CHEMICAL TREATMENT OF DRILLING FLUIDS

A COLLOID CHEMICAL AND RHEOLOGICAL STUDY

PROEFSCHRIFT

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Aan mijn Ouders

Aan mijn Vrouw

Het in dit proefschrift beschreven werk werd uitgevoerd in het „Koninklijke Shell Laboratorium" te Amsterdam en - wat het Röntgen- en electronenmicroscopische gedeelte betreft - in de afdeling van dit laboratorium welke gevestigd is in het „Laboratorium voor Technische Physica" van de Technische Hogeschool te Delft. De pompproeven op technische schaal werden uitgevoerd met een diepboorinstallatie van de „Nederlandsche Aardolie Maatschappij" gevestigd te Oldenzaal, tijdens een proefboring te Gramsbergen.

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Mijn bijzondere erkentelijkheid moge ik hier uiten voor de opbouwende kritiek van mijn collega's van het „Koninklijke Shell Laboratorium" en voor de voortreffelijke hulp bij de experimenten van mijn laboratoriumassistenten en leden van het personeel van de „Nederlandsche Aardolie Maatschappij".

Mijn „Alma Mater" is de Rijksuniversiteit te Utrecht, waar ik in 1936 het doctoraalexamen scheikunde aflegde. Hier was het dat mijn belangstelling voor de colloidchemie gewekt werd door de boeiende lessen van Prof.Dr.H.R.Kruyt en door mijn contact met zijn school in het van 't Hoff Laboratorium.

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CONTENTS

INTRODUCTION

In rotary drilling of oil wells the circulation of a drilling fluid is conditio sine qua non: its primary functions are to cool and lubricate the bit and to remove the drill cuttings. Thus the function of a drilling fluid is comparable with that of a cutting oil in metal cutting operations.

In principle, therefore, a single fluid (oil or water) or a fluid emulsion would do the job. However, an additional function of a drilling fluid is to keep the hole intact: the weight of the mud column should restore the disturbed equilibrium of the formation pressures. In most cases the specific gravity of the mud should be greater than 1 to achieve this, particularly when high pressure gas reservoirs are encountered: the fluid column may then prevent a blow-out. The fluid should therefore be weighted, either by suspending heavier material or by dissolving such materials in the fluid (e.g. brines). In the case of suspensions the settling of the suspended matter should be prevented which may be achieved by the addition of colloidally dispersed matter.

In most cases the use of suspensions will be imperative: usually porous formations are encountered where a single fluid or solution would get lost by penetration into the formation. A suspension, on the other hand will filtrate on the porous wall, leaving behind a rather impermeable filter cake, preventing further fluid losses. This phenomenon is called the "plastering" of the formation by the mud. Also for this purpose the presence of colloidal matter which is known to improve the impermeability of the filter cake, will be highly desirable.

In general, therefore, the principal components of a drilling fluid are the fluid phase, suspended weighting materials and colloidally dispersed suspending and plastering material. The latter will often require the addition of peptising agents in order to regulate the state of peptisation of the colloids.

In addition, special compounds may be added for special purposes, e.g. to prevent the dispersion of clays of the formations drilled, to improve the plastering on extremely porous formations, to improve the removal of the mud cake which is formed on the productive zone ("deplastering") and to counteract the taking up of gas ("gas cutting").

The requirements to be met by a drilling fluid in circulation may be summarized as follows:

They should

1. adequately lubricate and cool the bit;
2. carry the drill cuttings in the upward stream;
3. release the cuttings in the mud ditch;
4. keep the weighting materials in suspension;
5. be easily pumpable;
6. keep the hole intact and prevent blow-outs by their weight;
7. have excellent plastering and deplastering properties;
8. not disperse the formations encountered;
9. resist gas-cutting;
10. be non corrosive and non abrasive.

The relevant properties to be considered are:
lubricating properties, heat conductivity and heat transfer coefficients in contact with steel in connection with (1).
rheological properties (1, 2, 3, 4 and 5)
specific gravity (6)
filtration behaviour (7)
interaction with the formation (8)
foaming tendency (9)
corrosivity and abrasiveness (10)

It is beyond the scope of this thesis to give a detailed discussion of this complex of properties or of the large variety of drilling fluid compositions, designed to meet the above requirements. Our attention will be focussed on two items which, at the present stage of development, are considered to be of primary importance.

First the rheological properties of drilling fluids will be discussed in relation to the problem of pumpability. Secondly the colloid chemical properties of the most widely used type of drilling fluids, viz the clay-water base muds will be dealt with. It is known that the adjustment of the colloid chemical properties of these clay suspensions have a direct bearing on their rheological behaviour and this forms the link between the two items under discussion. The pumpability study is a typical engineering problem, as we are here handling many tons of drilling fluid in circulation over large distances. In the colloid chemical investigation, on the other hand, we must think in terms of particles of colloidal dimensions. However, the distribution of charges at the surfaces of the extremely small clay particles determines the pressures required to pump the drilling fluid in bulk. This is, in our opinion, the particular charm of the combination of an engineering with a colloid chemical study.

The pumpability and the colloid chemical problem are discussed in part I and II, respectively. In part III the link between the two will be dealt with.

PART I

RHEOLOGY, VISCOMETRY AND PUMPABILITY OF DRILLING FLUIDS

SUMMARY

Mud rheology and mud viscometry are discussed from the pumpability point of view. First, mud flow in the rotary circuit is analysed. On the strength of this analysis the rheological information required to attack the pumpability problem is formulated and finally a suitable viscometer is developed enabling the determination of those rheological constants from which pumping pressures may be calculated.

With this instrument, a modified Stormer viscometer, a number of muds has been tested, particularly clay base muds before and after chemical treatment. It appeared that the muds, under the conditions prevailing in the circuit, behave as either Newtonian or Bingham plastic systems. Chemical treatment was found to affect mainly the Bingham yield stress of a mud, the small differential viscosity remaining practically unaltered. In the laminar flow region this results in a decrease of the pumping pressure, since in this region the pumping pressure is mainly governed by the Bingham yield stress. In the turbulent flow region it was not known whether yield stress reduction would lower the pumping pressures since insufficient information is obtainable in the literature. Therefore a number of semi technical scale and one full scale pumping experiment have been carried out with simultaneous determination of the rheological behaviour of the muds. It was found in this, still limited, amount of tests that pressure losses in the turbulent region are higher than predicted from differential viscosity data but at constant differential viscosity a variation of the yield stress from practically zero to about 150 dynes/ cm^2 appeared not to affect the turbulent flow pressure losses. It was, however, shown that the critical circulation capacity for the onset of turbulence increases with increasing yield stress. As a consequence, in some ranges of circulation velocities the mud with the higher yield stress which is still in the laminar flow region may be more easily pumped than that with the lower yield stress which is in the turbulent flow region. Particularly with weighted muds, where turbulent flow pressure losses are extremely high due to the high specific gravity, the yield stress may be raised in order to keep pumping pressures low by the maintenance of laminar flow.

PART I RHEOLOGY, VISCOMETRY AND PUMPABILITY OF DRILLING FLUIDS.

INTRODUCTION

The mud pump and circulation system are the heart and veins of the rotary drilling equipment. If blood thickens the heart fails and life stops, if mud thickens, the pump fails and drilling must be stopped. This may demonstrate the importance of the rheological properties of rotary drilling fluids. In a given mud circuit the maintenance of a minimum rate of circulation required to cool the bit and to carry the drill cuttings, entirely depends on the adequate adjustment of the rheological behaviour of the mud.

When oil wells were drilled to shallow depths and slush pumps were driven with steam power, the pumpability of the mud was never a very serious problem. In present-day deep-drilling operations, however, and where the pumps are driven by Diesel engines, pumping pressures are more critical. Consequently, increasing attention is being devoted to the pumpability of muds and the effect of their rheological characteristics on the pumping pressures. Although much thought has been given to both pumpability and rheology of muds, their relation is still not sufficiently known.

This is mainly due to the lack of appropriate viscometers to supply the required rheological information. The usual apparatus like the MacMichael and Stormer instruments or the Marsh funnel etc. are arbitrary instruments in which the flow pattern is ill defined, and although the results may be used in a relative way in the daily routine control of mud samples, no basic data are obtained for use in pressure loss calculations. Therefore the need was felt for a viscometer-preferably a routine type instrument-which would supply these fundamental data.

Generally speaking, when handling such a problem of applied rheology, the practical problem should be analyzed carefully. Therefore the relation between the rheological characteristics of muds and their pumpability must be discussed first. Then on the strength of the analysis of mud flow in the rotary circuit, the fundamental rheological information required for pressure loss calculations can be formulated. Finally a suitable viscometer may be developed.

A limited number of pumping experiments on a semitechnical scale and one full scale experiment have been carried out in order to check the relations between viscometer readings and pumping pressures in a rotary circuit.

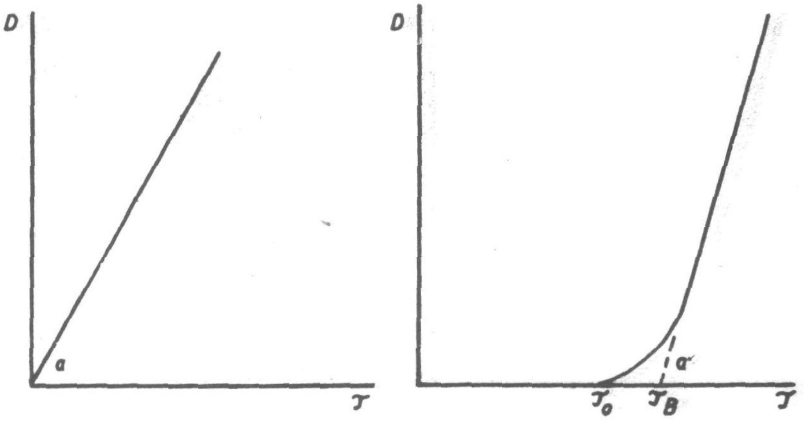
A. RHEOLOGICAL DEFINITIONS USED.

As will be shown, later, under the conditions prevailing in the mud circuit, drilling muds approximately obey the equations for either Newtonian or Bingham plastic flow. Their flow behaviour may thus be represented by one of the following formulas:

$\tau = \eta D$ for Newtonian flow and $\tau - \tau_B = n.D$ for Bingham flow where
τ = the shearing stress applied (dynes/cm^2 or N/m^2)
τ_B = the Bingham yield stress
D = the rate of shear (sec.$^{-1}$)
η = the viscosity (dyne/sec./cm^2 = "poise" or N sec./m^2)
n the differential viscosity

(between brackets the c.g.s. and practical units, respectively: if pressure losses according to the formulas given are calculated in dynes/cm^2 they may be converted into p.s.i. or atmospheres by multiplying by 14.5×10^{-6} or by 0.986×10^{-6} respectively.)

These relations are represented in fig. I, 1, showing the τ-D diagrams.



"NEWTONIAN FLOW"
$\tau = \eta \cdot D$
$\eta = \cot a$

"BINGHAM FLOW"
$\tau - \tau_B = \eta \cdot D$
$\eta = \cot a$

FIG. I, I

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For Bingham flow the extrapolated "Bingham" yield stress is larger than the yield stress defined as the minimum stress causing flow (τ_0). The deviation from the straight line at low rates of shear is, however, of no interest for the pumpability problem. At the high rates of shear prevailing in the circuit, therefore, the system may be treated as an ideal plastic system obeying the equation $\tau - \tau_0 = n.D$, substituting τ_B for τ_0.

Most muds show the phenomenon of thixotropy or isothermal sol-gel transition. Thus the τ-D relation is not a fixed relation but depends on the history of the mud. However, in the pumpability studies one is mainly interested in the τ-D relation which is valid for the mud in circulation or, in other words, which is valid for the mud at the "thixotropic level" prevailing in the circuit.

All this applies to laminar flow where the stream lines are parallel. With increasing fluid velocities the ratio of inertia forces and frictional forces increases, and beyond a certain critical velocity this results in turbulent flow. This critical velocity is usually connected with the critical ratio of inertia and frictional forces by means of the dimensionless Reynolds Number. As soon as flow becomes turbulent the specific gravity of the mud enters the pressure loss formulas.

B. ANALYSIS OF MUD FLOW WITH RESPECT TO THE PRESSURE LOSSES IN THE CIRCUIT.

Pressure losses in the circuit occur in the surface connexions (standpipe, hose, swivel, kelly and drill collars), the drill pipe, the tool joints, the bit nozzles, the bottom of the hole, where the mud stream is reversed and the annulus, i.e. the annular space between drill pipe and bore hole or casing. The slight difference of the specific gravity of the mud in drill pipe and annulus due to the presence of the drill cuttings in the latter, requires a small additional pumping pressure.

A short survey may be given of the pressure-loss equations in the different parts of the mud circuit for both a Newtonian and a Bingham plastic system.

a. Pressure-loss formulas for Newtonian liquids ($\tau = \eta.D$)

1. Flow through the drill pipe.

The pressure-losses for laminar flow are governed by Poiseuille's law:

$$P = \frac{8\ L\ \eta . V}{R^2} = \frac{8\ L\ \eta . Q}{\pi R^4} \qquad (1)$$

where R and L are the internal radius and length of the drill pipe;

Q = the volume rate of flow

V = the average linear velocity of the fluid = $Q/\pi R^2$.

The maximum shearing stress at the wall of the pipe is $\tau_R = \frac{PR}{2L}$, the maximum rate of shear $\dot{D}_R = \frac{PR}{2L\eta} = \frac{4Q}{\pi R^3} = \frac{4V}{R}$.

Flow is laminar up to the critical value of the Reynolds number

$$Re = \frac{4mV\rho}{\eta} = \frac{2RV\rho}{\eta} = \frac{2Q\rho}{\eta . \pi R}$$

where ρ = the density of the fluid and m the mean hydraulic radius of the pipe $m = \frac{R^2}{2\pi R} = R/2$.

The critical value is dependent on the shape of the ends of the tube and may be assumed to be ca 2000 in this case.

