selection of clay or by blending. Moreover, the very considerable thixotropy of the bentonite and the Mojave Desert clay is shown by the vertical difference in the two shear strength curves for each slurry, this property being almost negligible in the Turner Valley clay. It may be seen from the magnitude of the shear strengths shown that cuttings of appreciable size can be carried upwards by the drilling mud ascending in the hole even at very low fluid velocities. Moreover, the increase in shear strength during standing resulting from the thixotropy of the aver-

---

* Consulting Chemist and Chemical Engineer, Los Angeles, California.

† The earliest clear description of thixotropy in a clay slurry which has come to the writer's attention is that of Weber in 1909.

( 269 )

https://doi.org/10.1346/CCMN.1952.0010124 Published online by Cambridge University Press

CROWN BLOCK

TRAVELING BLOCK

SWIVEL

ROTARY HOSE

DRILL STEM

STAND PIPE

HOIST

MUD PUMPS

ENGINE HOUSE

MUD DITCH FROM FLOW PIPE

FLOW PIPE

ROTARY TABLE

SURFACE CASING

DRILL PIPE

CONDUCTOR PIPE

MUD PIT

CELLAR

CASING

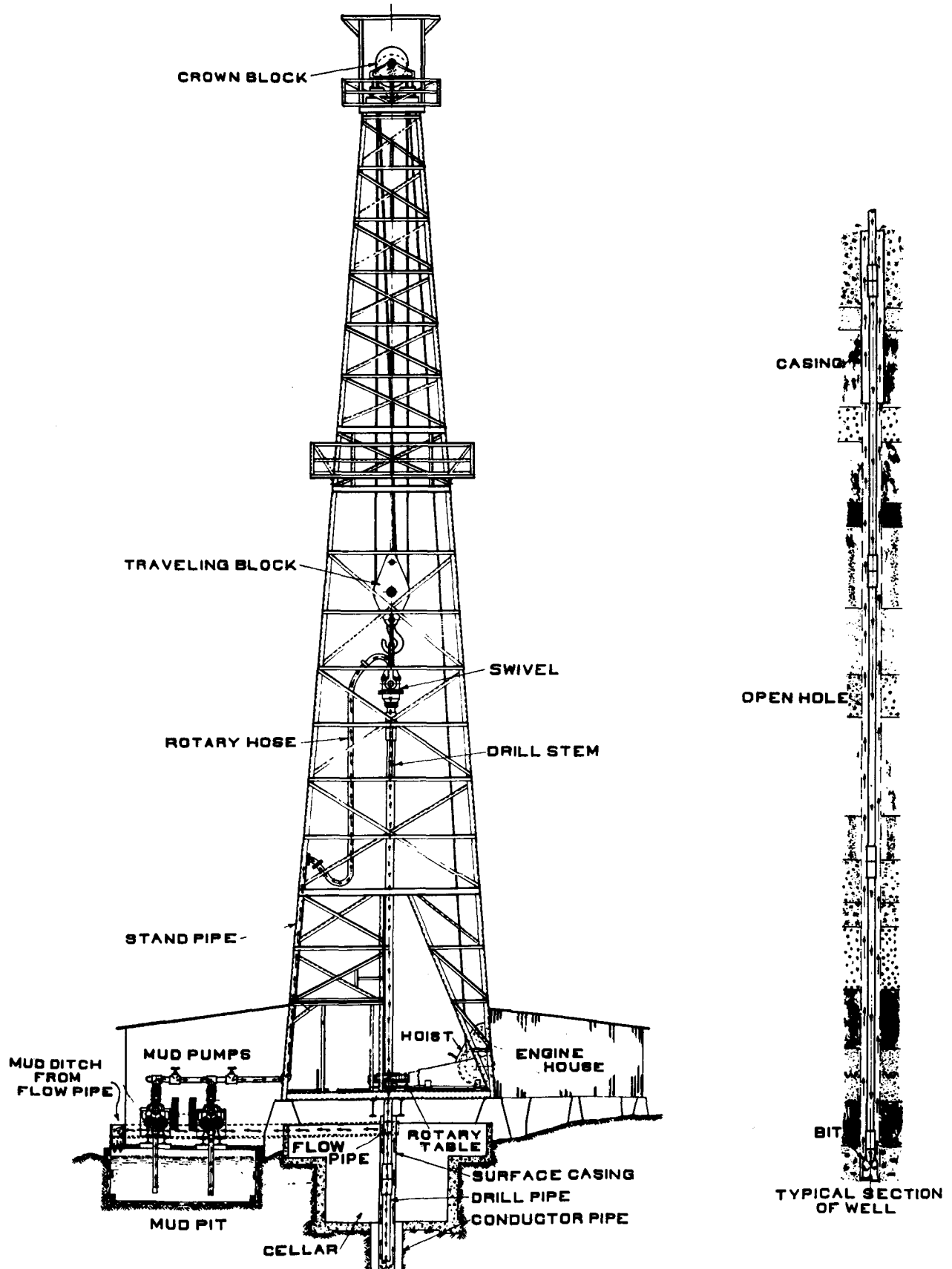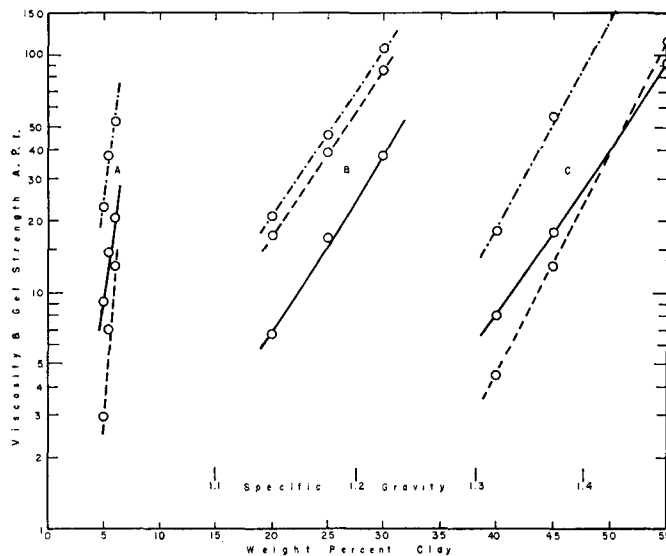OPEN HOLE

BIT

TYPICAL SECTION OF WELL

FIGURE 1.

FIGURE 2.

age mud is of value in preventing the settling of cuttings should circulation be interrupted for any reason. A highly plastic, poorly thixotropic mud would be undesirable as high pump pressures would be needed to circulate it, the jetting action of the mud as it emerges from the bit would be diminished, and release of cuttings at the surface would be impeded. The usual method of obtaining a higher density in drilling muds than is obtainable by the use of clay and water alone consists of adding a finely divided dense material such as ground barite or ground hematite to the drilling mud. If this is ground exceedingly finely, for example to the 1-micron range, then mud to which it is added will be excessively thickened and the increase in density will be relatively small. On the other hand, if a weighting material is too coarse, for example around 60 or 80 microns in diameter, it will tend to settle out or even be removed by the same mechanism designed to remove sand from the mud. Weighting materials used in drilling muds are, accordingly, generally in the particle size range of about 5 to 40 microns, and here again at least a slight shear strength of the mud is desirable and necessary to prevent settling.

Much work has been done and reported on the rheology of drilling muds, and much progress has been made particularly in the last five years. The work of Evans and Reid (1936), the various papers of Herrick (1932), Pigott (1942), Cardwell (1942), Beck, Nuss and Dunn (1948), Hall, Nuss and Thompson (1950), Melrose and Lilienthal (1951), Williams and Bruce (1951), Métrot (1951) and van Olphen (1950, 1950a, 1950b) is of note. The monographs of Babbitt and Waldwell (1939, 1940), while dealing only indirectly with drilling muds, are also of value. At the present time, the flow of drilling mud in pipes and through orifices can be fairly well determined and related to measurements made on small samples of the mud, such as these made with a rotational viscometer, useful in turbulent flow, and in plastic flow where thixotropy is negligible. Much work remains to be done, however, particularly with thixotropic muds, even though a significant beginning was

made as long ago as 1935 by Ambrose and Loomis (1935). As far as the writer is aware, no one has quantitatively correlated the measure of thixotropy given by measurements of shear strength of mud made at difference lengths of time of standing quiescent with the obviously related measure of thixotropy obtainable by measurements made during flow or rotation at different rate of shear, including transient values as the rate of shear is changed. The difficulties involved are naturally formidable, particularly since the anisodimensional nature of the fine particles of most muds leads to flow orientation which can probably have an effect on thixotropic gelation akin to rheopexy (Hauser and Reed, 1936); but many important phases of down-the-hole behavior, such as channeling of mud flow past enlarged spots in the hole, the fall of cuttings through a thixotropic mud in which flow has been suspended, and the like, cannot be adequately handled on the basis of studies made so far.