As soon as the critical Reynolds number is exceeded flow becomes turbulent, and then the pressure-losses are given by the Fanning-Darcy law:

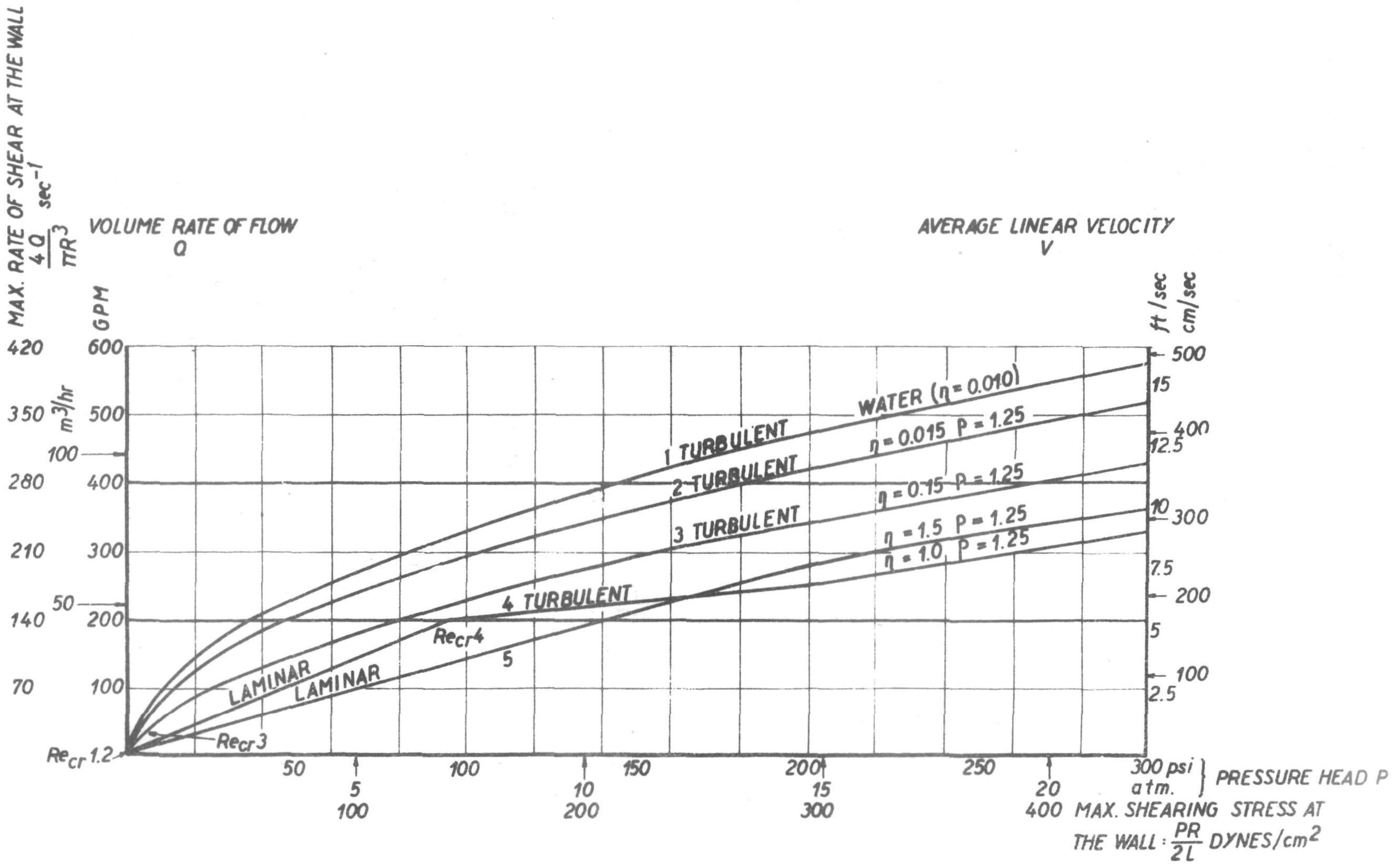
$$P = f. \frac{L\rho V^2}{2m} = f. \frac{L\rho V^2}{R} = f. \frac{L\rho Q^2}{\pi^2 R^5} \qquad (2)$$

where f is the "friction factor" an empirical constant, which varies with the value of the Reynolds number. The relation of f and Re depends on the roughness of the tube. According to Blasius $f = 0.079\ Re^{-1/4}$ for Reynolds numbers between 2000 and 100.000 and the pressure losses become proportional to

$$P \sim \frac{L . V^{1.75}}{R^{1.25}} . \rho^{0.75} . \eta^{0.25} \qquad (2a)$$

At still higher Reynolds numbers f becomes gradually less dependent on the viscosity and P then becomes directly proportional to the density. This will result in high pressure requirements when pumping barytes weighted muds into deep wells.

The pressure losses P as a function of the rate of circulation Q for some Newtonian liquids are presented in fig. I. 2a. The data are calculated for flow through 3000 ft of 4½ in.O.D. drill pipe. For low viscosity fluids parabolic turbulent flow curves are obtained at any practical rate of circulation (curves



η in poise

FLOW OF NEWTONIAN LIQUIDS THROUGH 3000 FT OF 4 1/2" OD DRILL PIPE
PRESSURE HEAD AS A FUNCTION OF VOLUME RATE OF FLOW (CALCULATED)

FIG. I, 2a

1, 2, 3). Flow will be laminar up to practical rates of circulation in the case of high viscosity fluids (curves 4,5). The shift towards higher pressures of curve 2 with respect to the curve for water (curve 1) is mainly due to the high specific gravity (1.25).

2. *Flow through the annulus*

For laminar flow the equivalent of the Poiseuille equation reads

$$Q = \frac{\pi P}{8L\eta}(R_1^2 - R_2^2)\left(R_1^2 + R_2^2 - \frac{R_1^2 - R_2^2}{\ln R_1/R_2}\right) \qquad (3)$$

where 2 R_1 = I.D. of the casing and $2R_2$ = O.D. of the drill pipe.

The Reynolds number for the annulus is

$$Re = \frac{4mV\rho}{\eta} = \frac{2(R_1-R_2)V\rho}{\eta} = \frac{2\ Q\ \rho}{\eta\pi(R_1+R_2)} \quad \text{since } m = \frac{\pi R_1^2 - \pi R_2^2}{2\pi R_1+2\pi R_2} = \frac{R_1-R_2}{2}$$

Theoretically, therefore, flow may be turbulent in the drill pipe at a certain volume rate of flow where the flow in the annulus is still laminar. However, in practice, the swinging and rotating drill pipe will certainly disturb laminar flow in the annulus. In the case of laminar flow eccentricity of the drill pipe results in smaller pressure losses than those calculated.

If the Reynolds number exceeds the critical value of ca.2000, flow in the annulus becomes turbulent and the pressure losses are calculated according to the Fanning-Darcy equation for the annulus:

$$P = f.\frac{L\rho V^2}{2m} = f.\frac{L\rho V^2}{R_1-R_2} = f.\frac{L\rho Q^2}{\pi^2(R_1-R_2)(R_1^2-R_2^2)^2} \qquad (4)$$

Theoretically, the pressure losses in the turbulent range are independent of the eccentricity of the drill pipe, the mean hydraulic radius remaining the same.

3. *Flow through the tool joints and bit nozzles.*

The pressure losses on passing a stricture where the difference in height is negligible is according to the Bernouilli theorem:

$$P = \frac{\tfrac{1}{2}\rho\ Q^2\ (1-\beta^4)}{C^2A^2} \qquad (5)$$

where β is the ratio of the diameters of the stricture and the drill pipe. A is the cross sectional area of the stricture and C is an empirical constant, the "coefficient of discharge" which depends on the shape of the stricture and the Reynolds number in the stricture.

For the bit nozzles C is usually found to be 0.8 and β^4 may be neglected, being small compared with 1.

For tool joints C is usually taken to be equal to 1.0 and it is found that about 70% of the total pressure loss is recovered after passing the tool joint. The value of β depends on the type of tool joint. For "regular" tool joints $\beta = 0.55-0.60$ and consequently the pressure losses are rather large, they are, however, negligible for "internal flush" joints where $\beta \approx 0.97-0.98$.

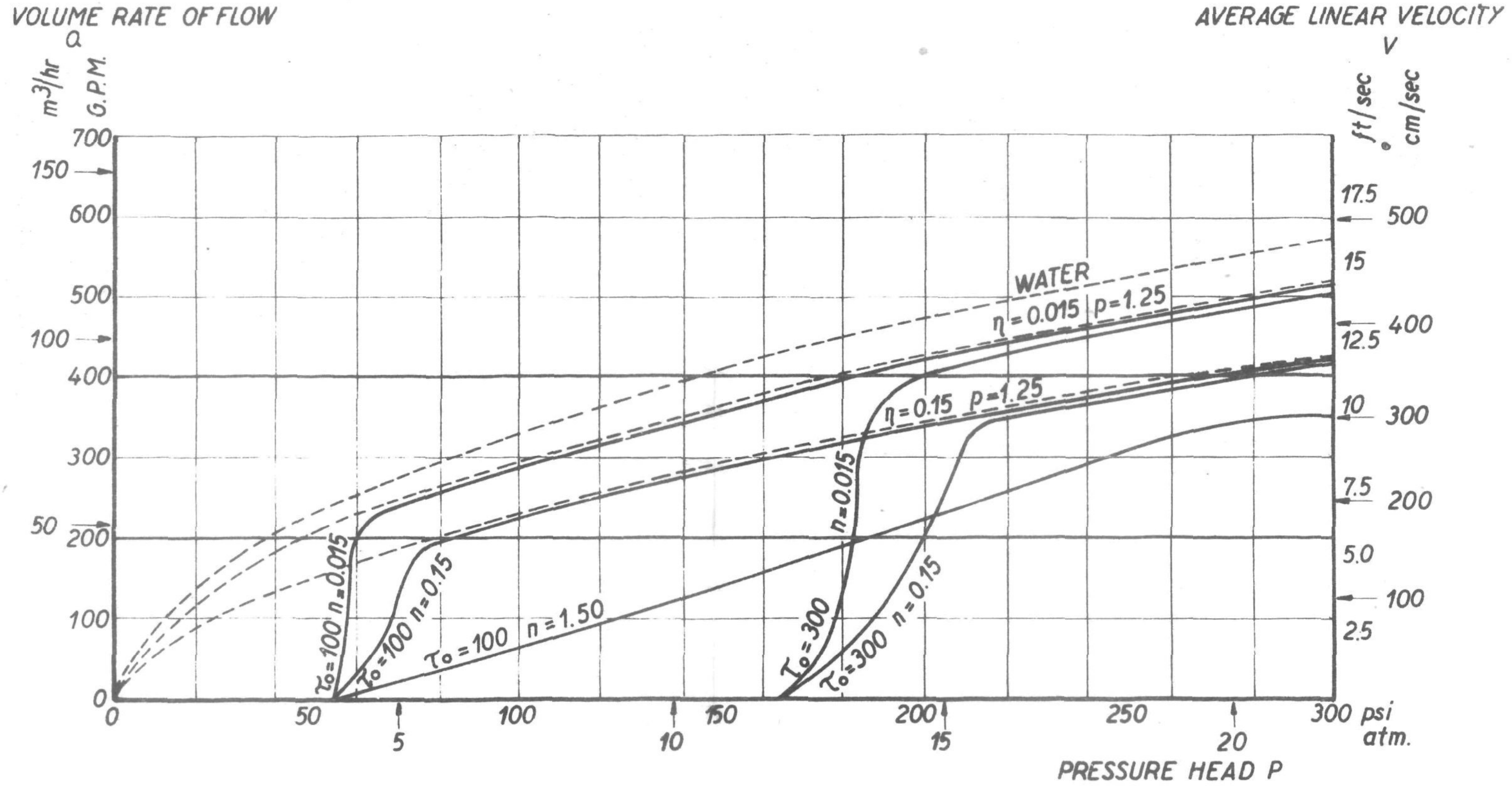
4. *Pressure losses in the surface connexions and at the bottom.*

The losses in the surface connexions are comparatively small: they may be roughly calculated from the number of bends, fittings and valves, which are to be expressed in equivalent lengths of pipe according to the engineering handbooks.

The pressure loss at the bottom of the hole where the mud stream is reversed, will not exceed $\frac{1}{2}\rho V_a^2$ where V_a is the linear velocity in the annulus, which is comparatively small.

As to the relative magnitude of the pressure losses in the various parts of the system, it is found that the losses in the annulus are usually small in comparison with those in the drill pipe. The losses in the bit nozzles become very high for small nozzles. This is an important consequence of the use of so-called jet bits, where the mud stream passing the small nozzles is directed onto the formation in front of the bit blades in order to take advantage of its erosive action. As an example the following pressure losses (p.s.i.) are obtained when circulating a 1.24 sp. gr. mud at a rate of circulation of 400 GPM.

Surface connexions:	50
3000 ft 4½ in O.D. drill pipe I.F.:	175
3000 ft annulus (8.83 in I.D. casing):	12
Two 5/8 in bit nozzles:	570
Two 1⅛ in bit nozzles:	55



FLOW OF IDEAL PLASTIC FLUIDS THROUGH 3000 FT. OF 4 1/2" O.D DRILL PIPE
PRESSURE HEAD AS A FUNCTION OF VOLUME RATE OF FLOW - (CALCULATED)

FIG. I, 2b

b. Pressure loss formulas for Bingham plastic systems.

In the regions where laminar flow may exist, viz. in the drill pipe and in the annulus, the pressure losses may be calculated from the Bingham-Buckingham equation. At practical rates of flow in the drill pipe this equation reads:

$$Q = \frac{\pi R^4}{8Ln} (P - 4/3\ p_B) \quad \text{where } p_B = \frac{2L\ \tau_B}{R} \tag{6}$$

which is represented by the asymptote of the steep part of the curves in fig.I, 2b. This asymptote cuts the P-ordinate at a point $4/3\ p_B$.

For turbulent flow in bit nozzles and tool joints and – at high rates of circulation – in drill pipe and annulus, formulas relating the pressure losses with both n and τ_B are not known. Although for pipe flow a parabolic relation between pressure loss and rate of circulation is found roughly, as indicated schematically in fig.I, 2b, the litarature data cannot be correlated with reliable data for both n and τ_B.

Pressure losses may again be expressed in a Fanning-Darcy equation $P = f \frac{L \rho V^2}{R}$ where the friction factor f should be related to the Reynolds number, but the problem is how to define a Reynolds number for these systems.

For ideal plastic systems where $\tau - \tau_o = n.D.$ (τ_o = the minimum stress causing flow or the normal yield stress), a correct mathematical deduction of a Reynolds number as a function of n and τ_o from the Bingham-Buckingham equation is given by McMillen (1). For the systems investigated by him the critical value of the Reynolds number according to his formulation is again around 2000. However, for many systems reported in the literature showing Bingham flow much lower critical values result from McMillen's equations. McMillen's expression for the Reynolds number contains the numerical value for the relative plug radius c. Since for an ideal plastic system the value of c under various conditions of flow will be different from that for a Bingham system it is evident that his formulas do not hold for the latter.

According to Binder and Busher (2) a critical value of 2000 is found for many data in literature if a Reynolds number is based on an apparent viscosity defined as $\eta_s = n + \frac{R}{3V}\tau_B$ which is derived from the analogy $\frac{PR}{2L} = \frac{4V}{R} . \eta$ (Poiseuille) with $\frac{PR}{2L} = \frac{4V}{R} (n + \frac{R}{3V} \tau_B)$ (Bingham-Buckingham asymptote).

The transition points of laminar to turbulent flow indicated in fig. I, 2b are actually calculated according to their definition. However, these authors do not relate turbulent flow pressure losses with this Reynolds number.

Dunn, Nuss and Beck (3) were the first to relate pressure losses in the mud circuit with viscometric data. They describe the turbulent flow pressure losses by the introduction of the "equivalent turbulent viscosity" η_T which is equal to the viscosity a Newtonian liquid would have which would give the same turbulent flow pressure losses as the plastic system under identical conditions. In other words a "Reynolds number" $Re' = \frac{2R\ V\ \rho}{\eta_T}$ is defined for the plastic system so that its f-Re' relation is identical with the f-Re relation of a Newtonian liquid with viscosity $\eta = \eta_T$. This procedure has been proposed earlier (2) but Dunn, Nuss and Beck relate η_T with viscometric data. However, they relate η_T with n only, thus neglecting the effect of the yield stress. This does not seem correct, although for a number of muds tested in the field, pressure losses could be calculated according to their procedure which agree with those measured to within 10%. As, however, for various systems reported in the literature, the yield stress certainly appears to affect the turbulent flow pressure losses in pipes and strictures, it is still questionable whether the yield stress may be neglected in the case of turbulent flow of drilling fluids. Further data will be required to settle this question.

C. CONSEQUENCE FOR MUD VISCOMETRY

Turning to the discussion of the significance of rheological data for the practical pumping problem, the above considerations may be summarized as follows.

The flow of *low-viscosity muds without a yield stress* is turbulent under all circumstances throughout the mud circuit. As the pressure losses vary only slightly with the viscosity (given by the friction factor-Reynolds number relation) no accurate determination of the viscosity is required in this case, and a rough estimate will suffice.

The flow of *high viscosity muds without a yield stress*, however, may be laminar in drill pipe and annulus up to practical

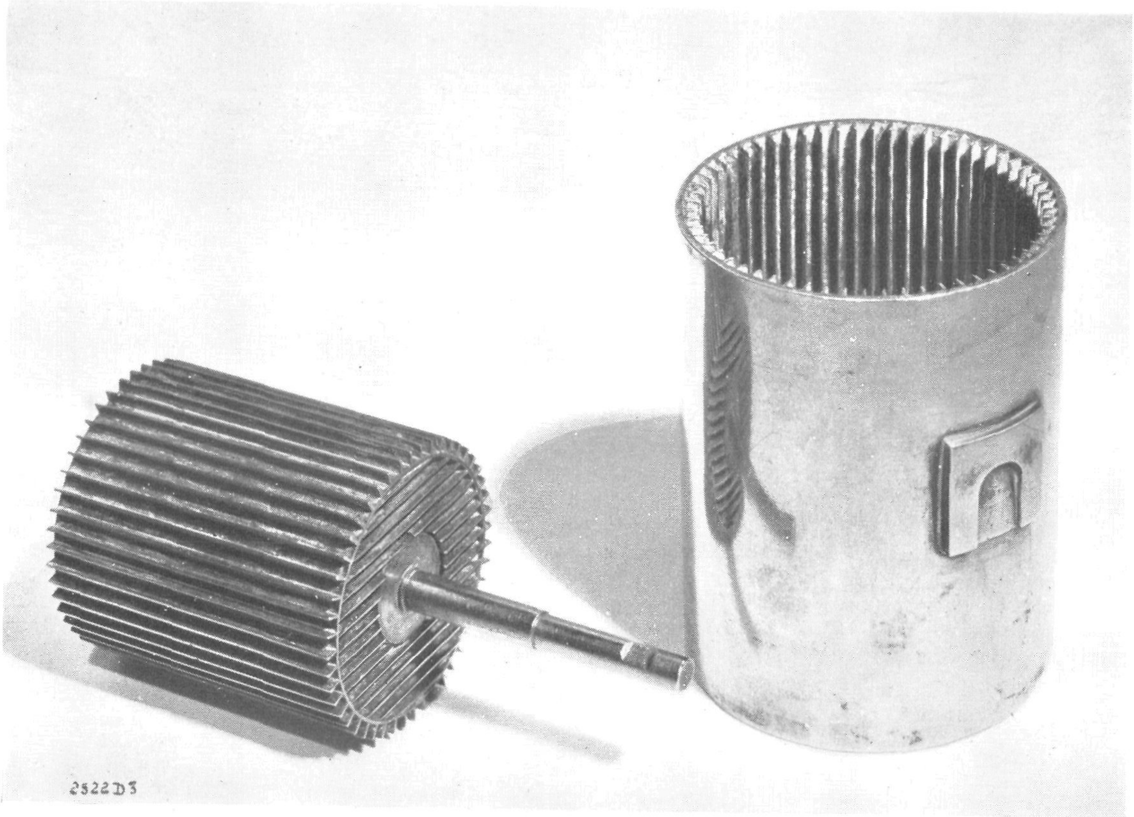


Fig. I. 3. Modified cup and rotor for the Stormer viscometer.

rates of flow. In this case the viscosity should be determined accurately, the pressure losses being proportional to the viscosity. Since the mud suspensions may only be approximately Newtonian, the viscosity should be determined under the conditions prevailing in practice i.e. at the rates of shear occurring in drill pipe and annulus (which may be estimated to cover the range of about 100 to 400 sec.$^{-1}$) and after subjecting the mud to a pretreatment, simulating the amount of shear in pump and bit nozzles. This shearing action will affect the viscosity in drill pipe and annulus, respectively, because of the thixotropic behaviour of most muds. The proper pretreatment has to be standardized on the strength of comparative experiments with samples taken from different parts of the mud circuit and with samples subjected to agitation in laboratory stirrers.

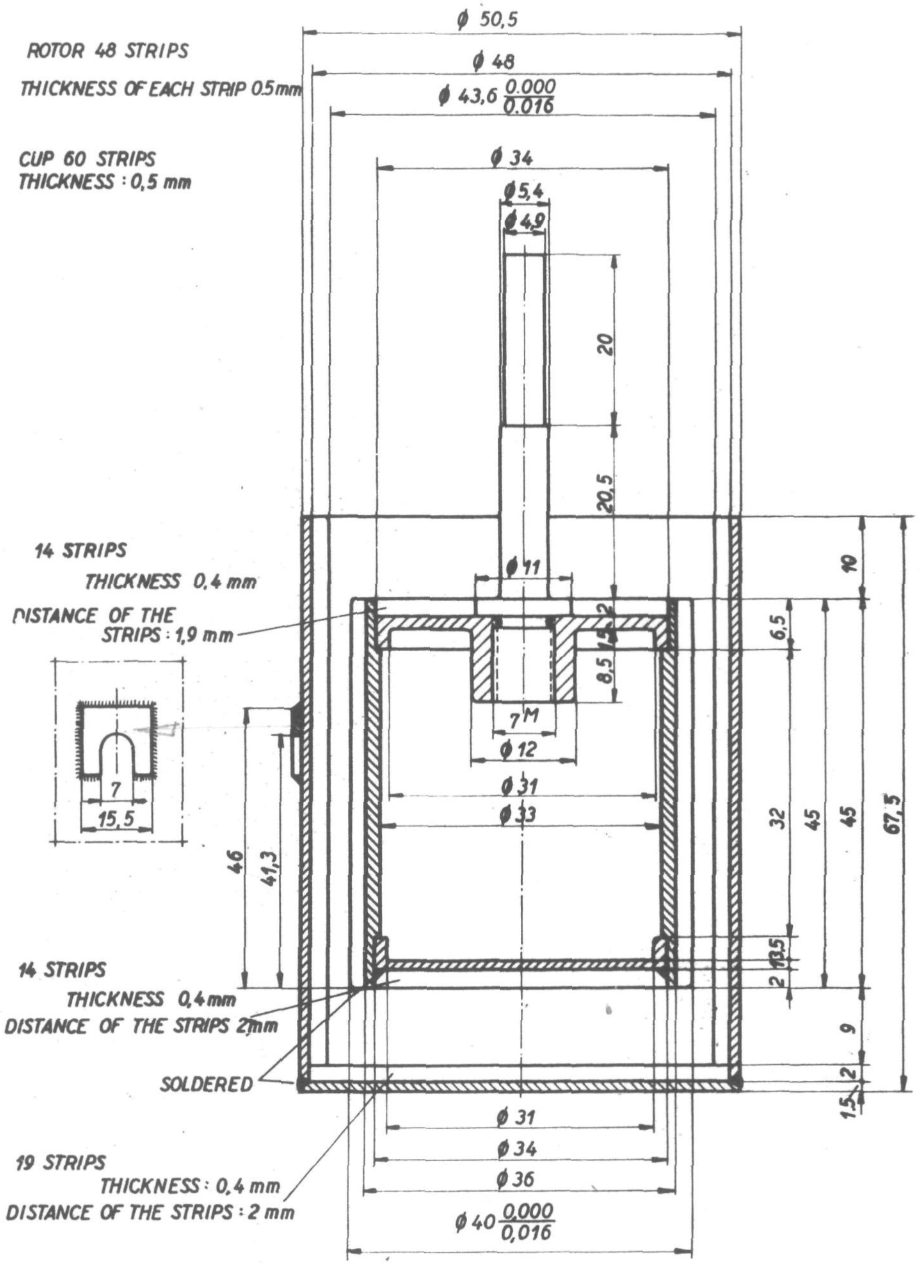
Also for *muds having a yield stress* flow may be laminar up to practical rates of flow in the drill pipe and annulus; then the pressure losses are determined by the position and slope of the curve in the P-Q diagram or, in other words, by the Bingham yield stress and n. It would be desirable, therefore, to determine a few points of the stress-rate of shear curve at some definite rates of shear in the shear region of 100-400 sec.$^{-1}$ and to extrapolate the curve in order to find the Bingham yield stress. Again the mud should be subjected to a proper treatment in order to measure at the thixotropic level prevailing in the circuit.

In practice there are still some other factors affecting the rheological properties viz. temperature and pressure. The former is easily taken into account by carrying out the determinations in a bath of the required temperature. It is believed that the pressures occurring in practice will not affect the rheological behaviour appreciably.

D. A MODIFIED STORMER VISCOMETER

For determinations at well-defined rates of shear a rotational cylinder type viscometer will be the most suitable instrument. Clearance between the cylinders should be small in order to keep the rate of shear between narrow limits. The dimensions are further dictated by the range of rates of shear at which the apparatus should operate e.g. 100-400 sec.$^{-1}$, which should be covered by a convenient range of rates of rotation.

In addition, due consideration should be given to the possibility of slip of the suspensions at the surface of the cylinders



ROTOR 48 STRIPS
THICKNESS OF EACH STRIP 0.5mm

CUP 60 STRIPS
THICKNESS : 0,5 mm

14 STRIPS
THICKNESS 0,4 mm
DISTANCE OF THE STRIPS : 1,9 mm

14 STRIPS
THICKNESS 0,4mm
DISTANCE OF THE STRIPS 2mm

SOLDERED

19 STRIPS
THICKNESS : 0,4 mm
DISTANCE OF THE STRIPS : 2 mm

THE UPPER AND THE LOWER SURFACE OF THE ROTOR AND THE BOTTOM OF THE CUP HAVE PARALLEL STRIPS

FIG. I, 3a

which would obscure the determinations. Parallel experiments with smooth cylinders and those provided with anti-slip strips have shown that in most cases both assemblies yield identical results. However, in some cases-particularly emulsion base muds and flocculated clay water base muds-viscosity and yield stress values are found which are 30-40% low if the smooth cylinders are used. Therefore, although slip is certainly not of common occurrence, the provision of anti-slip strips will ensure the general applicability of the instrument.

A suitable cup and rotor have been developed along these lines and they have been adapted to the well known Stormer viscometer, an apparatus which is already in common use for the testing of muds. The original cup and rotor of the Stormer did not comply with the above requirements as wide variations of the rate of shear are encountered between cup and rotor, as well as inside the hollow rotor. Further the design of the original Stormer is fairly favourable for the development of turbulence which limits its applicability to low rates of shear. The usual determination of the "600 rpm Stormer viscosity" is certainly carried out in the turbulent range and cannot be converted into fundamental data. Finally slip is not avoided. The apparatus itself, however, is of reasonable mechanical design and the modification can be restricted to a modification of the cup and rotor. Fig. I,3 shows a photograph of the new cup and rotor, Fig.I,3a the construction and dimensions.

E. CALIBRATION OF APPARATUS

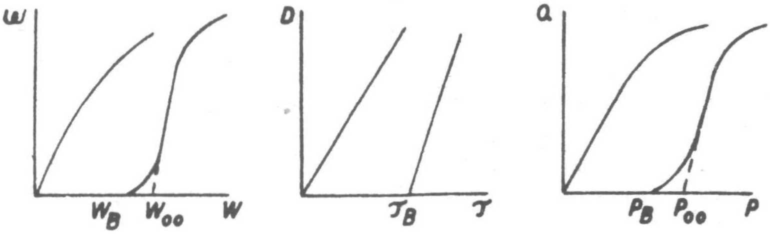
With the modified Stormer viscometer the relation driving weight-rate of rotation (W-ω) is measured, from which the fundamental τ-D diagram may be derived which is again translated into the practical P-Q diagram. This procedure is schematically sketched in fig.I, 4.

The "translation" procedure B → C was dealt with in section A. For the translation A → B the apparatus constants of the viscometer must be determined either by calibration or by calculation.

a. Newtonian flow, apparatus constant for the calculation of the viscosity.

The moment on the rotor is given by $M = \frac{W.g.a}{s}$ where

W = driving weight (g)
a = radius of pully + radius of cord (= 1.45 cm)
s = gear ratio (= 11 in the instrument used)
g = the acceleration due to gravity.



A
VISCOMETER DIAGRAM

B
FUNDAMENTAL DIAGRAM

C
PUMPING PRESSURE-RATE OF FLOW DIAGRAM

FIG. I, 4

8276-2-B4

The viscosity can be calculated from the speed of rotation (r.p.m.) caused by a driving weight W according to the formula $\eta = k.\ W/\omega$ where k = the apparatus constant for the calculation of the viscosity. This constant may be determined either by calculation or by calibration with oils of known viscosity.

1. calculation

The relation between the angular velocity Ω and the moment on the rotor, valid for the space between the two cylinders is

$$\Omega = \frac{M}{4\pi.\,\eta.\,h}\left(1/R_1^2 - 1/R_2^2\right) \qquad (8)$$

where Ω = the angular velocity = $\frac{2\pi.\,\omega}{60}$

h = height of rotor; R_1 = radius of rotor; R_2 = radius of cup; which may be converted into:

$$\eta = \frac{60\ \text{a.g.}}{8\pi^2 \text{h.s.}}\left(\frac{R_2^2 - R_1^2}{R_1^2\ R_2^2}\right) W/\omega = k_1\ .\ W/\omega \qquad (8a)$$

resulting in $k_1 = 0.886$.

The shearing stress varies between

$\tau_{R_1} = \frac{M}{2\pi R_1^2 h}$ and $\tau_{R_2} = \frac{M}{2\pi R_2^2 h}$ or between 1.146 W and 0.962 W dynes/cm².

Thus the average shearing stress in the modified cylinder set is 1.05 W dynes/cm² ± 10%.

The rate of shear varies between:

$$D_{R_1} = \tau_{R_1}/\eta = \frac{\pi}{15}\,\frac{R_2^2}{R_2^2-R_1^2}\,\omega \quad \text{and} \quad D_{R_2} = \frac{\pi}{15}\,\frac{R_1^2}{R_2^2-R_1^2}\,.\,\omega$$

or between 1.291 ω and 1.082 ω sec.$^{-1}$.
Thus the average rate of shear is 1.186ω sec^{-1} ± 10%.