## SEALING PROPERTIES

Clay was first used in mud to prevent loss of the mud fluid itself; however, some of the mud is lost as it filters though the cake that seals permeable formations. The filter cake on the wall of the hole thus increases in thickness at a rate which depends upon many factors, including the thickness of the cake already formed, the viscosity of the fluid phase of the mud (generally a function of the prevailing temperature), the pressure differential across the cake, and, most important of all, the permeability of the cake itself. Cake permeability in turn depends upon the nature of the solids in the mud, their state of flocculation, and to some extent the pressure differential across the cake, some cakes being relatively compressible. In view of the obvious disadvantage of having a filter cake build up against a permeable formation, reducing the diameter of the hole, it seems strange that so long a time elapsed between the introduction of the use of clay slurries for rotary drilling and the first study of caking properties of clays. A study of the pioneering work of Knapp (1923), in the middle twenties, followed by that of Jones and Babson (1936) and Jones (1938) will enable the reader to trace the development of cake permeability testing, generally known as filtration testing or wall-building testing. Several years ago the industry adopted a method of evaluating the filtration behavior of all types of muds. A full description is given in the Code for the Field Testing of Drilling Fluids published by the American Petroleum Institute. In the test, which determines what is probably the most important characteristic of mud, mud is filtered under pressure through a filter paper under specified conditions of time, temperature, and pressure, so that the loss of filtrate, rate of cake growth, and the physical nature of the cake can be determined. Methods of evaluating the data as well as variations in test procedures are given in publications of Larsen (1938), Byck (1940), Williams and Cannon (1939), Prokop, and others.

Table 1 shows the A.P.I. filter loss, or "water loss," as it is commonly termed, for fifteen different clays made up into slurries of fifteen centipoises viscosity, A.P.I., in distilled water. Measurements of cake weight and solids content, made at the same time, permitted the

*Table 1. Filter loss of clay.*

| | Base-exchange capacity | Yield in bbls. 15 cp mud per ton | Solids in filter cake (Percent by weight) | A. P. I. water loss at 15 cp | Filter cake permeability microdarcys | pH |
|---|---|---|---|---|---|---|
| 1. Hectorite, pure (California) | 70 | 160 | 6.5 | 7 | 0.85 | 8.6 |
| 2. Bentonite (Wyoming) | 77 | 125 | 10 | 11 | 1.8 | 8.2 |
| 3. Bentonite (Randsburg, California) | 56 | 71 | 16 | 15 | 2.1 | 8.7 |
| 4. "Subbentonite" (Fayette Co., Texas) | 67 | 18 | 50 | 11 | 1.5 | 7.5 |
| 5. Illite (Fithian, Illinois) | 16 | 13 | 67 | 57 | 38. | 7.4 |
| 6. Kaolin (Dry Branch, Georgia) | 3 | 14 | 70 | 190 | 285. | 7.0 |
| 7. Attapulgite (Florida) | 33 | 105 | 23 | 105 | 68. | 7.1 |
| 8. Halloysite (Las Animas Co., Colorado) | 16 | 17 | 60 | 35 | 15. | 7.7 |
| 9. Clay (Frazier Mt., California) | 51 | 28 | 37 | 22 | 5.5 | 8.9 |
| 10. Clay (El Paso County, Texas) | 32 | 15 | 58 | 20 | 3.7 | 7.4 |
| 11. Clay (Rosamond Lake, California) | 39 | 14 | 64 | 27 | 6.5 | 8.9 |
| 12. Clay (Rogers' Dry Lake, California, upper layer) | 40 | 15 | 63 | 21 | 6.6 | 9.6 |
| 13. Clay (Rogers' Dry Lake, California, lower layer) | 37 | 9½ | 66 | 8 | 1.3 | 9.2 |
| 14. Clay (Coalinga, California) | 28 | 16 | 55 | 43 | 19. | 9.4 |
| 15. Clay (McKittrick, California) | 12 | 26 | 53 | 28 | 5.4 | 7.6 |

Note: Clays 1-15, inclusive, do not necessarily correspond to clays now marketed for drilling mud use. The names of clays 9-15, inclusive, are geographical localities, and not trade names.

calculation of filter-cake permeabilities, and these are shown in microdarcys in the next column of table 1. It may be seen that a rough parallelism obtains between water loss and cake permeability, but it is the latter which is more important, so that it should be computed whenever possible as a matter of routine from the results of the A.P.I. test.* The great variation in filter-cake permeability among the different clays shown is striking, and makes it clear why relatively few clays are suitable for drilling mud use.

Many clay deposits which were extensively used two and three decades ago as sources of drilling mud have now been abandoned, since it was found that these gave muds having poor filtration characteristics. On the other hand, careful prospecting in known clay deposits in many cases has yielded bodies of clay with excellent filtration behavior, and it is common for processors of bentonite and other clay to make careful filtration tests as one means of product control. Of course a clay ex-

hibiting good filtration behavior does so only under favorable conditions; any environmental conditions tending to bring about flocculation of the clay and other solids in the mud will in general increase the filter-cake permeability of the mud.

A filter cake is actually a sediment formed under pressure, so that for a slurry of a given clay, the sedimentation volume should determine filter-cake permeability, other factors remaining the same. Flocculation and deflocculation determine sedimentation volume, however. This is illustrated in table 2 (1946), which shows how deflocculation and flocculation of a typical drilling mud reduce and increase, respectively, the filter-cake permeability, the "sedimentation volume" of the filter cake,

* For the standard A.P.I. test conditions, the filter cake permeability is approximately $0.7 \times 10^{-7} \times$ (water loss in cc) $\times$ (cake thickness in 32nds inch).

*Table 2. Clay A (Run-of-mine Hector clay, 5 percent in water)*

| Treatment of suspension | A. P. I. viscosity | Permeability of filter cake | Specific volume of filter cake[2] | Specific volume of sediment[3] |
|---|---|---|---|---|
| Thinned with Graham's Salt | 15 | 0.7 | 6.6 | 1.6 |
| No treatment | 25 | 1.2 | 7.4 | 2.4 |
| Thickened with MgO | 115 | 8.1 | 11.6 | 25. |

[1] Microdarcys, calculated from A.P.I. filtration test.
[2] Cc of cake per gram of clay, A.P.I. filtration test.
[3] Cc of sediment per gram of clay, sediment centrifuged from 10:1 dilution of the clay suspension with distilled water.
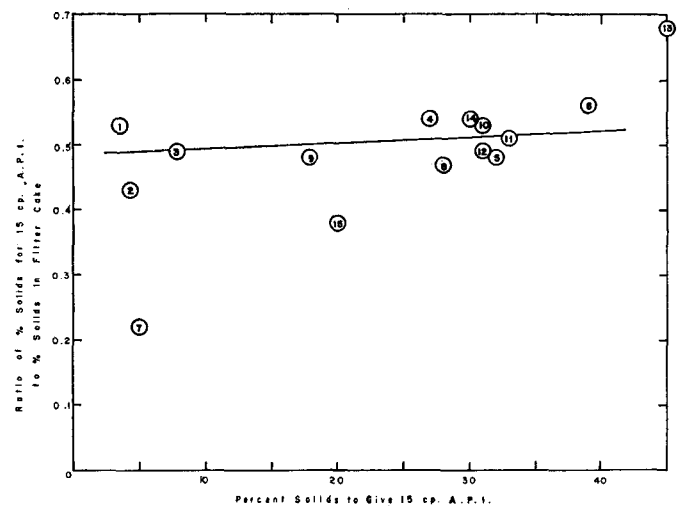


FIGURE 3.

and the sedimentation volume of the clay as determined by centrifuging portions of the diluted mud.

### Miscellaneous Functions of Clay in Mud

It is of some interest to note that Speller (1936; 1938) several years ago found that bentonite contributed toward the reduction of corrosion fatigue of steel when used in drilling muds. Of course, the simple type of clay-water or bentonite-water mud is somewhat less widely used now than formerly, and data do not appear to be available for the corrosion properties of the more highly chemically-treated muds, such as will be discussed in detail below.

Clays are of importance in emulsion muds, where they function as emulsifying agents, and they also play an important part in some types of oil-base muds. Discussion of these functions will be reserved for a later portion of the paper.

## SOURCE AND NATURE OF CLAYS USED IN DRILLING FLUIDS

### Clays Encountered During Drilling

Unless special measures are taken, any dispersible clay encountered during the course of drilling with a fresh-water mud is generally taken up by the mud and becomes part of its dispersed solids. This action is of course modified by such factors as the type of bit used and therefore the size of the cuttings produced, the length of time of upwards travel of the cutting in contact with the mud before reaching the surface, the average temperature of the mud, and the like. Where a relatively small amount of dispersible clays is encountered, the over-all effect may be beneficial, as it may reduce or eliminate the necessity for purchasing clays and weighting materials. However, when long intervals of such clays must be drilled through, incorporation of the clay into the mud can give serious trouble, particularly if the mud has been weighted with a commercial weighting material such as ground barite. Prior to about six or eight years ago, one had a choice only of diluting the mud with water, thereby increasing its total volume and wasting a portion of any weighting agents present, or of adding dispersing agents to the mud so that even though the clays were incorporated in the mud, gel strength reduction would be brought about by the addition of such chemical agents. In more recent years, however, techniques have been developed which make it possible to drill through colloidal, normally dispersible shales and either avoid the incorporation of very much of the shale into the mud or, with some types of treatment, reduce the normally gelatinous character of the shales so that they make scarcely any contribution to the viscosity and shear strength of the mud.

A detailed account of clays encountered during the course of drilling and which are taken up by the mud is somewhat outside of the scope of this paper, and more properly belongs to a study of the petrography of formations in oil-producing regions. However, mention should be made at least of the so-called heaving shales encountered in the Gulf Coast region of the United States, particularly in the course of drilling adjacent to salt domes. Shales of this type have given much trouble in the past not only by thickening the mud by dispersion but also by sloughing or "heaving" into the hole. Grim reported (personal communication) finding iron-rich montmorillonite as the chief constituent of Vicksburg shale from West Columbia, Texas, and of Miocene shale from the Allen Dome in Texas, and a mixed-layer type of mineral consisting of intergrown montmorillonite and illite as the chief clay mineral in Yegua shale from the Esperson Dome in Texas, and points out that the mixed-layer type of material would particularly be expected to be subject to ready dispersion.

Fancher and Oliphant (1943) a few years ago made a mineralogical study of two natural shale muds used in Gulf Coast drilling, each of which represented a composite of the shaly strata drilled through. Separate determinations were made on different particle sizes, fractionation having been effected by the use of a supercentrifuge. Illite was found to be the most abundant of the clay minerals in the muds tested.

### Surface Clays

It has been universal practice for many years in rotary drilling to make use of nearby clay deposits as a source of drilling mud. The use of such local clays is probably as highly developed in California as anywhere else in the world, so that a general description of California localities and a brief mention of others elsewhere will be illustrative. Table 1 is intended to give a cross section of the more or less pure clays used, some typical surface clays, and some types of clay minerals, not used in muds, for comparison. Table 1 also gives for each clay the so-called yield of the clay (not to be confused with yield point or yield value), which is generally taken to be the number of barrels (of 42 U. S. gallons) of drilling mud of 15 centipoises A.P.I. viscosity which can be prepared from one ton of the dry clay. This has turned out to be a most useful index not only in the use of the various clays, but in their classification. Naturally, the more highly colloidal clays, particularly those containing a substantial proportion of clay minerals of the swelling type, will give the highest yield, as is shown in table 1. Table 1 also shows the percent solids in the filter cake formed by a slurry of the clay when filtered at 100 pounds per square inch in the standard A.P.I filtration test. For normal clays, at least, this is an index of what might be called the effective volume of the clay in water, and it is of considerable interest that while the swollen filter cake is essentially a pressure sediment, there is a close relationship between the volume occupied by the clay in the cake and the effective volume occupied by the clay in a more dilute slurry, as judged from its rheological characteristics. In figure 3, the ratio of the percent solids in slurries of 15 centipoises A.P.I. viscosity (which may be computed from the yields figures given in table 1) to the percent solids in the mud cake formed from the same slurry (as given in table 1) is plotted against the percent solids to give the 15 centipoise slurry. It will be seen that this ratio is astonishingly constant at about 0.5, and is even approximately the same for the very high yield bentonites on the left-hand side as it is for the very low yield local clays on the right-hand side of the figure. The three exceptions will be discussed later. The fact that this ratio is as constant as it is suggests that

perhaps the A.P.I. viscosity, as determined at 600 rpm, is a valid rheological index of drilling muds even though it combines several independently determinable properties in a single value.

*Clays of Relatively Low Yield.* Probably the majority of surface clays used for drilling mud purposes in the United States are of the so-called low-yield type. That is, they require 25 to 40 percent clay by weight of mud to give a workable viscosity, corresponding to a density in the range of about 1.2 to 1.2 or a yield, as defined above, of from about 10 to 20 barrels of 15 centi-poise mud per ton of clay.

Deposits of this type which have been extensively used include, for example, one near El Paso, Texas, that has been commercially mined for at least 20 years, several California deposits widely used in the past, but now abandoned because of poor mud properties, such as localities north and northwest of Coalinga, west and southwest of Kettleman Hills, and clays in the surface layer of some dry lakes in the Mojave Desert region. Such top layers tend to concentrate soluble salts that have an adverse effect on the mud. Some of the dry lakes in the Mojave Desert region, including Rosamond (Fancher, 1943), Buckhorn, and Rogers (better known as Muroc), north and northeast of Palmdale, California, have yielded large tonnages of drilling mud clays. Some clays from the localities just named are of considerable interest for their clay-minerals. Grim (personal communication) has found a clay from a lower lying stratum from the central part of Rogers Dry Lake to contain a substantial proportion of a finely divided zeolite and analcite, together with an interlaminated clay made up of illite and a hectorite-like mineral. This may well contribute to the rather high base exchange capacity of some of these playa clays. The inclusion of fine, relatively isodimensional, non-swelling particles in this clay (No. 13 on table 1) may account for its unusually compact filter cake for its slurry viscosity (see fig. 3). Finely divided zeolites may be more common than generally suspected in surface clay deposits; Ross (1941) reported finding analcite as an alteration product of glassy volcanic ash in a deposit near Wikiup, Arizona, and Yovanovich (1936) identified zeolites in smectic clays of Algeria and Morocco. Certainly there is a vast field for future study in the California dry lake clays, and almost nothing has been reported on their petrography. (For a clay mineral analysis of nearby soils, see Brown and Drosdorff 1940).

J. Endell (1950) has recently reported that clays used for drilling muds in northwestern Germany for the most part consist of kaolin and mica-like clay minerals, and have a quite low yield.

West of McKittrick, California, clay has been extensively taken from a playa-type deposit, one of the constituents of which has been found by Grim to be a fibrous type of clay mineral. The fibrous clay would be expected to give a particularly bulky filter cake, quite in contrast to the zeolite of the Rogers Dry Lake clay.

*Surface Clays of Medium Yield.* A number of clay deposits have been worked for drilling mud purposes which give drilling muds at a moderate yield, of perhaps 20 to 40 barrels per ton. Representative of such deposits are Wilmington Slough clay taken from a slough just north of Wilmington, California; Frazier Mountain clay, from a deposit at an elevation of about 5,000 feet on the west slope of Frazier Mountain, just south of the San Andreas rift in the Tehachapi Mountains of Southern California; a surface deposit east of Midland, Texas, and the extensive deposits of so-called sub-bentonites in Gonzales and Fayette Counties, Texas. With the exception of some of the Texas clays which have been established to be calcium-type montmorillonite, substantially nothing appears to have been reported on the petrographic nature of the other deposits mentioned.

### Relatively Pure Clays Used in Muds

*Montmorillonite.* Montmorillonite of the swelling type is widely used throughout the world in drilling muds. Most of the material of this type, generally known as bentonite, comes from the Black Hills region of Wyoming and South Dakota, although some European and North African bentonites are used in Europe and the Middle East. This type of bentonite will give a workable drilling mud at concentrations as low as $5\frac{1}{2}$ to 7 percent by weight of mud, with water alone, corresponding to a yield of from 80 to more than 100 barrels of mud per ton of bentonite. Lesser amounts are used as an additive to muds which have already been made up, and particularly in connection with the use of weighting materials. Bentonite is prized for its property of giving a low filter-cake permeability, as well as for the softness that it gives to the filter cake and to the thixotropic character that it imparts to the mud. Its extraordinarily high yield makes shipment for long distances practicable, and Wyoming bentonite is actually used in drilling in substantially all parts of the world.