The total apparatus constant is found from that for the cylinder surfaces and that for the top and bottom plate. The latter may be estimated from the friction of a disc which is given by:

$$M = \frac{32}{3}\eta\,.\,\Omega\,R_1^3 \quad \text{or} \quad = \frac{180\ \text{a.g.}}{64\ \pi.\text{s.}R_1^3}\,.\,W/\omega = k_2\,.\,W/\omega \tag{9}$$

resulting in $k_2 = 14$.

The total apparatus constant for the calculation of the viscosity may be found from $1/k = 1/k_1 + 1/k_2$ since if $\eta = 1$, top and bottom of the rotor will rotate with a speed $\omega = 1$ with a driving weight $1/k_2$, the cylinder with a weight $1/k_1$ and both together with a weight $1/k_1 + 1/k_2$.

This calculation results in a total apparatus constant $k = 0.883$.

2. *calibration*

The speeds of rotation at various driving weights were measured at 25°C for a number of oils of known viscosity. The speed of rotation is calculated from the time required for the rotor to make 100 revs. In order to avoid inertia effects at the start the time for 100 revs. was measured between the 20th and 120th revolution of the rotor (the speed proved to become constant within the first 20 revs). The driving weights applied should be corrected for friction in the apparatus. To this end the weight was determined which would give the same rate of rotation of the rotor in air and this weight was subtracted from the weights used with the calibration oils. The calibration data for five different oils are given in Table IA.

TABLE IA

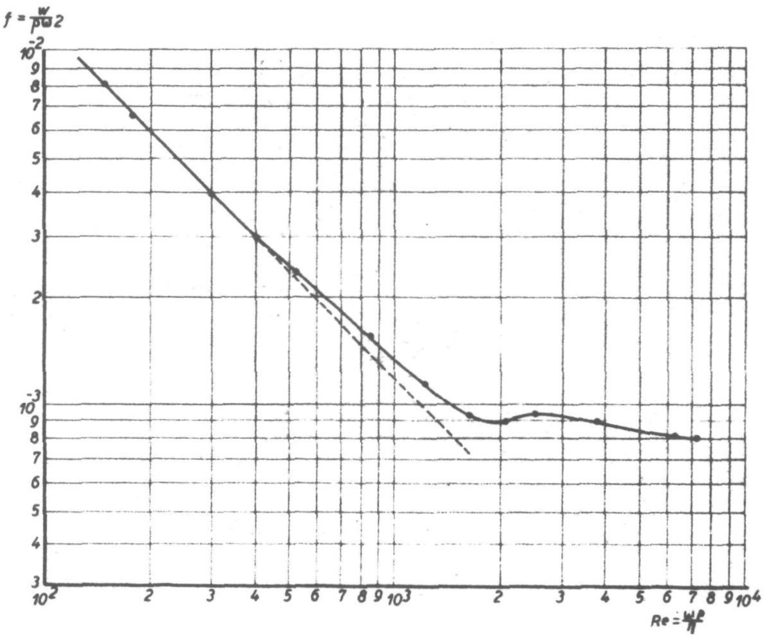
CALIBRATION DATA FOR THE APPARATUS CONSTANT FOR THE VISCOSITY

VISCOSITY (POISES)	ω/W	k
0.211	4.00	0.84
0.578	1.44	0.83
0.975	0.86	0.84
3.97	0.212	0.84
11.04	0.0752	0.83

The calculated constant appears to be in good agreement with that found by calibration. Apparently, the effective radius of cup and rotor are indeed given by the radius of the cylinders enveloping the ends of the strips since these were introduced in the calculations.

The determinations of viscosities in the range of rates of shear of 100-400 sec.$^{-1}$ should be carried out at rates of rotation of 85-340 r.p.m.

In the viscometer, too, flow becomes turbulent at high rates of rotation. The lower the viscosity the lower the critical rate of rotation. However, the region of laminar flow in the viscometer fully covers the region of laminar flow in the mud circuit. For those low viscosity muds which show turbulence both in the circuit and in the viscometer we are only interested in the estimated order of magnitude of the viscosity which would enable a sufficiently accurate calculation of the pressure losses.



CALIBRATION OF CUP AND ROTOR. THE RELATION OF f AND Re
LAMINAR AND TURBULENT FLOW REGION

FIG. I, 5

A method for the estimation of the viscosity from data obtained in the turbulent region of the viscometer is advised by Squires and Dockendorff (4) and also quoted by Wilhelm and Wroughton (5). Analogous to the flow in pipes we may define a Reynolds number in the rotational cylinder viscometer to be proportional to $\omega\rho/\eta$ and a friction factor proportional to $W/\rho.\omega^2$. From the calibration data for oils of known viscosity, f and Re may be plotted on log-log paper in both the laminar and the turbulent flow region. A curve of the same type as that found for flow through pipes is obtained (Fig. I, 5).

For a mud showing turbulent flow in the viscometer, the value of f is calculated for a certain observed combination of W, ρ and ω values and the Reynolds number belonging to this value of f is obtained from the graph; then η may be calculated from Re, ρ and ω. The method supplies rough data which are, however, accurate enough.

b. Bingham flow, apparatus constant for the calculation of the differential viscosity and the Bingham yield stress.

The ω-W relation for a Bingham plastic system is represented in Fig. I, 4. The curved lower part applies to plug flow in the viscometer, the straight line portion (which is not an asymptote as in the case of the P-Q diagram) is a plot of the following formula:

$$\Omega = \frac{M}{4\pi n h}\left(1/R_1^2 - 1/R_2^2\right) - \frac{1}{n}\tau_B \ln R_2/R_1 \qquad (10)$$

in which the effect of the top and bottom plate of the rotor is neglected. Equation 10 may be written:

$$\omega = \frac{60}{2\pi}\cdot\frac{M}{4\pi n h}\left(1/R_1^2 - 1/R_2^2\right) - \frac{60}{2\pi}\frac{\tau_B}{n}\ln R_2/R_1 \qquad (10a)$$

$$\text{or } \omega = k_1.\frac{W}{n} - b\,\frac{\tau_B}{n} \qquad (11)$$

Since for $\omega = 0$ $W = W_{oo}$ equation (11) becomes $\frac{1}{n}(k_1 W_{oo} - b\tau_B) = 0$

$$\text{and } W_{oo} = \frac{b.\tau_B}{k_1} = \tau_B\,\frac{60}{2\pi}\,\frac{1}{k_1}\ln R_2/R_1 \qquad (12)$$

Substituting $b\tau_B = k_1 W_{oo}$ in (11):

$$n = k_1\frac{W - W_{oo}}{\omega} \qquad (13)$$

Thus the differential viscosity n is found from the slope of the straight line portion by multiplying with k_1. In analogy with the Newtonian systems the correction for the top and bottom plate will be accounted for by using the value of k instead of k_1.

The Bingham yield stress τ_B is connected with W_B by the relation

$$W_B = \frac{2\pi R_1^2 h}{\frac{g.a}{s}} \cdot \tau_B \tag{14}$$

which is valid for the cylindrical surface. In practice W_{oo} is determined by extrapolation of the straight line portion to $\omega=0$. There is, however, a fixed ratio between W_B and W_{oo} depending on the apparatus dimensions as calculated from (12) and (14):

$$W_{oo}/W_B = 2\,\frac{R_2^2}{R_2^2 - R_1^2}\ \ln R_2/R_1 \tag{15}$$

This ratio amounts to 1.08, thus W_{oo} is 8% larger than W_B. Taking into account the top and bottom of the rotor in the calculation of both W_{oo} and W_B it may be assumed that for the complete rotor W_{oo} will also be about 8% higher than W_B. Since the relation of W_B and τ_B for the complete rotor is

$$\tau_B = \frac{W_B\,\frac{g.a}{s}}{2\pi R_1^2 h + \frac{4}{3}\pi R_1^3} = 0.88\ W_B$$

the apparatus constant for the calculation of the Bingham yield stress from W_{oo} amounts to 0.81, thus: $\tau_B = 0.81\ W_{oo}$ dynes/cm^2.

F. RESULTS OBTAINED WITH THE MODIFIED STORMER VISCOMETER

The best procedure to determine the stress-rate of shear diagrams which are derived from the driving weight-r.p.m.diagrams is to use a fresh sample for the determination of each point of the curve after submitting the sample to the required pretreatment. If, alternatively a complete curve is determined on one sample only, thixotropic changes during each run may be superimposed on the true curve. If, after the pretreatment, the mud stiffens only slowly, both procedures yield practically identical results.

All muds tested appeared to approximate very closely Bingham or Newtonian flow. Some examples, demonstrating the general shape of the curves obtained are collected in Figs. I, 6 and I, 7, whereas a number of test data are collected in table IB. From these results the following general rules may be drawn up:

The differential viscosity of clay water base muds generally varies between 5 and 25 cp. Oil base and emulsion base muds *) usually show higher values: between 35 and 100 cp. The Bingham yield stresses vary within a wide range from zero to 300 dynes/cm^2.

It is seen from the table that *chemical treatment of clay base muds primarily results in a decreasing yield stress,* although the differential viscosity may decrease at the same time. A definite increase of the differential viscosity accompanied by a decreased yield stress was noticed after lime treatment of a red mud.

An increasing clay content gives rise to an increase of both yield stress and differential viscosity and an analogous effect is observed on the addition of barytes.

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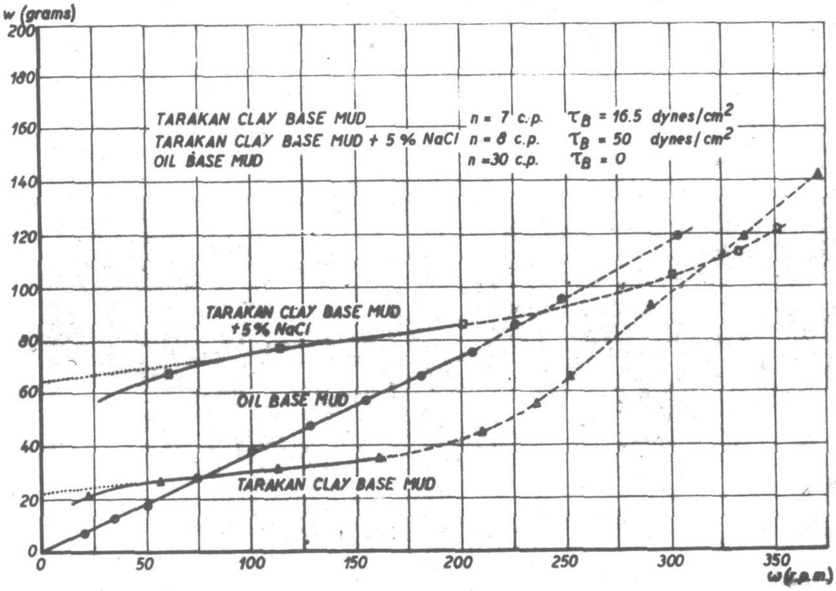
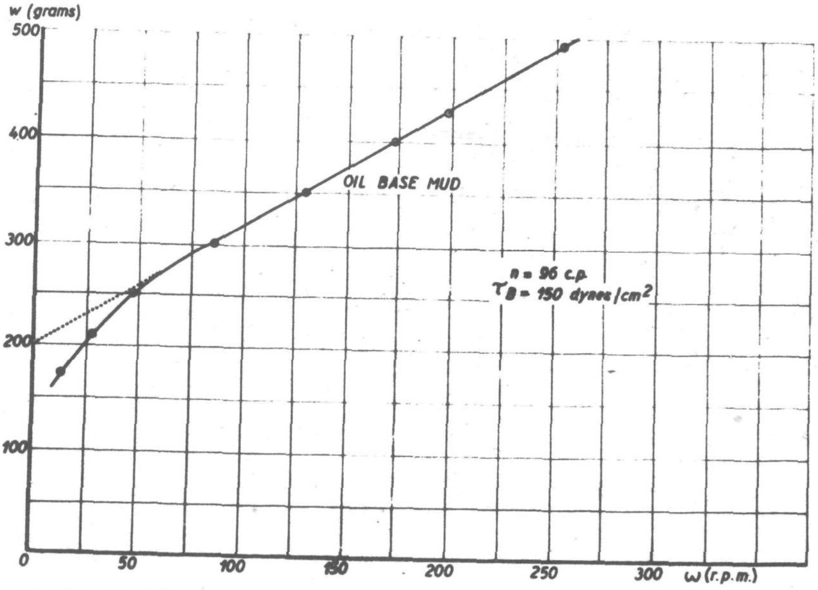
*) "Oil base muds" are usually prepared from a low viscous oil in which blown asphalt as colloidal material and ground limestone as weighting material are incorporated.
"Emulsion base muds" are usually emulsions of a clay-water mud and a low viscous oil.



DRIVING WEIGHT (W) - RATE OF ROTATION (ω) CURVES FOR VARIOUS MUDS

——— laminar flow region ·········· extrapolation to ω = 0
-------- turbulent flow range

FIG. I, 6



DRIVING WEIGHT (W)-RATE OF ROTATION(ω) CURVES FOR AN OIL BASE MUD

——— LAMINAR FLOW REGION ·········· EXTRAPOLATION TO ω=0

FIG. I, 7

TABLE IB

RHEOLOGICAL DATA OF MUDS OBTAINED WITH THE MODIFIED STORMER VISCOMETER

Mud base Chemical treatment	differential viscosity centipoises	Bingham yield stress dynes /cm^2
Talang Djimar clay mud s.g. 1.15	14.5	53
1.20	26.8	150
Tarakan clay base mud s.g. 1.15	<5	<5
1.20	8.1	14.5
1.30	13.7	52
1.40	58	600
Tjepoe clay base mud s.g. 1.15	8.3	106
1.20	13.8	285
Talang Djimar clay mud s.g. 1.15	14.5	53
+ 10% NaCl	16.1	114
+ 1% starch	35	63
+ 1% starch + 20% NaCl	12.8	55
+ 0.1% Na polymetaphosphate	9.3	21
+ 1/4% Na polymetaphosphate	6	8
+ 1/2% Na polymetaphosphate	29.2	10 (s.g.1.80)
+ 0.1% Na metasilicate	<5	<5
+ 0.1% NaOH	<5	23
+ 0.1% NaOH + 0.1% quebracho	11.4	9
Talang Djimar clay mud s.g. 1.20	26.8	150
+ 0.05% Na polymetaphosphate	25.5	124
+ 0.1% Na polymetaphosphate	25.5	106
+ 0.05% Na metasilicate	25.5	114
+ 0.1% Na metasilicate	19.4	68
+ 0.05% Na citrate	20.8	105
Tjepoe clay mud s.g. 1.20	13.8	285
+ 0.2% Na polymetaphosphate	<5	60
+ 0.2% Na polymetaphosphate + barytes	23.7	178 (s.g. 1.80)
+ 0.3% quebracho + 0.2% NaOH	17.1	68
lime treated red mud without starch	40.3	23
Emulsion base mud A	35	65
Emulsion base mud B	87.5	220

Note

It may be remarked that the viscometer is also suitable for the determination of the yield stress τ_0 of the system determining the minimum pressure required to start circulation after a period of closing down as well as its thixotropic change. These data may be obtained by determining the minimum driving weight causing rotation of the rotor, chosing an arbitrary valve for the rate of rotation (or rate of shear) which should be considered the beginning of flow of the mud.

G. SEMI TECHNICAL-SCALE PUMPING EXPERIMENTS

In the preceding chapters the relation between the rheological behaviour and the pumpability of muds has been discussed. It appeared that *in some cases these relations are still* insufficiently known, e.g. turbulent flow pressure losses for Bingham systems.

Therefore a number of semi-technical scale pumping experiments was carried out with muds which were simultaneously tested with the modified Stormer viscometer. Although a full account of these experiments is beyond the scope of this thesis, some results will be described which are illustrative for the discussions in the previous sections.

1. *equipment*

The mud was pumped through 3/4 in. pipe by means of a high pressure piston pump driven by a Diesel engine, the maximum delivery being ca 5 m^3/h for 37 m of pipe where the pressure losses for the thicker muds amount to ca 10 kg/cm^2.

The rate of circulation was measured by means of measuring tanks and the pressure drop with Bourdon type manometers for the full length and with mercury manometers for part of the length of the pipe. Simultaneously the Bingham yield stress and the differential viscosity of the muds were measured, taking samples from the flow line.

2. *Drilling mud*

A clay water base mud of specific gravity 1.33 was used and the rheological properties were adjusted by metasilicate treatment or by partial flocculation with salt.

The results of the viscometer readings are reported in Table I, C.

TABLE I, C

VISCOMETER DATA

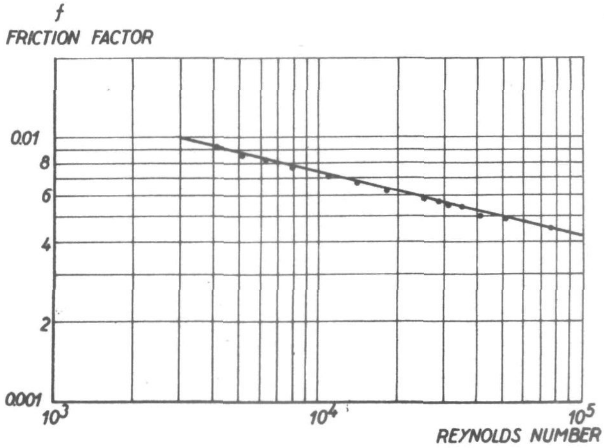
Mud condition in run No.	diff. viscosity centipoises	Bingham yield stress dynes/cm^2
I	11	14.5
II	9.5	43.5
III	8	77
IV	10.5	107.5
V	5.5	156
VI	10	214
VII	14.5	306

Results

In Fig. I, 8 the results are shown for the calibration of the pipe with water in terms of the friction factor-Reynolds number relation. The empirical formula derived from these data reads:

$$f = 0.0701\ \mathrm{Re}^{-0.244}$$

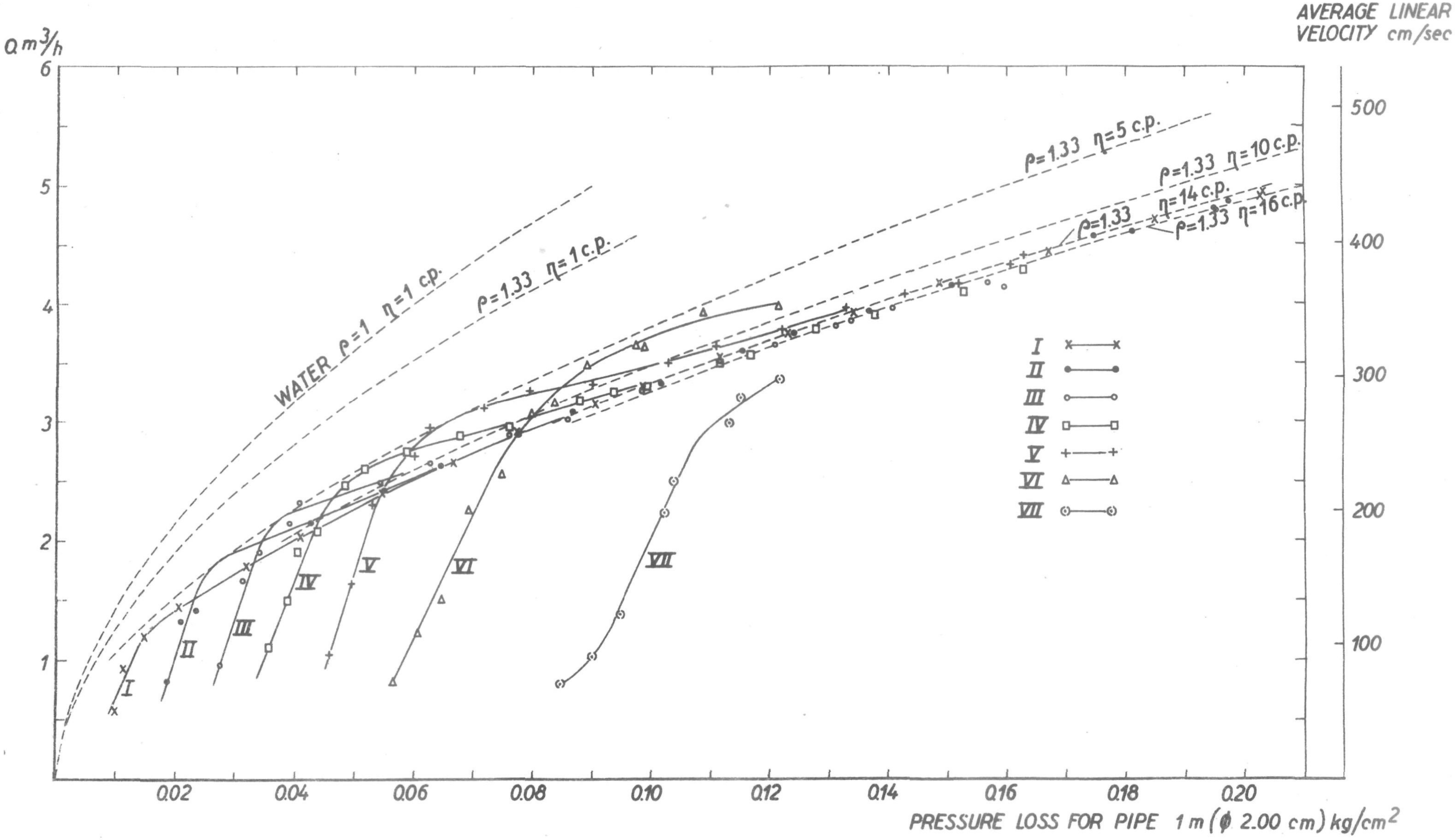
which is practically identical with the Blasius equation (see page 8).



f-Re RELATION FOR PIPE FROM CALIBRATION WITH WATER   FIG. I,8

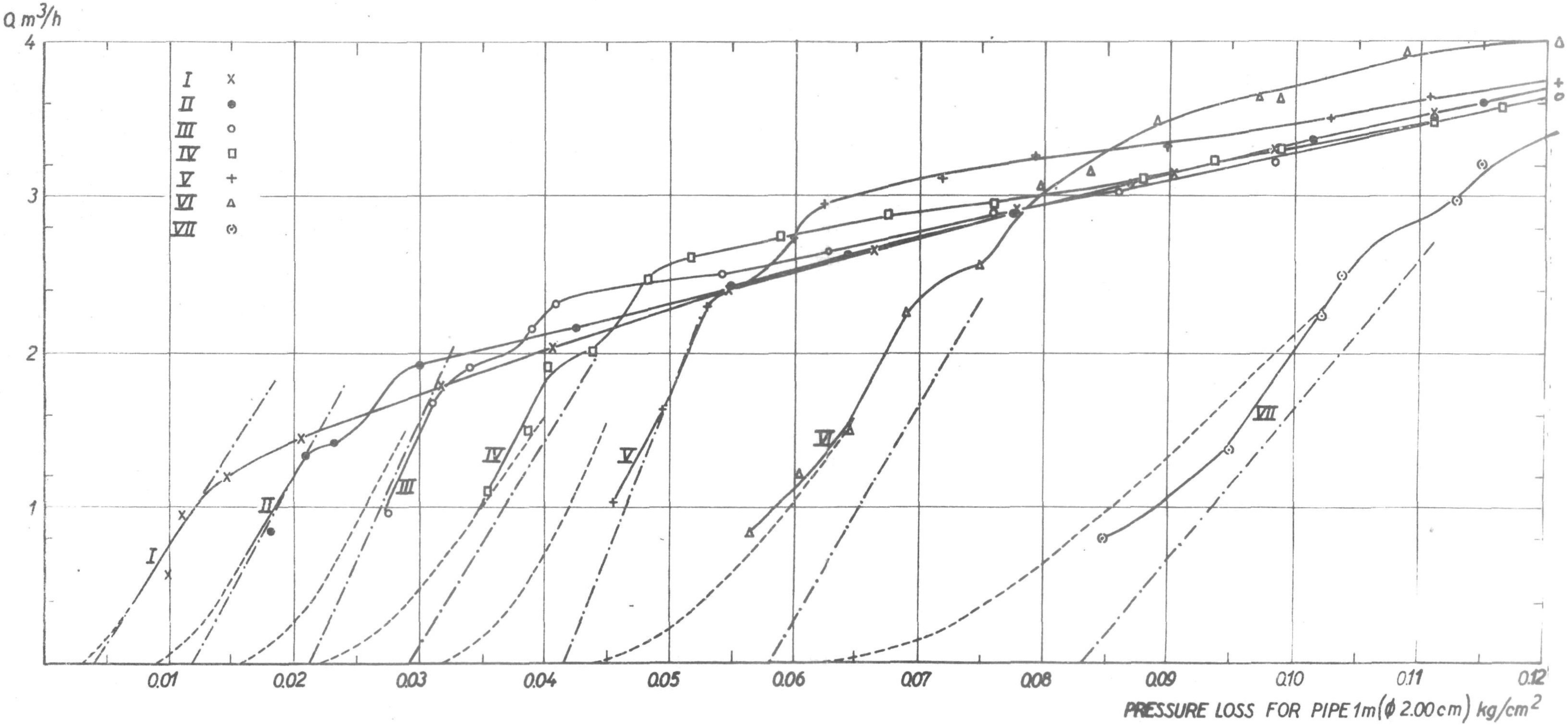
A comprehensive graphical representation of the results for muds with different yield stresses is given in Fig.I, 9 and an enlargement of the laminar flow parts of the curves in Fig.I, 10. In the latter graph the dotted curves are those calculated from the viscometer readings (the straight lines are the calculated asymptotes). Although at low rates of circulation the measured points are somewhat scattered around the calculated curves, the general agreement of measured and calculated data is reasonable, keeping in mind that at low rates of circulation thixotropic effects are less easy to control. For the various muds, with increasing Bingham yield stress (and only slightly varying differential viscosity) the critical rate of flow for the onset of turbulence appears to increase.

Passing a small region of unsteady flow, parabolic turbulent flow curves are obtained. Turning to Fig.I,9, it is seen that at high rates of circulation the pressure losses for the various muds become practically the same, despite their largely differing yield stresses. The dotted curves in this graph refer to the turbulent flow pressure losses calculated for hypothetical Newtonian liquids having the same specific gravity as the mud, but varying viscosities (the latter are indicated on the curves). A comparison of these dotted curves and those measured for muds indicates that the "equivalent turbulent viscosity" of the muds gradually increases with higher rates of circulation. In the beginning, η_T is equal to about 5 cp while at higher mud velocities a value of about 16 cp is reached for all muds tested. Thus the equivalent turbulent viscosity approximates a value which is roughly 1½ times the differential viscosity on an average. This result is in disagreement with that obtained by Dunn, Nuss and Beck (3) who report that η_T is only about 1/3 of the differential viscosity. In their work, however, a f-Re relation was used which was not obtained from calibration of their circuit but from literature. The difference between their f-Re relation and ours accounts for the discrepancy between the results.



PRESSURE LOSS-VOLUME RATE OF FLOW DATA FOR VARIOUS MUDS. SEMI TECHNICAL SCALE PUMPING EXPERIMENTS

FIG.I,9



PRESSURE LOSS-VOLUME RATE OF FLOW DATA FOR VARIOUS MUDS. LAMINAR FLOW REGION (ENLARGED)

K.S.L.A.
FIG. I,10

H. FULL SCALE PUMPING EXPERIMENT

One full scale experiment has been carried out in a deep well after cementing a 7 in casing at ca 8000 ft. Pumping pressures were measured at different rates of flow and with various lengths of drill pipe inserted in the casing. Also the size of the bit nozzles was varied. At the same time the rheological properties of the mud used were determined with the viscometer. Only one mud was tested and no calibration experiments with water have been carried out.

a. Equipment and circuit

The rates of flow were measured by means of a rectangular measuring tank with a cross section of 200 x 220 cm. The pumping pressures were read on manometers ranging from 0–19 and 0–150 kgs/cm^2. The manometers were connected to the stand pipe via a gas buffer in order to level out the pressure fluctuations of the pump. The gas buffer was filled from a nitrogen cylinder in order to ensure a sufficiently large cushion of gas at high pumping pressures.

The rate of circulation was varied by varying the speed of the engine or – at greater depths – by using either one or two parallel pumps.

Readings were taken for the following circuits

a. surface connections including 1 stand of drill collars inserted in the 7 in casing.
b. (a) + bit with two 5/8 in nozzles
c. (a) + bit whith two 1 in nozzles
d, e, f, g, h, i, j, k
(c) + 224, 473, 973, 1473, 1973, 2660, 2632 and 2660 meters of 3½ in O.D. drill pipe with F.H. tool joints in the 7 in casing respectively.