Some years ago, it was common to add alkaline-earth alkalis, such as slaked lime or burned magnesite, to high-grade swelling bentonites, even, as a dry admixture. It was found that when such a mixture, containing perhaps one percent of the alkaline earth material, was added to water, substantially larger gel strengths were obtained at a given percentage of bentonite. This practice was abandoned, however, when filter cake permeability tests became generally adopted, since it was found that the filtration properties of muds made from the treated bentonites were inferior. On the other hand, it has been the practice for many years to treat calcium bentonites with sodium carbonate in an attempt to produce a sodium bentonite therefrom (Atom . . . , 1935; Deibner, 1951). This has been a common practice in Europe, where commercial deposits of highly swelling bentonites are relatively rare.

Some calcium apparently increases the yield of a swelling type bentonite. This is not unexpected, as the yield depends upon the apparent Stormer viscosity which in turn depends more on the shear strength in a bentonite slurry than upon any other parameter. Roth (1951), working on Wyoming bentonite, points out the function of calcium ions—at least when not present to too great an extent—in creating two types of disorder, which he believes leads to readier dispersion of the bentonite. The first is from exchangeable calcium ions which give rise to double water layers rather than the single water layers associated with exchangeable sodium ions, thus expediting slaking. The second arises from calcium

ions isomorphously substituted in the octahedral positions, which distorts the lattice structure; again, the contortion of the layer is believed to facilitate dissociation of the clay platelets. More recent work directed to a systematic investigation of the effect of exchangeable bases, as between sodium and calcium in montmorillonite of the Wyoming type, has been reported by Williams, Neznayko and Weintritt (1952). In this investigation, homoionic montmorillonites were prepared, and the drilling-mud properties at different relative saturations of the bases were determined.

In this country, the naturally occurring calcium bentonite—chiefly the Texas sub-bentonites—are generally used with little or no treatment prior to being incorporated into mud, for their properties are satisfactory without beneficiation. Clay 4 of table 1 is representative. Most clays are adversely affected by the presence of even relatively small amounts of salt dissolved in the mud, but the two exceptions are some of the Texas sub-bentonites and clays of the attapulgite type. The former are widely used where slight salt contamination is encountered.

*Hectorite.* A celebrated and apparently unique deposit of a clay, the chief constituent of which is a mineral of the montmorillonite, or montmorillonoid, group in which magnesium appears in place of aluminum in the center of the lattice (Marshall, 1937), occurs a short distance south of Hector, California (Foshag and Woodford, 1936). Large amounts of this clay have been used in the past in drilling muds. The swelling and filter-cake permeability properties of hectorite—the clay mineral constituent of this deposit—are remarkably good (see Clay 1 of table 1, a hand-picked specimen), and even though the clay as mined regularly contained as much as 50 percent finely divided calcite and other nonclay material, the run-of-the-mine clay produced a mud of properties that compared favorably with that of high-grade Wyoming bentonite of much higher clay-mineral content. The fact that the hectorite platelets are lath shaped (Shaw and Humbert 1941) apparently is no bar to a low filter-cake permeability; this may well be connected with the tendency of the hectorite to disperse into flakes of unit cell thickness in a fashion similar to that of montmorillonite of the Black Hills variety.

*Attapulgite.* Quite different from other clays used in drilling muds is attapulgite, which is sold for drilling-mud purposes in this country from deposits in Georgia and Florida. Attapulgite has a fibrous structure (Bradley, 1940; Shaw and Humbert, 1941) in contrast to the platy or at least lath-shaped particles of most other clays, and the possibility of dispersing in water under favorable conditions to needle-shaped particles of cross-sectional dimensions comparable in magnitude to that of the unit cell gives rise to a type of plasticity which apparently is of the brush-heap type, quite in contrast to the gels produced by swelling montmorillonite. Attapulgite suspensions are only feebly thixotropic, as might be expected from their structure, and, moreover, have the interesting and useful property of possessing shear strength and viscosity quite independent of electrolyte concentration. A dispersion of five grams per centiliter of attapulgite in saturated sodium chloride solution has

about the same consistency when measured in a Stormer viscometer as a dispersion of five grams per centiliter in pure water. The suspension in pure water is substantially unaffected by the deflocculating and degelling agents commonly used with ordinary clays such as the polyphosphates, tanstuffs, and humic acids. Attapulgite finds extensive use, therefore, in areas in which rock salt is drilled through, and in which the mud thereupon becomes saturated, or nearly so, with salt. In such a solution, ordinary clays fail to swell and complete loss of gel strength is the usual result. Attapulgite is added to such muds to give the gel strength necessary and desirable for cuttings removal, weighting material suspension, and the like.

The acicular nature of attapulgite particles causes them to behave essentially as filter aids, much in the fashion of asbestos or diatomaceous earth. One result of the fibrous structure is that muds made up with attapulgite have a very high filter-cake permeability, even though pure water has been used. Where it is necessary to have low cake permeability with such a mud, organic colloids that are so completely hydrophilic that they are unaffected by the presence of salt are generally added. Such colloids may be gelatinized starch, generally added in a thin-boiling, pregelatinized form (Larsen, 1947); gums such as gum tragacanth (Harth, 1935) and gum karaya (Kennedy and Teplitz, 1943); or cellulose derivatives, such as sodium carboxymethylcellulose (Wagner, 1947) and hydroxyethyl cellulose (Himel and Lee, 1951).

*Illite.* Much clay of the illite type becomes incorporated in drilling muds from shales encountered during drilling, as has been noted. The only relatively pure deposit of an illite-type clay mined and sold for drilling mud use which has come to the writer's attention is the clay from Grundy County, Illinois, sold as grundite. Although this deposit is inactive at the present time, its properties have been described in a paper by Grim (1939). The properties of an illite by itself, as represented by clay from a type deposit, clay 5 of table 1, are not favorable for a mud because of the fairly high cake permeability.

*Halloysite.* Some attempt was made about ten years ago to market for drilling mud purposes a halloysite clay occurring in Colorado. No other halloysite, or even a clay rich in halloysite, is known to the writer as currently used in muds.

*Kaolinite.* There is no a priori reason to expect that either halloysite or kaolinite would be well adapted for drilling mud use in relatively pure form, an expectation borne out by table 1. A Tennessee ball clay is currently being marketed for use in mud for water-well drilling and for drilling shot holes for seismographic exploration; the demands on such a mud are not generally severe.

## CHEMICAL TREATMENT OF CLAY MUDS

### Addition of Degelling Agents

In the ordinary course of drilling, clay-water muds tend to increase in consistency, which results is an increase in gel strength. The change in consistency may be the result of drilling through mud-making formations, or the result of the addition of soluble salts such as sodium

chloride, calcium sulphate, and the like. In the early days of drilling with rotary mud, notably in the 1920's, attempts were made to treat such thickened muds with the materials found useful in ceramic slips, particularly sodium hydroxide, sodium carbonate, and sodium silicate. Such attempts were largely unsuccessful; the mechanism of the production of the gel is still controversial, but it may arise from quite different causes than are operative in china clays. For example, the addition of a small amount of sodium hydroxide to a slip of kaolin in water will bring about marked thinning, whereas the addition of a like amount of caustic soda to a bentonite suspension will cause thickening. Most clay-water drilling muds tend toward behavior of the latter type, and until the early 1930's the problem of degelling drilling muds by chemical treatment was largely unsolved. Today the chemical agents used for this purpose fall largely into two groups: inorganic complex phosphates, and organic weak acids of generally high molecular weight such as tanstuffs and humic acids. An early anonymous publication (1932) of the Shell Laboratories in Amsterdam lists many organic compounds useful for thinning muds.

The introduction of the molecularly dehydrated phosphates as drilling-mud thinners was made by Wayne (1942) in the early 1930's. At the present time, sodium pyrophosphate, both in the tetrasodium and the disodium dihydrogen forms; sodium tripolyphosphate; and the glassy sodium phosphates of obscure structure but ranging in composition from the so-called tetraphosphate to the hexametaphosphate are widely used. Analogous compounds such as the stannates (Wayne, 1951) and vanadates have been proposed but are not commercially used at the present time because of their scarcity and high price. Orthophosphates are used scarcely at all, and other simple sodium compounds which remove calcium, such as sodium carbonate and sodium bicarbonate, are used only for special treatments and generally in combination with other materials.