TABLE I,D

series	A mud. wt	measuring tank sec	cm	Q m^3/h	P kgs/cm^2	P_c	$P_{t.j.}$	$P_{d.p.}$ $+P_{ann.}$	$P:$ $(f_a \times 100)$ calc.	$f_{d.p.} \times 100$	Summary of various pressure losses (kgs/cm^2) $P_{d.p.}$	$P_{t.j.}$	$P_{ann.}$	$P_{s.c.}+P_{bit\ 1\alpha}$	
a surface	1.26	170	100	93	11										
		232	70	30.2	3.5										
b a + 5/8" bit	1.26	340	128	59.5	21.5										
		310	94	47.8	12.5										
		180	96	84.2	40.5										
		206	110	84.2	40										
c a+1"bit	1.26	187	110	93	14.5										
		240	77	50.7	5										
d 224 m+c	1.28	193	110	90	32	13.5	1.5	17	26.6	0.465	15.5	1.5	1.5	13.5	
		270	110	64.3	20	7	0.5	12.5	13.5	0.675	11	0.5	1.5	7	
		253	80	50	11.5	5	0.5	6	8.2	0.535	5.5	0.5	0.5	5	
		231	110	74.2	26.5	9.5	1.0	16	18.5	0.63	14.5	1.0	1.5	9.5	
e 473 m+c	1.28^5	202	110	86	56	12	2.5	41.5	51.5	0.59	37.5	2.5	4	12	
		211	80	60	30	6.5	1.5	22	25	0.643	20	1.5	2	6.5	
		254	70	43.5	17	4.5	0.5	12	13.2	0.665	11	0.5	1	4.5	
		216	110	80.5	50	10.5	2.5	37	45	0.600	33.5	2.5	3.5	10.5	
f 973 m+c	1.29	305	110	57	47	6	2.5	38.5	46.5	0.605	34.5	2.5	4	6	
		179	70	62	52	6.5	2.5	43	55.2	0.57	38.5	2.5	4.5	6.5	
		179	70	62	53.5	6.5	2.5	44.5	55.2	0.59	40	2.5	4.5	6.5	
		174	50	45.5	30.5	4.5	1.5	25.5	29.7	0.627	23	1.5	2.5	4.5	
		254	50	31	16.3	3.5	0.5	12.3	13.8	0.65	11	0.5	1.2	3.5	
g 1473 m+c	1.29	187	70	59	75	6	3.5	65.5	75.8	0.63	59	3.5	6.5	6	(2 pumps)
		254	70	43.5	42.5	4.5	2	36	41.2	0.64	32.5	2	3.5	4.5	
		256	50	30.8	24	3.5	1	19.5	20.6	0.69	17.5	1	2	3.5	
		174	70	63.5	79	6.5	4.5	68	87.5	0.565	61	4.5	6	6.5	(2 pumps)
h 1973 m+c	1.29	174	70	63.5	112	6.5	6	99.5	117.5	0.62	89.5	6	10	6.5	(2 pumps)
		222	70	50	70	5	3.5	61.5	73	0.615	55.5	3.5	6	5	
		235	50	33.5	35	3.5	1.5	30	32.6	0.67	27	1.5	3	3.5	
		180	70	61.5	101	8.5	5.5	9	110	0.59	80	5.5	9	6.5	(2 pumps)
i 2660 m+c	1.29	179	70	62	137	6.5	7.5	123	151	0.595	110.5	7.5	12.5	6.5	(2 pumps)
		248	70	44.5	75	4.5	4	66.5	77.6	0.625	60	4	6.5	4.5	
		236	50	33.4	46	3.5	2.5	40	43.8	0.665	36	2.5	4	3.5	
		181	70	61	142	6.5	7.5	128	146	0.64	115	7.5	13	6.5	(2 pumps)
j 2632 m+c	1.29	129	50	61.2	126	6.5	7.5	112	145	0.565	101	7.5	11	6.5	(2 pumps)
		186	50	42.5	72	4.5	4	63.5	70	0.662	57	4	6.5	4.5	
		243	50	32.5	42	3.5	2	36.5	41	0.65	33	2	3.5	3.5	
k 2660 m+c	1.29	175	70	63.2	140	6.5	8.0	125.5	157	0.585	113	8	12.5	6.5	(2 pumps)
		190	50	41.5	69	4.5	3.5	61	67.5	0.66	55	3.5	6	4.5	
		235	50	33.5	46	3.5	2.5	40	44	0.665	36	2.5	4	3.5	
		182	70	61	136.5	6.5	7.5	122.5	146	0.612	110	7.5	12.5	6.5	(2 pumps)

P_c	pressure loss at surface connections and 1" bit nozzles according to c.
$P_{t.j.}$	calculated pressure losses at the F.H. tool joints.
$P_{d.p.} + P_{ann.}$	pressure losses at drill pipe and annulus together calculated from the measured pressure loss minus ($P_c + P_{t.j.}$)
$P : (f_a \times 100)$	pressure losses at drill pipe and annulus together divided by the friction factor in the annulus x 100, calculated from $P = f_{d.p.} \frac{L \rho Q^2}{\pi^2 R^5} + f_a \frac{L \rho Q^2}{\pi^2 (R_c - R_o)(R_c^2 - R_o^2)^2}$, where $f_{d.p.} = 0.73\, f_a$

The measured pressure losses at the surface connections (a) were applied as a correction to calculate the losses at the bit nozzles (b–a and c–a). The losses in drill pipe and annulus at various depths were calculated by subtracting the loss at the surface connections and at the 1 in bit nozzles from the measured losses (d–c, e–c etc.).

Readings were made with the bit at bottom (2660 m) and at one stand above bottom (2632 m) in order to evaluate any effect of immediate reversal of the mud stream after passing the nozzles. The experiments were carried out without rotating the drill pipe but after each run the drill pipe was rotated for about one minute to check whether rotation of the drill pipe would affect the pressure. It may be mentioned already here that neither immediate reversal of the mud stream nor the rotation of the drill pipe showed any significant effect on the pressure losses.

b. *Drilling mud*

The mud was a cement contaminated salt water mud which was in a flocculated condition. The mud showed settling and therefore the specific gravity was found to increase slightly with greater depths despite the fact that prior to the series of experiments the mud was homogenized by three hours circulation at full depth. In addition the mud was circulated before each test run during 20 min. to an hour depending on the depth of the drill pipe.

The rheological properties were measured during each run at the temperature and thixotropic level of the mud by taking the samples from the flow line directly in the cup of the viscometer Owing to the rapid settling of the mud the readings in the viscometer could not be too accurate but a differential viscosity of about 7 centipoises and a Bingham yield stress of about 15 dynes/cm2 may be considered a fair average valid for all of the experiments.

c. *Results*

The results of the experiments are collected in Table I, D. Fig. I, 11 represents the measured pressure loss-rate of circulation relations.

d. Evaluation of the results.

The flow of the rather thin mud may be expected to be turbulent in any part of the circuit at the rates of flow investigated.

1. The *coefficient of discharge* (C) in the pressure loss formula for the bit nozzles may be calculated from the results. For this calculation only the results for the 5/8 in bit nozzles can be used since those for the 1 in nozzles are not accurate enough, the pressure losses being rather low.

The values for C were found to decrease slightly with increasing rate of circulation (or with increasing Reynolds number) as shown in Table I E. These values are in close agreement with the value reported by Nolley, Cannon and Ragland (6) who give the figure C ≈ 0.8.

TABLE I E

COEFFICIENT OF DISCHARGE (C) AS A FUNCTION OF RATE OF CIRCULATION FOR 5/8 IN BIT NOZZLES

Q (m^3/h)	C
50	0.884
60	0.844
70	0.833
80	0.833
85	0.820

2. The *friction factor* (f) in the formula for pressure losses in both drill pipe and annulus may be calculated as follows:

When evaluating the experimental results, the comparatively small pressure losses in the tool joints are calculated and subtracted from the losses in the drill pipe, tool joints and annulus together. From the resulting pressure losses in drill pipe and annulus together the empirical constants in the formulas: f_{dp} and f_a, the friction factors in drill pipe and annulus, may be calculated, since the ratio of these constants is known. According to Blasius the friction factor is proportional to $Re^{-¼}$, thus

$$f_{dp} : f_a = \left(\frac{2}{R_i}\right)^{-¼} : \left(\frac{2}{R_c + R_o}\right)^{-¼} \quad \text{or} \quad f_{dp} = 0.73 . f_a$$

The results of the calculation are collected in table I, D and in Fig. I, 12 where f_{dp} is plotted as a function of the rate of circulation on log-log paper.

The log f_{dp} - log Q relation is shown in fig. I, 12. The results applying to shallow depths which are less accurate are indicated by triangles.

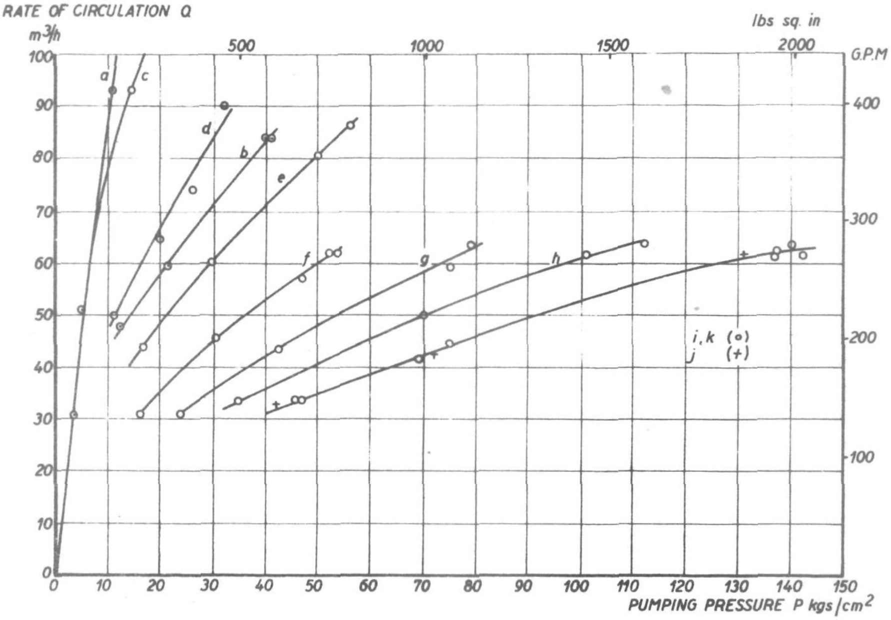


FIG. I, 11

PUMPING PRESSURE VERSUS RATE OF CIRCULATION
DATA 8000 FT WELL

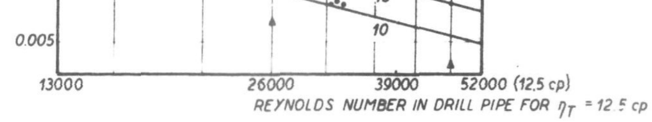


FIG I, 12

EXPERIMENTAL FRICTION FACTOR-RATE OF FLOW
RELATION FOR THE DRILL PIPE

The log f-log Q relation is principally equivalent to the log f - log Re relation. Re being proportional to Q. The f-Re relation according to Blasius, assuming an equivalent turbulent viscosity of 10, 15 and 20 cp respectively is drawn in the figure. Most points are found in the region between 10 and 15 cp, so that an average equivalent turbulent viscosity of 12.5 seems to be a reasonable figure, allowing for a spread of ± 7% which is well within the experimental error. The Reynolds numbers applying to this viscosity value are indicated on the Q ordinate. The results show, however, that with increasing rates of circulation (or increasing Reynolds numbers) the equivalent turbulent viscosity tends to increase from ca 10 cp at 30 m^3/h to ca 17 cp at 80 m^3/h.

Summarizing it may be concluded from these preliminary results of both semi technical and full scale pumping experiments, that in the turbulent flow region the equivalent turbulent viscosity of the muds tends to be higher than the differential viscosity and increases slightly with increasing rates of flow. And although the actual value of the Bingham yield stress was found to have little effect on the turbulent flow pressure losses at sufficiently high rates of circulation more experimental data will be required to settle this point definitely.

Finally it may be remarked that the observed increase of the critical rate of flow for the onset of turbulence with increasing yield stress of the system as shown by Fig. I, 10 may have the following practical consequence: In some ranges of flow rates the mud with the higher yield stress which is still in the laminar region may be more easily pumped than that with the lower yield stress which is in the turbulent region. Therefore, particularly in the case of weighted muds, where turbulent flow pressure losses are extremely high due to the high specific gravity, the yield stress may be raised in order to keep the pumping pressures low by the maintenance of laminar flow.

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PART II

COLLOID CHEMICAL STUDY OF THE MECHANISM OF CHEMICAL TREATMENT OF CLAY WATER BASE DRILLING FLUIDS

SUMMARY

In part I the effect of chemicals on the rheological properties and pumpability of muds was analyzed. The chemicals appeared to mainly affect the Bingham yield stress of the muds which explains their favourable effect on the pumpability. The present part deals with the stability conditions in treated clay suspensions from a colloid chemical point of view, aiming at an understanding of the mechanism of chemical treatment. The investigation is confined to montmorillonitic clays.

Submicroscopical particles of these clays are extremely thin plates. Their thickness to diameter ratio corresponds with that of a 0.1 mm razor blade. Just as the razor's edge is the most essential part of the blade, it is the edge surface of the flat clay particles where the play of chemical treatment is essentially enacted. The chemicals have a charging effect on the lateral surface which results in a strong repulsive force between the edges of different plates. Thus edge to edge association and consequently the formation of a voluminous rigid network is prevented and the suspension remains a readily flowing liquid. This is how the primary purpose of chemical treatment is achieved. Thanks to the relatively small lateral surface area of the plates the chemicals are active at remarkably low concentrations. Also in practice muds containing, say, 30% of technical clay can be effectively treated with a few tenths of a percent of chemicals only.

The above mentioned picture is derived from a detailed study of the charge distribution on the clay particles and the stability conditions in dilute clay sols, which may be summarized as follows:

The particles are assumed to have a dualistic character, the flat surface bears a negative charge due to imperfections of the lattice whereas the lateral surface charge may certainly be positive in the neutral sols. Here the tetrahedrical silica and octahedrical alumina sheets are broken. The double layer formed opposite the latter will be positive like that of an alumina sol micelle. Also the exposed silica sheets may obtain a positive

charge owing to the presence of traces of aluminum and hydroxyl ions in the intermicellar liquid. Several supports for a positive edge charge could be obtained. Owing to the unlike charges of the two surfaces a structure is formed in a dialyzed sodium montmorillonite suspension by edge to surface association (gel). On addition of an electrolyte the original gel becomes a sol. This is attributed to a reduction of both surface potentials resulting in a reduction of the edge to surface association. On further addition of electrolyte, however, the repulsive potentials will become so small that edge to edge and surface to surface association is no longer prevented and a new structure is formed, again resulting in a stiffening of the suspensions. Such a stiffening of the suspension can be avoided - and this is the purpose of chemical treatment - if chemicals are added which have a charging effect on one or both parts of the clay surface. It has been found that such an effect of the conventional mud treating chemicals indeed exists. They convert the originally positive edge charge into a stronger negative charge, thus creating a repulsive potential at the lateral surface which prevents structure formation up to relatively high salt concentrations.

The point of view of the conversion of the positive edge charge into a negative one is based on the observation of analogies between the response to chemical treatment of montmorillonite and of some positive sols, viz. positive quartz and positive alumina sols. These sols are considered a model for the broken silica and broken alumina sheets, respectively, which are exposed at the lateral surface.

The observed analogies are quite general: they apply to treatment with phosphates, metasilicate, oxalate, citrate and alkali and even to tannate treatment. The latter has been studied by using the trivalent phenol pyrogallol as a model for the ill defined polyphenol mixtures of which the natural tannins are composed. Also tannate treatment in the presence of lime could be studied with pyrogallol and model sols.