The mechanism of degelling by complex phosphates is no less obscure than the mechanism of the gelling of the muds in the first place. Grim (1947) has suggested that gelling may be ascribable to the building up of layer upon layer of hexagonally disposed water molecules on the surface of the clay particles, and that degelling by complex phosphates may result from the fit of polyphosphate chains and rings onto the same surface, thereby interfering with the building up of oriented water layers. Van Olphen (1951) has advanced the hypothesis that the edges of montmorillonite flakelets are at least in parts positively charged, that the gelation of bentonite in aqueous suspensions therefor comes about from an edge to face orientation which would naturally give a gel of low solids content, and that accordingly the action of the polyphosphates is essentially one of adsorption at the loci of positive charges with the consequent neutralization or even reversal of charge at these points.* These are both reasonable proposals, and the most that can be said at this time is that more work must be done on the problem. The complete solution will no doubt involve full consideration of the structure of polyphosphates as compared with those of orthophosphates: the

existence of P-O-P bonds with tetragonal coordination of oxygen ions about the phosphorus ions, analogous to silicates; the relatively high ionization constants of the polyphosphates (as evidenced, for example, by the feeble alkalinity of tetrasodium polyphosphate and the actually neutral pH of many metaphosphates, including Graham's salt—the so-called sodium hexametaphosphate), which would enable neutralization of the postulated positive charge of the montmorillonite flake by one portion of the polyphosphate molecule and the presentation of a negative charge by another portion; probably also the ability of certain polyphosphates to sequester calcium ion; and finally the ability of polyphosphates to prevent growth of certain crystals where it is possible for them to fit on the lattice of the growing crystal, such as on calcite. Cyclic trimetaphosphate neither thins mud initially, nor prevents the growth of calcite crystals, but after hydrolysis has taken place and the ring is split, it becomes an excellent thinner. This is in complete accord with the findings of Raistrick (1949), who found that nucleation of calcite crystals was not prevented by tri- and tetrametaphosphate at first, but was after hydrolysis of these ring compounds. It is significant that the principal effects of the addition of polyphosphates to a drilling mud is reduction in shear strength rather than increase in Bingham fluidity (or reduction of differential viscosity). (Melrose and Lilienthal, 1951; van Olphen, 1951.)

The organic compounds that have proved most useful in thinning drilling muds are the several tanstuffs, of which quebracho extract is the most widely used, and humic acid, generally derived from certain lignites. The fact that these materials thin best at an alkaline pH, and indeed at pH's high enough so that fairly complete ionization of the acids can be assumed, suggests that the mechanism may be related to that which gives the polyphosphates their effectivness. Indeed, at pH's of 12 or higher, gelatinized starch acts as a thinner for clay-water muds in a way very like the tanstuffs, and the higher pH involved is in accordance with the much lower ionization constant of the alcoholic hydroxyl groups in starch as compared with the phenolic and even carboxylic groups in tannic and humic acids. A discussion of some aspects of the behavior of tanstuffs and polyphosphates in thinning muds is given in several articles including which may be mentioned those by Loomis, Ford and Fidiam (1941), Garrison (1940), and van Olphen (1950 b, 1951). A special usage of tanstuffs and humic acids, aside from simple thinning in normal, moderately alkaline pH range is discussed below.

*Lime Muds.* The term "lime muds" as currently used needs some explanation. In the early days of drilling, limestone was often added to mud, occasionally as ground massive limestone and sometimes as beet-sugar-factory waste lime, and such muds were occasionally called "lime muds." Also, calcium hydroxide, as ordinary slaked lime, formerly was added to mud when a thickening effect was desired, but the adverse effect upon filter-cake permeability led to its abandonment. Within the last decade, the new and almost revolutionary technique has been developed of using slaked lime in clay-water drilling muds at a high pH and in the presence of a protective colloid, which may be of the

---

* J. Endell (1950) has recently published an electron micrograph showing particles of a gold sol (presumably negatively charged) adhering to the edges of kaolinite platelets.

class of tanstuffs and humic acid derivatives, or gelatinized starch. The term "protective colloid" has been deliberately used, because the system is quite completely flocculated without the organic material, and it has only been through knowledge of the proper use of these organic materials in conjunction with lime that the latter has been usable at all. The pH range of such muds is high, generally between 12 and 13, and is achieved generally by the joint use of caustic soda and hydrated lime. The concentration of the organic material is likewise high, ranging upward from 4 or 5 pounds of organic material per barrel of mud. When clay is added to such a mud, either as a drilling-mud clay deliberately added or as ground-up cuttings encountered during drilling, even though the clay would normally readily become dispersed in water, dispersion in the lime type of mud is at a minimum, and only a slight contribution is made to the consistency of the mud. This effect is of enormous advantage in drilling through long intervals of mud-making shale, and indeed, with proper mud control, there seems to be no limit to the footage of normally dispersible shales which can be so drilled. Such muds are characterized principally by very low gel strength both after agitation and after a period of quiescence, and by quite low filter cake permeability. Substantial contamination by salt can occur without harming the mud, particularly when gelatinized starch is present. Muds of this type are generally made from a mud already in use, and the conversion of ordinary muds into high pH lime muds calls for a great deal of skill on the part of the mud engineer, since the initial flocculation which takes place results in great thickening of the mud, which, however, is temporary. The usual explanation given for the behavior of such a mud is that the presence of the calcium ion prevents swelling of any normally swelling clays, as well as collapsing clays of that type present in a mud undergoing conversion, that the organic thinner, together with any starch which may also be present, prevents adhesion between the particles so treated by the calcium ion. Field technology of such muds is at the present time still much more of an art than a science, and although fairly precise control techniques have been developed, involving for the most part the reaction of the mud and the filtrate to chemical titrations of several kinds, control and remedial treatments are largely empirical. However, it appears that too high a concentration of calcium ion is undesirable, and in practice the calcium-ion concentration is carefully controlled, possibly at a level somewhat under that which would correspond to complete calcification of the clays present. This is suggested by the ability of bentonite, when added to such a mud, to behave in a nearly normal manner as regards filter-cake-permeability reduction; although the recent work of Gruner and Vogel (1950) on the swelling of calcium bentonite at high pH's suggests a possible mechanism. The quantities of lime consumed during the course of drilling through shales are substantial, and obviously considerable base exchange takes place during the use of such a mud. Lime muds of this type have been the subject of several recent reviews (Goins, 1950; Lancaster and Mitchell, 1949; McCray, 1949).

A recent development in lime-base muds of particular interest to clay mineralogists is the discovery that certain of these muds, when used for drilling at great depths where unusually high bottom-hole temperatures are encountered, undergo a solidification to an extent occasionally so great that the mud resembles set portland cement. A laboratory method of reproducing the various solidification phenomena on a small scale has been described by Gray, Cramer and Litman (Gray, Cramer, and Litman, 1951); and an investigation from the standpoint of the mineralogical changes involved has recently been published by Gray, Neznayko and Gilkeson (1952), who found that calcium silicates, among which analcite and xonotlite could be identified, were formed, apparently from the clay and quartz originally present. It was found that retardation of the solidification could be brought about by the use of organic dispersing agents of the type which are effective as portland-cement retarders.

### Salinification of Muds

Interstitial clays occuring in oil sands, either as clays laid down with the sediment itself or possibly formed in place, have recently received much attention from the standpoint of their interaction with fluids intruding from the well bore (Darley, 1947; Griffiths, 1946; Grim, 1947; Johnston and Beeson, 1945; Suter, 1948). Prior to disturbing the reservoir by drilling, such clays are of course in equilibrium with any interstitial water present, which almost universally is substantially saline in character, and quite generally contains ions of alkaline earth metals as well as of alkali metals. Unless a drilling mud is of a special type, the filtrate therefrom is likely to have a much smaller ionic strength than that of interstitial reservoir waters, an effect which indeed has been recognized from the earliest days of electrical welllogging. One must, for a variety of reasons, prevent intrusion of drilling-mud filtrates in the producing formations as much as possible, not only for the reason discussed here, but also because of the possibility of reducing the permeability of the sands to oil from purely capillary effects. However, with practically all muds having an aqueous base, some loss of filtrate is nearly unavoidable, and severe reduction in permeability of oil-bearing strata to the flow of fluids of any kind has been shown to be the result of intrusion of relatively fresh water filtrates, particularly when the sands contain appreciable amounts of clay. Even where the clay is not of a swelling type, undoubtedly a reduction in adhesion of the clay or other minute particles to the surface of the sand grains can be brought about by the intrusion of fresh water in accordance with the principles of adhesion capability investigated by von Buzágh (1930). Table 3, taken from von Buzágh (1937), shows the reduction in adhesion of quartz particles to a quartz plate, in the presence of distilled water and of increasing concentrations of NaCl and CaCl$_2$. The sine of the angle of tilt necessary to dislodge the quartz particles by gravitational action is shown for different concentrations of the salts. The great increase in adhesion for even quite dilute electrolyte concentrations as compared with fresh water is clearly seen, as well as the difference between sodium and calcium chlorides at the same concentrations. The possibility of the dislodgement of fine particles normally adhering to the surface of sand grains by the interposition of fresh water or weak brines of alkali-

| Concentration in millimols per liter | NaCl | | CaCl₂ | |
|---|---|---|---|---|
| | Percent | sinα | Percent | sinα |
| 0 | 0 | 0.095 | 0 | 0.095 |
| 5 | ---- | ---- | 0.055 | 0.317 |
| 10 | 0.058 | 0.165 | 0.111 | 0.414 |
| 20 | 0.117 | 0.342 | 0.222 | 0.573 |
| 40 | 0.233 | 0.43 | ---- | ---- |

metal salts alone, whereby such very small particles can move to block the fine openings in the capillaries, is evident from table 3, so that swelling clay or even clay of any kind does not have to be present to explain many of the results obtained in fluid-permeability investigations. Investigation of the swelling of microsamples of the fine fraction obtained from oil-sand cores subject to permeability reduction by fresh-water filtration by means of the Enslin (1933) apparatus, carried out in 1947 by Foster (Foster, 1947), showed a relatively feeble swelling, yet the core was from a formation particularly subject to permeability reduction from fresh-water intrusion. (It is not intended here to minimize the importance of clay swelling in formation permeability, but merely to call attention to another factor which has perhaps been overlooked in the past, and may be found to be of some importance.) Recent work by the research group of the Union Oil Company of California has included the investigation from a very fundamental and very thorough standpoint of the clay-mineral content of the fine fractions of California oil-sand cores (Nahin, et al., 1951; Nowak and Kruger, 1951).

The treatment of drilling muds so that their filtrates will fail to have a swelling or dislodging effect or both upon interstitial clays and other fine particles has been given much attention in recent years. The usual expedient, as one might deduce either from clay-swelling data or adhesion data of the von Buzágh type, is to salinify the mud, particularly with salts of di- and trivalent cations (Cross and Cross, 1937; Darley, 1947; Griffiths, 1946; Sherborne, 1951; Temple, 1951). Calcium chloride has been used in concentrations of several percent by weight of the fluid phase of the mud, and even soluble aluminum salts have been used. Naturally, the effect intended for the interstitial clays is not without a like effect on the clays in the drilling muds themselves, and unless special measures are taken the mud properties will be adversely affected by the addition of such salts. Fortunately, gelatinized starch is fully effective to obtain low filter-cake permeability in such cases, and is generally used with such a mud. The filtrate from a lime mud such as has been discussed in the previous section falls somewhat short of ideal performance in this connection, partly no doubt because of its very high pH.

### Reversal of Charge

Some have suggested not merely converting a mud to a calcium-base clay, but reversing the charge to a positive micelle. Perhaps the most elaborate work along these lines is that of Bond (1944), who used such materials as methylene blue for producing a positively charged bentonite for use in drilling muds. With such a mud any

swelling or even dispersion of normally hydratable clay encountered during the course of drilling is of course out of the question. Muds of this particular type do not appear to have been used commercially, however, probably because of their relatively high cost and also because of the intervention of the high-pH-lime technique, which has solved most of the problems in connection with heaving-shale drilling.

## USE OF CLAYS IN MUDS CONTAINING OILS
### Emulsion Muds

Within the past decade the use of emulsions as drilling fluids has become fairly widespread. Both types of emulsion, that is, oil-in-water and water-in-oil, have been used, but the former is much more common. Substantially all of the oil-in-water type of emulsion drilling fluids presently used contain clay, and indeed are most generally made up by the addition of oil to a clay-water mud which has already been in use. The ability of colloidal clays, particularly bentonitic clays, to act as emulsifying agents for oil-in-water emulsions is so well known that little need be said here. In fact, it has been found that some clays are such good emulsifying agents in themselves that no additional emulsifiers need be added, but this property is seldom relied upon in actual practice, since the use of organic emulsifying agents in a clay-water mud can readily be made to give great stability to the emulsion. One function of clays in such muds which is generally overlooked, but which nevertheless is most important, is that of providing a preferentially water-wettable filter cake for the mud to filter against. The fact that the walls of the pores in such a clay filter cake are hydrophilic prevents the passage of the minute droplets of emulsified oil, which presumably are then enabled to block off the pores and to reduce the over-all permeability of the cake. The filtrate from such a mud, when the emulsion is properly stabilized, is substantially 100 percent water, and all of the oil is retained by the cake, which is in accordance with the picture just presented, as is also the very considerable reduction in over-all fluid loss resulting from the emulsification of oil into the clay-water base mud.

An interaction of the clay with the emulsifying agent used in a particular emulsion mud has been studied by Doscher (1949); the particular mud proposed is of interest as it makes use of calcium ions for tying the emulsifying agent to the clay particle as well as to prevent swelling of clays both in the emulsion and such as may be contacted by filtrate from the emulsion.

### Oil Base Muds

The attempt to keep intruded water entirely away from oil-bearing formations has led to the development of drilling fluids made up with oil instead of water, the so-called oil-base muds. For the most part, such drilling fluids do not have clay added, and since they are not ordinarily used for "making hole" as distinguished from drilling into an oil-bearing formation, clays encountered during drilling with such a mud are generally of little consequence, aside from the fact that they are generally not dispersible in the fluid in the first place. Clays are of importance, however, in particular oil-base muds which have been used. Rolshausen and Bishkin

(1937) proposed the incorporation of bentonite in an oil-base mud in order to take up any free water encountered during drilling. A recent article by Lummus and Dunn (1952) describes a recently developed type of oil-base drilling fluid made up from oil and a dry concentrate, which is stated to consist of "a chemically treated mixture of clay and weighing material."

Another and most interesting type of oil-base mud in which mortmorillonitic clays play an all-important part is that patented by Hauser (1950), which makes use of the swelling properties in oil of reaction products of long chain amines and bentonite, also discovered by him (1950; and Jardan, 1952). Such oleophilic bentonites, which are substantially completely coated by the hydrophobic organic cation through a base-exchange reaction, impart both gel strength and, because of their platy character, low fluid loss to oil-base muds, and also enable the emulsification of any water encountered during use into the mud as a stable water-in-oil emulsion. A particular advantage is that the organophilic clay retains its gelling ability even at very high temperatures, thus avoiding a difficulty often encountered with other types.

## DISCUSSION

**H. F. Coffer:**

I would like to have further discussion on the reactions of chemicals in thinning muds.

**W. T. Cardwell, Jr.:**

The work of Loomis, Ford, and Fidiam (1941) several years ago is still basic. Their work showed a correlation between the calculated surface areas of the clay particles and the amount of pyrophosphate required in a suspension to attain minimum viscosity. This amount was just sufficient to form a monomolecular layer of the pyrophosphate on all the surfaces of the clay in the suspension. The adsorption of pyrophosphate on the clay surfaces presumably prevents the formation of an extended water structure. Formation of this extended water structure is thought to account for the viscosity.

**H. van Olphen:**

Actual adsorption studies indicate that adsorption of the polyphosphate is not complete. It is, however, sufficient to be explained as lateral surface adsorption. A minimum in the "viscosity" curve occurs owing to a balance between the peptization by the polyphosphate anion and the flocculation by the Na+ ions; at high concentrations the Na-polyphosphate finally flocculates the clay completely (van Olphen, 1951a).

As I see it the phosphate-anion adsorption charges the particle edges and prevents their edgewise association. Hence no voluminous clay-particle network is built up and the yield stress of the system is reduced. (The so-called "viscosity" reduction of the drilling fluid is primarily yield-stress reduction.)
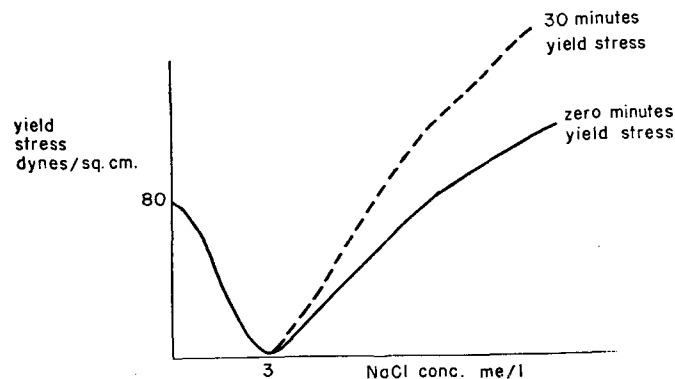


FIGURE 4.

The question of the rheological properties of clay—liquid systems beyond the point of gelation—is of utmost importance in drilling fluids, ceramic slips, and soils and is quite interesting from a colloid chemical point of view.