The stabilisation effect on the broken silica sheets is seen as the result of the removal of adsorbed aluminum hydroxyde which is responsible for the positive charge at this point, leaving behind a negative silica surface. The stabilisation effect on the broken alumina sheets is attributed to anion adsorption via an aluminum link, resulting in a negative charge. The total effect of a peptiser is a superposition of both effects. If a stabilising effect on the alumina part of the lateral surface is lacking the total effect is usually rather small. If the octahedrical sheet contains more trivalent Fe the effect of most chemicals is reasonable since contrary to alumina a ferric hydroxide sol is stabilised by most peptisers.

In lime/tannate treated suspensions, the silica sheets are peptised by the adsorption of anions which are linked to the silica via calcium which is inferred from the analogous effect of lime tannate treatment on a montmorillonite and a quartz sol.

The contribution of the flat surface potential to the overall stability is only apparent at low peptiser concentrations or in untreated suspensions.

PART II COLLOID CHEMICAL STUDY OF THE MECHANISM OF CHEMICAL TREATMENT OF CLAY WATER BASE DRILLING FLUIDS

INTRODUCTION

On preparing a drilling mud by dispersing clay in water, the virgin suspension is usually in the flocculated state owing to the presence of flocculating salts in both the raw clay and the water used. Such a flocculated mud is – apart from other defects- too stiff to be readily pumpable. According to common experience the remedy is to peptize the suspension. This might be achieved by dialysis but this is an uneconomical procedure in the field. Fortunately, clays can be peptized by a large variety of chemicals, most of which are active at remarkably low concentrations, particularly as compared with the rather high concentration of clay (a few tenths of a percent on 30-50% of clay). The striking result of such a chemical treatment is the conversion of the stiff suspension into a readily flowing liquid. As has been shown in part I this is a matter of a sharp..decrease of the yield stress of the suspension, rather than a result of a viscosity change.

Some of these chemical treating agents have been discovered accidentally, others were given a trial on the strength of more or less hypothetical concepts of the mechanism of peptisation. In order to give an idea of the variety of chemicals which are used in drilling practice, the experience in this field may be summarized as follows:

a. Since the particles of a clay suspension are negatively charged, the flocculating concentration of polyvalent cations will be lower than that of monovalent cations. These strongly flocculating polyvalent cations – particularly Ca! – may be rendered ineffective by precipitation or complex formation with various sodium salts. Thus the polyvalent cation will be replaced by an equivalent amount of the monovalent sodium ions which are harmless to the clay up to a reasonably high concentration. Well-known examples are sodium metasilicate ("sil"), sodium oxalate, sodium polymeric phosphates etc.

b. Tannins like quebracho extract often cause a strong deflocculating effect. Their application together with alkali or with alkali + lime has led to the development of so called "red muds" and "lime red muds". In connection with the remarks under

(a) the activity of these compounds in combination with lime, which has been discovered accidentally, is certainly a rather paradoxal effect.

c. Adjustment of the pH of the mud by alkali or by CO_2 has been successful in some cases.

d. Hydrophilic materials like starch are successfully applied, particularly in salt water muds where they may act as protective colloids.

Obviously there is a considerable choice of chemicals for the treatment of muds. The empirical approach has indeed solved many problems in the field, but failures still do occur. It is also obscure why a certain treatment is successful for one type of mud but fails for another mud, why a treatment is excellent for one well but fails in another well. Difficulties are sometimes encountered when the mud takes up flocculating electrolytes from the formations drilled which will require frequent readjustment of the treatment. Furthermore in deep wells the high temperature may have a detrimental effect on the treated mud. In order to understand this and to find the proper remedies the analysis of the mechanism of chemical treatment will be imperative. At the present state of development the empirical approach seems to have reached its limits and further progress will require a fundamental attack. A first attempt is made in the work presented in this part.

A suitable system had to be chosen for the work. In practice a large variety of local clays is used for the preparation of muds. These clays are usually mixtures of representatives of the three main groups of clay minerals viz. the montmorillonite, the illite and the kaolin group. In fundamental work, however, a well defined clay is to be preferred and although the study of pure representatives of all three groups should be included in an extensive investigation, the work reported here is limited to the study of one type of clay only, viz. bentonite which belongs to the group of the montmorillonites. A montmorillonite was chosen since the suspensions of this clay mineral exhibit the most pronounced rheological effects.

The preparation and colloid chemical characteristics of dilute montmorillonite sols and the mechanism of the effect of chemical treatment on the stability of these sols will be dealt with in the following chapters.

Chapter 1

PREPARATION AND PROPERTIES OF FRENCH MONTMORILLONITE SOLS (1)

A. STRUCTURE OF MONTMORILLONITE

It is a favourable condition for a fundamental attack of the drilling mud stabilisation problem that during the last few decades the structure of clay minerals has been extensively studied, particularly by X-ray and electronmicroscopical investigation together with differential thermal analysis and other physical techniques. As a result of the combination of these techniques the general structural relationships of clays are fairly well known (2), although different interpretations are still found in the literature and many details still remain to be explained. In our working hypothesis we have adapted the Hofmann structure for montmorillonite (2a) as well as the views of Ross and Hendricks (2b) regarding the origin of the cation exchange capacity of montmorillonite which are also based on the Hofmann concept *).

The clay minerals belong to the silicates, the structural element of which is the practically regular $Si\text{-}O_4$ tetrahedron. In the clay minerals these tetrahedrons share three of their four oxygen atoms with three neighbouring tetrahedrons, thus forming a sheet of tetrahedrons "T". The empirical formula of such a sheet is $(Si_2O_5)_n$. According to Hofmann the apexes of all tetrahedrons are at the same side of the sheet.

The second structural element of the clay minerals is an octahedrically arranged sheet "O" of Al or Mg atoms, surrounded by 6 O and/or OH groups, analogous to the structure of certain modifications of the corresponding hydroxides (hydrargylite and brucite, respectively).

The tetrahedrical and octahedrical sheets are linked by primary valencies, building lattice layers, which in the case of montmorillonites consist of 2 "T" and 1 "O" in between. The clay consists of a pile of these lattice layers which are linked by Van der Waals forces.

An idealized unit cell is sketched in Fig.II, 1 which shows the projection on a plane perpendicular to the layer. As shown on

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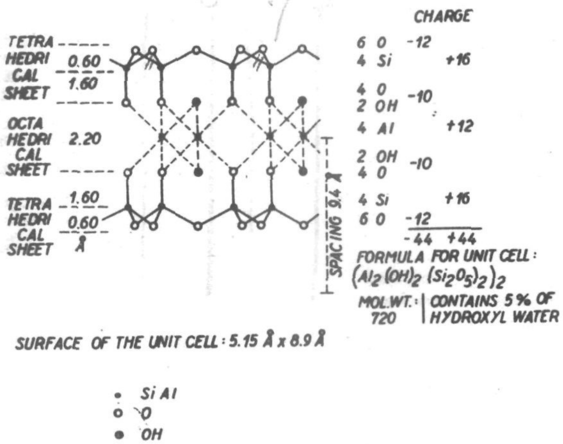
*) For different concepts we refer to (2c).

niet geheel korrekt SiO4 tetraëders hebben slechts een O gemeen



PROJECTION OF IDEAL UNIT CELL OF MONTMORILLONOIDS FIG. II, 1

the right hand side in the figure, the ideal lattice is electroneutral. This is realized in the mineral pyrophyllite. If 2 Al are substituted by 3 Mg, occupying the third vacant octahedrical position as well, the structure of the mineral talcum is obtained which is also electroneutral. These two minerals do not display clay properties. In the lattice of the clay minerals indicated by the name montmorillonites – to which bentonite = montmorillonite belongs – electroneutrality is disturbed mainly by isomorphous substitutions in the octahedrical sheet. In the case of bentonite trivalent Al in octahedrical position is replaced by divalent Mg ① which is not compensated by a full occupation of the third octahedrical position. The result is a surplus of negative charge and this surplus charge is compensated by adsorption of cations like Na^+ or Ca^{++} at the layer surfaces. These are the exchangeable cations of the clay. Their hydration results in adsorption of water between the layers causing the swelling of the layer lattice. The base exchange capacity of bentonite usually amounts to about 100 m.eq./100 g which can be roughly accounted for by an isomorphous substitution of ca 17 % Al by Mg. A more detailed account of the base exchange capacity will be given in section E.

It will be clear that in the case of pyrophyllite and talcum neither swelling nor any cation exchange will be observed since no compensating ions are required in these minerals.

The X-ray diffraction patterns of the clay minerals show two types of reflections: those connected with the arrangement of the atoms or ions in the two dimensional layers ("prism reflections") and the reflections connected with the stacking of the layers ("base reflections"). In the montmorillonites the place of the latter is also determined by the water content of the clay, the water being adsorbed between the lattice layers. Consequently the corresponding spacing may vary between 10 and 20 Å.

Since the layers are bound by the comparatively weak Van der Waals forces, they are easilv split along a plane parallel to the layers. The result is that suspended clay particles are very thin plates which can be demonstrated by electromicrographs.

B. PREPARATION OF MONTMORILLONITE SOLS

In order to study the peptisation of montmorillonite sols both in the presence of Ca^{++} and in Ca^{++} free systems, a sodium and a calcium montmorillonite sol were prepared. As a suitable base material a bentonite of French origin was chosen, which according to X-ray analysis did not contain any other clay mineral than montmorillonite.

After destruction of any organic matter by H_2O_2 treatment, the colloidal fraction of the bentonite was separated and converted into a calcium or a sodium bentonite, respectively, by base exchange (repeated treatment with $CaCl_2$ or NaCl). The sols were purified by dialysis (washing on an ultrafilter). Since on prolonged washing there is a risk of the sols being converted into hydrogen bentonite (by base exchange with the H^+ of the water) dialysis was discontinued as soon as the pH of both sol and ultrafiltrate was just a little over 7.0, which should be considered an arbitrary choice.

A detailed description of the procedure is given below.

Preparation of Na montmorillonite sols.

50 g of raw bentonite were digested with 100 cc of 30% H_2O_2 in order to destroy any organic matter present in the bentonite. After standing overnight the excess peroxide was decomposed by heating on a steam bath.

Subsequently a 1% suspension of the bentonite was prepared in distilled water and the coarse fraction allowed to settle. After decantation the suspension was centrifuged during 2h at 500 r.p.m.

The radius of the centrifuge from the central shaft to the bottom of the tubes was 28 cm and the liquid column in the tubes had a length of 15 cm. About 75% of the bentonite was discarded in this way leaving a 1/4% suspension of the fine fractions of the bentonite.

Three parts of this suspension were flocculated with 1 part of 1 N NaCl. The flocculated suspension was centrifuged in 100 cc portions and the supernatant liquid was decanted. The remaining sediment of about 1 cc in each tube was suspended in 100 cc of fresh 1 N NaCl solution and again centrifuged. The decantation, the suspending in fresh NaCl solution and centrifuging were repeated four times after which no calcium ions could be detected in the decanted NaCl solution by means of the oxalate reaction. Then the sediment was taken up in distilled water and centrifuged. After decantation, the sediment was again digested with distilled water and this manipulation was repeated until the suspension became peptised. Next the peptised suspension was dialysed by ultrafiltration and washing with distilled water on a collodion membrane mounted on a Buchner funnel. In order to prevent conversion into hydrogen bentonite dialysis on an ultrafilter was preferred to electrodialysis, the former being easier to control.

Washing was continued until the pH of both sol and ultrafiltrate was just a little over 7.0. The sol had to be washed with about four times the original sol volume of distilled water.

Preparation of calcium montmorillonite sol.

Ca montmorillonite was prepared in a similar way, however using $CaCl_2$ instead of NaCl for the conversion of the original bentonite into calcium bentonite.

C. SIZE AND SHAPE OF THE MONTMORILLONITE MICELLES

The knowledge of the size and shape of the micelles of the sols to be investigated is desirable with a view to the quantitative interpretation of possible adsorption reactions with chemical treating agents.

On ultramicroscopical observation the sols show the image of a hydrophobic sol: ultramicrons in brisk Brownian motion. The plate like shape of the micelles is obvious from the intermittent scattering of light due to the rotational movement of the plates which is superimposed on the translatorial Brownian motion.

In order to determine the average diameter and the average height of the plates, the results of two methods were combined: From the relative viscosity of dilute suspensions the ratio of height and diameter of the plates is calculated according to the Peterlin-Burgers equation (3). In these calculations the plates are considered as flat ellipsoids of rotation. Their axis ratio is an approximate figure for the height-diameter ratio. From ultramicroscopical counting of the number of micelles the volume of one micelle may be determined, the total volume of clay in the suspension being calculated from the weight percent of clay and a specific gravity which is based on an assumed degree of hydration of the micelle.

Let ρ_a be the specific gravity of the micelle which is assumed to be 2.70 for montmorillonite dried at 105°C and $\frac{(100-a)2.70 + a}{100}$ for montmorillonite containing a% of water.

Let g_a be the weight concentration of the sol of montmorillonite with a% of water, expressed in g/100 ml of the sol, thus

$$g_a = g + \frac{a}{100} g$$

where g is the weight concentration of dry clay.

Let φ_a be the relative volume of the micelles containing a% of water, thus $\varphi_a = 0.01\, g_a/\rho_a$.

The ratio of height to diameter of the plates (p) - or the axis ratio of the ellipsoids - is found from the Peterlin-Burgers equation:

$$\frac{\eta_s-\eta_o}{\eta_o} = \left(1.19 + \frac{4}{3\pi p}\right) \cdot \varphi_a \quad \text{or} \quad \text{since} \; \frac{\eta_s-\eta_o}{\varphi_a\, \eta_o} >> 1.19$$

in the case of montmorillonite micelles we may write:

$$\frac{\eta_s-\eta_o}{\varphi_a\, \eta_o} \cdot \frac{1}{0.425} = 1/p \qquad (1)$$

where η_s = viscosity of the sol and η_o that of water.

Let n be the average number of particles (average of 200 determinations) in the cylindrical counting volume v of the ultramicroscope with a height of 3.0 μ and a diameter of 19.3 μ. Therefore $v = 0.878 \,.\, 10^{-9}$ ml.

Before counting the sol is diluted to V times its original volume. Then the number of micelles pro 100 ml of the original sol is 100 . nV/v and the volume of one micelle will be

$$\frac{100\, \varphi_a}{100 . \frac{nV}{v}} = \frac{v}{nV} \cdot \varphi_a$$

Writing $nV/v = N_o$ (the number of micelles pro ml of original sol) the volume of each micelle will be φ_a/N_o which is equal to $\pi r^2 h$ where h = 2 r.p. and thus

$$2\pi r^3 . p = \varphi_a/N_o \qquad (2)$$

Combining (1) and (2) we find:

$$2\pi r^3 = \frac{\eta_s - \eta_o}{\eta_o} \cdot \frac{1}{0.425} \cdot \frac{1}{N_o}$$

$$\text{or } r = \sqrt[3]{\frac{\eta_s - \eta_o}{\eta_o} \cdot \frac{1}{N_o} \cdot 0.375} \qquad (3)$$

Thus the radius of the micelles is independent of the degree of hydration assumed in the calculations.