If a washed neutral sodium-Wyoming-bentonite sol is concentrated by ultrafiltration to a concentration of about 3 percent, a gel is obtained with a yield stress of about 80 dynes per sq cm. The gel is non-thixotropic. On addition of very little neutral salt to this gel, the yield stress is reduced to zero, but with more than about 3 me./l of the salt the system gels again, now establishing a thixotropic gel.

In the uncontaminated system the formation of the non-thixotropic gel is puzzling since the protecting double layers would be expected to be highly developed. The counter ions, the exchangeable sodium ions, are there, and the electrolyte content of the intermicellar liquid is low so that optimum repulsion between the particles should be realized. Still the non-thixotropic gelation suggests particle association. Admittedly, a yield stress can be developed in dispersed systems with predominant repulsion, but those systems show the phenomenon of dilatancy and not that of non-thixotropic gelation.

Also particle association in the purified gels could occur in the long range energy minimum owing to the difference in decay of the double layer repulsion and van der Waals' attraction as pointed out by Verwey and Overbeek. However, such an associated network would show thixotropy due to the shallowness of the minimum. Moreover, this association would be expected to become more pronounced on the addition of neutral salts but actually the reverse is true.

An explanation of the particle association and gelation in purified systems may be given on the basis of the assumption that despite the overall negative electrophoretic charge of the clay particles, the edges bear a positive charge so that the gelation would be the result of edge-to-flat-surface association, a kind of internal mutual flocculation. The lack of an energy barrier for such an association and the rather deep minimum in the attraction potential curve would explain the instantaneous set of the gel after stirring. Also this type of association would explain the large gel volume at relatively low clay concentration. The assumption of a positive edge charge appears to be able to explain quite a diversity of facts observed in clay suspensions, particularly stabilization by anions as practiced in drilling-mud treatment and ceramic slips. The origin of a positive edge charge may be sought in the presence of alumina at the edges where the octahedral sheets are broken. Also traces of aluminum ions which are present in the intermicellar liquid may charge the broken silica sheets positively as they do with a quartz sol. Therefore the presence of a positive edge charge would be in line with general colloid chemical experience.

Turning to the reduction of the yield stress of the pure gel by addition of about 3 me./l of NaCl, Na2SO4, NaOH, or CaCl2, this may be seen as the result of the compression of the double layer on both flat surface and lateral surface, thus reducing the mutual attraction of the two. On further addition of these salts, however, both double layer potentials will be so far reduced that edge-to-edge or flat-surface-to-flat-surface association is no longer prevented and the system gels again owing to dominant van der Waals' attraction. However, this gel is thixotropic and has a completely different character. This is the condition of a virgin drilling fluid when prepared from impure clay and water. The reduction of gelation by treating chemicals is now achieved by adsorption of anions to the positive edges, which gives the edges a protective negative charge, edge-to-edge association is prevented, and the main contribution to the formation of a voluminous network is eliminated. It may be mentioned that the major rheological effect of treating agents on the gelled clay suspension is a reduction of the Bingham yield stress of the system, the differential viscosity remaining essentially the same.

**E. A. Hauser:**

The development of organic-reacted bentonites has completely revised the old theory of thixotropy for we are now dealing with a system where electrokinetic forces are no longer involved. A thixotropic gel can be formed by reactions such that the individual particles develop a balance between the solvated layer and the van der Waals' attraction forces. The moment this balance is reached, the system sets up as a thixotropic gel.

## SELECTED REFERENCES

Ambrose, H. A., anl Loomis, A. G., 1935, Fluidities of thixotropic gels: bentonite suspensions: Physics, v. 4, pp. 265-273.

Anonymous, 1932, Die Behandlung der in der Bohrtechnik üblichen Dickspülung zwecks Viskositätscherabsetzung: Petroleum Zeitschr., v. 28, no. 44, pp. 7-8.

Atom Studiengesellschaft für Erze, Steine und Erden, 1935, Verfahren zur Gewinnung hochquellfähiger anorganischer Stoffe: German Patent 613,037, of May 17, 1935.

Babbitt, H. E., and Caldwell, D. H., 1939, Laminar flow of sludges in pipes with special reference to sewage sludge: Univ. Illinois, Eng. Exper. Sta. Bull., 319.

Babbitt, H. E., and Caldwell, D. H., 1940, Turbulent flow of sludges in pipes: Univ. Illinois, Eng. Exper. Sta. Bull. 323.

Beck, R. W., Nuss, W. F., and Dunn, T. H., 1948, The flow properties of drilling muds: Am. Petroleum Inst., Drilling and Production Practice 1947, pp. 9-22.

Bond, D. C., 1944, Positive colloid muds for drilling through heaving shale: Am. Inst. Min. Eng. Tech. Pub. 1674, 10 pp.

Bradley, W. F., 1940, The structural scheme of attapulgite: Am. Mineralogist, v. 25, pp. 405-410.

Brown, L. C., and Drosdorff, M., 1940, Chemical and physical properties of soils and of their colloids developed from granitic materials in the Mojave Desert: Jour. Agr. Research, v. 61, pp. 335-362.

von Buzágh, A., 1930, Über die Haftfähigkeit Mikroskopischer Teilchen an einer Wand von Gleicher Beschaffenheit. II.:Kolloid-Zeitschr., v. 52, pp. 46-61.

von Buzágh, A., 1937, Colloid systems, London.

Byck, H. T., 1940, Effect of temperature on plastering properties and viscosity of rotary drilling muds: Am. Inst. Min. Eng. Trans., v. 136, pp. 165-175.

Cardwell, W. T., Jr., 1942, Drilling fluid viscometry: Am. Petroleum Inst., Drilling and Production Practice, 1941, pp. 104-112.

Cross, R., and Cross, M. F., 1937, Drilling fluids: U. S. Patent 2,073,413, of March 9, 1937.

Darley, H. C. H., 1947, The application of the principles of clay chemistry to problems encountered when drilling in Trinidad clays: Inst. Petroleum Jour., v. 33, pp. 219-229.

Deibner, L., 1951, Techniques du laboratoire utilisées dans l'étude de l'activation chimique, acide ou alcaline, des argiles. II. Activation alcaline des argiles colloïdales: Chimie analytique, v. 33, pp. 95-100, 138-142.

Doscher, T. M., 1949, Characteristics of detergent suspended drilling fluids: Oil and Gas Jour., v. 48, no. 8, pp. 75-76, 79-80.

Endell, J., 1950, Tone in der Erdölindustrie: Erdöl und Kohle, v. 3, pp. 105-109.

Enslin, O., 1933, Über einen Apparat zur Messung der Flüssigkeitsaufnahme von quellbaren und porösen Stoffen und zur Charakterisierung der Benetzbarkeit: Chemische Fabrik, v. 6, pp. 147-148.

Evans, P., and Reid, A., 1936, Drilling mud: its manufacture and testing: India Min. and Geol. Inst. Trans., v. 32, pp. 1-261, i-xxx.

Fancher, G. H., and Oliphant, S. C., 1943, The nature of Hastings drilling mud by supercentrifuge and X-ray analysis: Am. Inst. Min. Eng. Trans., v. 151, pp. 221-232.

Foshag, W. F., and Woodford, A. G., 1936, Bentonitic magnesian clay-mineral from California: Am. Mineralogist, v. 21, pp. 238-244.

Foster, J. F., 1947, An investigation of the clay-content-permeability relationship of oil sands: Univ. Southern California, M. S. Thesis.

Garrison, A. D., ten Brink, J. C., and Elkin, P. B., 1940, A study of some phases of chemical control in clay suspensions: Am. Inst. Min. Eng. Trans., v. 136, pp. 175-194.

Goins, W. C., Jr., 1950, A study of limed mud systems: Oil and Gas Jour., Jan. 19, 1950, pp. 52-54, 72.

Gray, G. R., Cramer, A. C., and Litman, K. K., 1951, Stability of muds in high temperature holes shown by surface tests: World Oil, v. 133, no. 3, pp. 149-150.

Gray, G. R., Neznayko, M., and Gilkerson, P. W., 1952, Solidification of lime treated muds at high temperatures: World Oil, v. 134, no. 4, pp. 101-104, 106.

Griffiths, J. C., 1946, Clay research and oil development problems: Inst. Petroleum, Jour., v. 32, pp. 18-31.

Grim, R. E., 1939, A unique clay from the Goose Lake, Illinois, area: Am. Ceramic Soc. Jour., v. 22, pp. 157-164.

Grim, R. E., 1947, Relation of clay mineralogy to origin and recovery of petroleum: Am. Assoc. Petroleum Geologists Bull., v. 31, pp. 1491-1499.

Gruner, E., and Vogel, R. E., 1950, Das Quellungsvermögen von Kalzium- und Natrium-Bentonit und seine Deutung: Kolloid-Zeitschr., v. 118, pp. 100-110.

Hall, H. N., Thompson, H., and Nuss, F. 1950, Ability of drilling mud to lift cuttings: Am. Inst. Min. Eng. Trans., v. 189, pp. 35-46.

Hamilton, Warren B., 1951, Playa sediments of Rosamond Dry Lake, California: Jour. Sedimentary Petrology, v. 21, pp. 147-150.

Harth, P. E., 1935, Application of mud-laden fluids to oil or gas wells: U. S. Patent 1,991,637, of Feb. 19, 1935.

Hauser, E. A., 1950, Modified gel forming clay and process of producing same: U. S. Patent 2,531,427, of Nov. 28, 1950.

Hauser, E. A., 1950a, Application of drilling fluids: U. S. Patent 2,531,812, of Nov. 28, 1950.

Hauser, E. A., and Jordan, J. W., 1952, Argiles "organophiles": Silicates Ind., v. 17, pp. 9-10.

Hauser, E. A., and Reed, C. E., 1936, Rheopexy in bentonite: Am. Chem. Soc. Jour., v. 58, p. 1822.

Herrick, H. N., 1932, Flow of drilling mud: Am. Inst. Min. Eng., v. 98, pp. 476-494.

Himel, C. M., and Lee, E. G., 1951, Drilling fluids and methods of using same: U. S. Patent 2,570,947, of Oct. 9, 1951.

Johnston, N., and Beeson, C. M., 1945, Water permeability of reservoir sands: Am. Inst. Min. Eng. Trans., v. 160, pp. 43-55.

Jones, P. H., 1938, Field control of drilling mud: Am. Petroleum Inst., Drilling and Production Practice, 1937, pp. 24-29.

Jones, P. H., and Babson, E. C., 1936, Evaluation of rotary drilling muds: Am. Petroleum Inst., Drilling and Production Practice, 1935, pp. 22-33.

Kennedy, H. T., and Teplitz, A. J., 1943, Drilling fluid: U. S. Patent 2,337,296, of Dec. 21, 1943.

Knapp, Arthur, 1923, Action of mud-laden fluids in wells: Am. Inst. Min. Eng. Trans., v. 69, pp. 1076-1100.

Lancaster, E. H., Jr., and Mitchell, M. E., Jr., 1949, Control of conventional and lime-treated muds in southwest Texas: Am. Inst. Min. Eng. Trans., v. 179, pp. 357-371.

Larsen, D. H., 1938, Methods of determining the filtration characteristics of drilling muds: Petroleum Eng., Sept. 1938, pp. 42, 44-46, 48 . . . Nov. 1938, pp. 50, 52, 56-58, 60.

Larsen, D. H., 1946, Colloidal features of drilling fluids, in Alexander, J., Colloid chemistry, v. 6, pp. 509-530.

Larsen, D. H., 1947, Well drilling fluid base material and process: U. S. Patent 2,417,307, of March 11, 1947.

Loomis, A. G., Ford, T. F., and Fidiam, J. F., 1941, Colloid chemistry of clay drilling fluids: Am. Inst. Min. Eng. Trans., v. 142, pp. 86-99.

Lummus, J. L., and Dunn, T. H., 1952, A new type of oil base drilling fluid: Am. Petroleum Inst., Paper presented at Spring meeting, Casper, Wyoming, April 24, 1952.

McCray, A. W., 1949, Chemistry and control of lime base drilling muds: Petroleum Eng., Nov. 1949, pp. B54, 56, 58.

Marshall, C. E., 1937, The colloidal properties of the clays as related to their crystal structure: Jour. Phys. Chemistry, v. 41, pp. 935-942.

Melrose, J. C., and Lilienthal, W. B., 1951, Plastic flow properties of drilling fluids. Measurement and application: Jour. Petroleum Technology, v. 3, no. 6, pp. 159-161.

Métrot, Roger, 1951, La rhéologie des suspensions. Application aux boues de forage: Rev. inst. franç. Pétrole, v. 6, pp. 3-19, 39-52, 67-82, 101-119, 191-206.

Nahin, P. G., Merrill, W. C., Grenall, A., and Crog, R. S., 1951, Mineralogical studies of California oil-bearing formations. I. Identification of clays: Jour. Petroleum Technology, v. 3, pp. 151-158.

Nowak, T. J., and Kruger, R. F., 1951, Effect of mud filtrates of mud particles on the permeabilities of cores: World Oil, v. 133, no. 1, pp. 125-126, 128, 130 . . . no. 3, pp. 152, 154, 156, 158, 161-162.

van Olphen, H., 1950, Verpompbaarheid, rheologie en viscosimetrie van boorvloeistoffen: Geologie en Mijnbouw, v. 12, pp. 188-194.

van Olphen, H., 1950a, Pumpability, rheological properties, and viscometry of drilling fluids: Inst. Petroleum, Jour., v. 36, pp. 223-234.

van Olphen, H., 1950b, Stabilization of montmorillonite sols by chemical treatment [in English]: Rec. trav. chim., v. 69, pp. 1308-1312, 1313-1322.

van Olphen, H., 1951, Chemical treatment of drilling fluids [in English]: Diss., Tech Hog. Delft.

van Olphen, H., 1951a, Rec. trav. chim. pays bas, v. 69, p. 1308, Delft [Thesis].

Pigott, R. J. S., 1942, Mud flow in drilling: Am. Petroleum Inst., Drilling and Production Practice 1941, pp. 91-103.

Prokop, C. L., 1952, Radial filtration of drilling mud: Jour. Petroleum Technology, Petroleum Trans., v. 195, pp. 5-10.

Raistrick, B., 1949, The influence of foreign ions on crystal growth from solution. I. The stabilization of the supersaturation of calcium carbonate solutions by anions possessing O-P-O-P-O chains: Faraday Soc., Discussions, v. 5, pp. 234-237.

Rolshausen, F. W., and Bishkin, S. L., 1937, Oil base hydratable drilling fluid: U. S. Patent 2,099,825, of Nov. 23, 1937.

Ross, C. S., 1941, Sedimentary analcity: Am. Mineralogist, v. 26, pp. 627-629.

Roth, Robert S., 1951, The structure of montmorillonite in relation to the occurrence and properties of certain bentonites: Univ. Microfilms, Pub. 2741, Microfilm Abstracts, v. 11, pp. 991-992.

Shaw, B. T., and Humbert, R. P., 1941, Electron micrographs of clay minerals: Soil Sci. Soc. America Proc., v. 6, pp. 146-149.

Sherborne, J. E., 1951, Rotary drilling fluids: U. S. Patent 2,551,768, of May 8, 1951.

Speller, F. N., et al., 1936, Report of special subcommittee on corrosion fatigue of drill pipe: Am. Petroleum Inst. Proc., sec. 4, v. 17, pp. 67-69.

Speller, F. N., 1938, Prevention of corrosion fatigue failures: U. S. Patent 2,132,586, of October 11, 1938.

Suter, H. H., 1948, Mineralogie und Petrographie in der Erdöl-industrie: Schweiz. Mineralog. und Petrograph. Mitt. Band 28, Heft 1, pp. 12-35.

Temple, Scott, 1951, Composition and treatment of drilling fluids: U. S. Patent 2,571,093, of October 16, 1951.

Verwey, E. J. W., and Overbeek, J. Th. G., 1948, Theory of the stability of lyophobic colloids: Elsevier Pub. Co., Inc.

Wagner, C. R., 1947, Drilling fluids and methods of use: U. S. Patent 2,425,768, of August 19, 1947.

Wayne, T. B., 1942, Treatment of drilling fluids: U. S. Patent 2,294,877, of September 1, 1942.

Wayne, T. B., 1951, Treatment of drilling fluids: U. S. Patent 2,553,224, of May 15, 1951.

Weber, E., 1909, The liquefaction of clays by alkalis, and the use of fluid clay casting in the ceramic industry: Ceramic Soc. [Eng.], Trans., v. 8, pp. 11-22.

Williams, C. E., Jr., and Bruce, G. H., 1951, Carrying capacity of drilling muds: Jour. Petroleum Technology, v. 3, no. 4, pp. 111-120.

Williams, F. J., Neznayko, M., and Weintritt, D. J., 1952, The effect of exchangeable bases on the colloidal properties of bentonites: Paper presented at Colloid Symposium, Los Angeles, June 16, 1952.

Williams, M., and Cannon, G. E., 1939, Evaluation of filtration properties of drilling muds: Am. Petroleum Inst., Drilling and Production Practice, 1938, pp. 20-28.

Yovanovich, B., 1936, À propos des argiles smectiques: Soc. Géol. France, Compte rendu 1936, pp. 104-105.