For various assumed values of a, the percentage of water of hydration, the following dimensions of the Na and Ca montmorillonite micelles are calculated: (the relative viscosity data are given for a dilution of 1:6 of the original 1.48% sol, where the relation of relative viscosity and concentration is still linear and the N_o values are derived from counting data in a dilution 1:1000)

TABLE II A

CALCULATION OF MICELLE DIMENSIONS FROM RELATIVE VISCOSITY AND COUNTING DATA

$a =$	0%	10%	25%	50%
$\rho_a =$	2.70	2.53	2.28	1.85
$g_a =$	0.246	0.270	0.307	0.369
$10^5 \times \phi_a =$	91	106	135	200
Na montm. $\frac{\eta_s - \eta_o}{\eta_o} = 0.0985$ $1/p =$	225	220	172	114
Ca montm. „ $= 0.0761$ $1/p =$	198	169	133	90
Na montm. $r_{Na} = \sqrt[3]{0.0985 \cdot \frac{6}{N_o} 0.375}$: $N_o = 1.98 \cdot 10^{12} \rightarrow r_{Na} = 4800$ Å				
Ca montm. $r_{Ca} = \sqrt[3]{0.0761 \frac{6}{N_o} 0.372}$: $N_o = 2.25 \cdot 10^{12} \rightarrow r_{Ca} = 4230$ Å				
Na montm. $h =$	37	43.5	56	84 Å
Ca montm. $h =$	42	49	63.5	92.5 Å

Deviations of the calculated and the real size may occur as a result of a number of factors that have been neglected in the calculations: Neither the effect of heterodispersity, nor the effect of the particle charge on the relative viscosity which should be accounted for by some Smoluchowsky term in the Peterlin-Burgers equation, were introduced. Moreover the specific gravity of bentonite and the water of hydration may not be additive owing to orientation effects of the hydration water between the layers. As a matter of fact the average radius of the Ca and Na montmorillonite sol micelles are calculated to be different although they may be expected to be equal, being prepared from the same parent material. A possible correction factor will be discussed later.

It may be concluded from these determinations that the micelles are extremely thin compared with their average diameter. The thickness corresponds with that of a packet of about 5 layers (ca 40 Å in dry condition).

In view of the incertainties involved in the calculation of the dimensions a further check by different methods was considered desirable. Both X ray and electronmicroscopical techniques were applied.

After concentrating the sols by ultrafiltration definite base reflections were obtained. This indicates that the hydrated plates may be estimated to be thicker than 100 Å *). The basal spacing being 19 Å this would correspond to the thickness of a packet of more than 6 layers. On dilution, however, the base reflections disappear before they are obscured by continuous water bands. At the same time the low angle scattering increases. Both observations point to a splitting up of the micelles on dilution. The base reflections of calcium montmorillonite are more persistent on dilution than those of sodium montmorillonite. The first are still visible on the background of a strong water band at a sol concentration of 3/4 %, the latter have disappeared at a concentration of 1½ %.

Analogous effects of dilution were encountered in the extremely diluted sols which are used for ultramicroscopical counting. The number of particles (calculated on the undiluted sol) increases with increasing dilution and also with the time elapsed between the preparation of the dilution and the observation. Some counting results are collected in Table II B. (250-500 particles were counted, amounting to an error of between 5 and 10%).

TABLE II B

EFFECT OF DILUTION AND TIME ON THE NUMBER OF PARTICLES OF MONTMORILLONITE SOLS

sol	dilution of 1.48% sol	$N_o . 10^{-12}$					
		direct	7 days	10 days	14 days	20 days	32 days
Na montm.	1 : 600	1.90		2.24			2.32
	1 : 1000	1.98	2.83		2.72	2.77	
Ca montm.	1 : 1000	2.25	2.44		3.05		
	1 : 1200	2.60					

Apparently a dynamic layer association-dissociation equilibrium exists in these sols, the position of which is dependent on the micelle concentration.

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*) This was pointed out by Ir.P.Franzen who carried out the X-ray work together with Miss. G.van Tilburg.

In view of this dependence of the particle size on the sol concentration it was not strictly correct, after all, to combine viscosity data with ultramicroscopical counting results which are obtained in different concentration ranges, although no large errors will be involved.

Electronmicroscopy *) was expected to supply a more direct check on the micelle dimensions. The electronmicrographs show rather irregular micelles having diameters of 1000-2000 Å, which is considerably smaller than calculated above. Some clusters of particles are observed, which may be due, however, to flocculation when preparing the samples on the supporting film. The transparency of the micelles indicate that they are really extremely thin and gold shadow cast micrographs show very small shadows. The length of the shadows indicates the above calculated micelle thickness (40 Å for the dry micelle) to be of the right order of magnitude.

Regarding the discrepancy between the observed and the calculated diameter it may be stressed that one should be careful in interpreting the electron micrographs. A breaking up of the thin crystal plates when the droplet of the sol is evaporated on the supporting collodion film is certainly conceivable and this would result in smaller diameters. In order to check this possibility a dilute sol was counted and evaporated to dryness under vacuum at room temperature. The residue was again taken up in the original amount of water and the sol was counted again. The result was that twice the original number of micelles was counted after the test, which may indeed be attributed to a breaking up of the thin crystal plates.

Summarizing the above, a thickness corresponding with that of a packet of ca 5 layers may be considered a reasonable figure. The magnitude of the micelle diameter, however, leaves more room for speculation.

D. SOL STABILITY AND CHARGE DISTRIBUTION ON THE MICELLES

Microelectrophoresis experiments, using the apparatus of Rutgers, Facq and van der Minne (4) show that the micelles are negatively charged. The electrophoretic mobility is comparatively small: for the sodium montmorillonite -2.1 μ/sec/Volt/cm and for

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*) The electronmicroscopical work was carried out by Ir. L. van Reyen, Mrs. N.M.C. van Veen-Tuyl Schuitemaker and J. Wolffes.

the calcium montmorillonite-1.0 μ/sec/Volt/cm at a sol concentration of 0.0003%.

The determination of the flocculation values of the sols was carried out by means of a centrifuge technique, developed by G.K.Jones *). The method is based on the determination of the sediment volume of the sols which undergoes a sudden increase when the sol flocculates.

The centrifuge used was a small electrically driven laboratory centrifuge fitted with six graduated, conical-bottomed 10 cc centrifuge tubes. The mean radius of rotation was 10.3 cm.
A flocculation experiment is carried out as follows:
An electrolyte solution is added to each of the six tubes in steadily increasing quantities from a micro-burette. Water, sufficient to make up the electrolyte volume to exactly 5.0 cc, is run in from another burette in such a way as to float on top of the electrolyte. Then, 5.0 cc of a 0.5% montmorillonite sol is pipetted into each of the tubes with the minimum of mixing. The tubes are stoppered immediately and shaken violently for about 30 seconds after which they are transferred to the centrifuge.
After the tubes have been centrifuged for 5 minutes at 1400 r.p.m., the depth of sediment in each tube is determined. The flocculation point is taken as that electrolyte concentration at which the first detectable increase in sediment volume occurs.

This method is more reliable than the subjective classical method of visual observation. The method is only sufficiently sensitive if the flocs are rather voluminous which limits its applicability to sols with anisodimensional or to those with hydrated particles.

Some flocculation values for Na and Ca montmorillonite sols are collected in Table II C.

TABLE II C

FLOCCULATION VALUES OF SODIUM AND CALCIUM MONTMORILLONITE SOLS

sol concentration ¼%	flocculation value (m.eq./l) for NaCl	 $CaCl_2$
Na montmorillonite	between 12 and 16	between 2.3 and 3.3
Ca montmorillonite	between 1.0 and 1.3	between 0.17 and 0.23

In accordance with the low electrophoretic mobility of the micelles the stability of the sols is low as compared with the stability of other negative sols towards flocculating salt. It is

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*) private communication.

apparent from both the electrophoretic mobility and the flocculation values that Ca montmorillonite sols are even less stable than Na montmorillonite sols.

① The negative charge of the micelles originates from the isomorphous replacements of Al by Mg in the lattice as was pointed out in section A. This surplus charge may be considered the inner coating of the double layer of the flat surfaces of the micelles. The exchangeable cations which are accumulated near the layer surfaces are the compensating "counter ions" of this double layer.

② Due consideration should be given to the situation at the edges of the plate-like micelles where electroneutrality will be disturbed owing to the disruption of the tetrahedrical silica and the octahedrical alumina sheets. Analogous to the formation of a double layer at the surface of most hydrophobic sol micelles due to incompleteness of the lattice at these surfaces, also a double layer will be formed at the broken edges of the plates. The problem is to make a reasonable assumption about the sign of the double layer at the edges. A priori, this potential may be either positive or negative: although the micelles are electrophoretically negative a positive edge potential may not be excluded since the effect of the negative surface layer potential may be preponderant.

(2a) When considering the possible charge distribution at the edges an analogy may be drawn with silica sols and alumina sols. It is known that silica sols are negative, alumina sols on the other hand may be positive up to a rather high value of the pH. Therefore, the broken silica sheets could be assumed to bear a negative charge (with silicate anions as potential determining ions) and the broken alumina sheets a positive charge (with Al^{+++} as potential determining ions). (Compare the views of Ford, Loomis and Fidiam (5)). The sign of the double layer potential is, however, not exclusively a matter of the distribution of potential determining ions. The presence should also be considered of ions which are able to reverse the sign of the double layer potentials of micelles e.g. the reversal of the charge of a negative colloid by polyvalent cations. This is a real possibility in bentonite ③ sols where small amounts of Al^{+++} or Fe^{+++} are present in the intermicellar liquid, the concentration of which is, however, sufficiently high to reverse the negative potential at the broken silica sheets into a positive potential. It is conceivable, therefore, that the total lateral surface potential is positive. If so, the montmorillonite micelle would have a rather exceptional structure, having two double layers of different sign, a negative one located at the layer surfaces and a positive one at the lateral surface

There is indeed a number of phenomena which may be seen as a support of the presence of two different charges on the micelle

i. The comparatively low electrophoretic velocity of the montmorillonite micelles may result from a counteraction of the contributions of the negative layer surfaces and of the positive lateral surfaces.

ii. In the case of kaolinite strong evidence of a positive charge of the edges was obtained by Thiessen (6): He has shown from electron micrographs that negative gold particles are exclusively adsorbed to the edges of the kaolinite micelles. Since the electrical conditions at the lateral surface of the kaolinite and the montmorillonite micelles may be expected to be rather similar this would point to a positive edge charge for montmorillonite as well.

iii. A viscosity anomaly was observed on addition of small amounts of a flocculating electrolyte to a sodium montmorillonite sol, which may be explained on the basis of the positive edge hypothesis.

On addition of a flocculating amount of NaCl or $CaCl_2$ to a Na montmorillonite sol a sharp rise of the viscosity is observed, whereas at the same time the number of particles and the electrophoretic mobility decrease (compare the data in Table II D). This is the normal behaviour caused by a decrease of both double layer potentials resulting in both edge to edge and surface to surface association of the micelles. The higher viscosity in the associated (flocculated) state may be seen as a consequence of the apparent volume of the porous particle agglomerates which is greater than the total volume of the individual particles. The effect is known as voluminosity effect and will depend on both degree and type of association of the micelles.

However, at a salt concentration which is fairly below the flocculating concentration, a slight decrease of the relative viscosity is observed (column 2 Table II D). Assuming a certain positive edge-negative surface association in the original sol as pointed out above, the decrease of the relative viscosity may be interpreted as a decrease of this type of association, since both double layer potentials will decrease at the same time and thus the electrical attraction between edges and surfaces.

TABLE II D

EFFECT OF SALT ON VARIOUS PROPERTIES OF SODIUM MONTMORILLONITE SOL

NaCl conc.m.eq./l	0 original sol	3	15 flocculated	80 sol
electrophoretic mob. μ/sec/Volt/cm sol conc. 0.006 %	2.9	2.7	2.1	
relative viscosity *)	1.10	1.07	1.42	1.55
number of micelles pro ml of 1.5% sol average of 200 dets. x 10^{-12}	1.9	1.3	1.15	0.3
assumed micelle association primarily	edge to surface	surface to surface	edge to edge and surface to surface and edge to surface	

*) The viscosity was measured at 25°C in an Ostwald viscometer. The dilute sols (0.25%) do not exhibit thixotropy when dialyzed. On flocculation, however, the viscosity decreases after previous agitation indicating a slight degree of thixotropy. In this case the system was left undisturbed during 5 minutes in the upper reservoir and capillary prior to the determination. Moreover, the viscosity was found to increase with the time elapsed after the addition of salt. The values reported are the maximum figures which are obtained after ½ - 1 hour.

If the above explanation holds, the calculation of particle size from relative viscosity and counting data should be corrected for the conglomeration effect in the case of sodium montmorillonite sols. The minimum relative viscosity after salt addition which is about 3% lower than that of the pure sol would be a more appropriate figure to be used in the calculations. The correction results in elimination of the discrepancy between the values for the radius of Na and Ca montmorillonite and also the figures for the axis ratio then become practically equal.

However, the interpretation given must not be considered a definite proof of the positive edge potential since two additional effects may contribute to the decrease of the viscosity: First the decrease may be seen as a small electroviscous effect (the electrophoretic mobility decreases) and secondly it may be a result of the formation of thicker packets with a smaller axis ratio, which might be due to a parallel association (the number of micelles decreases!). Generally speaking the interpretation of viscosity behaviour is rather involved. A more direct indication of the formation of structural agglomerates may be obtained from yield stress determinations in more concentrated systems.

iv. The development of rigidity in dialyzed bentonite suspensions at relatively low concentrations and the effect of small amounts of salts on the yield stress and thixotropy of these systems has indeed supplied a rather strong support for the positive edge hypothesis.

A detailed discussion of these effects will be given in chapter V dealing with a different montmorillonite, which proved to be more suitable for this work than the French montmorillonite used in the beginning of the investigation. In this thesis, we thus follow the progress of the work in the course of time. The above supports for the positive edge hypothesis, however weak, were considered to have sufficient reality to warrant adaptation of this assumption as a possible working hypothesis.

E. THE BASE EXCHANGE CAPACITY

1. Location of the exchangeable cations on the micelle

The base exchange capacity of montmorillonites is usually of the order of 100 m.eq./100 gram of clay. The surface occupied by one exchange able ion may be calculated at about 125 Å^2, corresponding with a charge density of 0.8×10^{14} esu/cm^2. The surface area of both sides of a unit cell is equal to $2 \times 5.15 \times 8.9 = 92$ Å^2. Therefore 0.73 exchangeable ion is present per unit cell, corresponding with a replacement of 0.73 of the 4 Al by Mg or a replacement of ca 18% of the Al. This calculation is only roughly corroborated by chemical analysis. In order to obtain a better correlation Ross and Hendricks (l.c) assume that the isomorphous substitutions are a little more complicated. In addition to replacement of Al by Mg in the octahedrical sheet also a replacement of Si by Al in the tetrahedrical sheet is supposed to take place to some extent. Moreover, the third vacant octahedrical position may be partly filled by Al or Mg. Thus the total excess negative charge of the lattice and therefore the exchange capacity is found from the excess negative charge due to Si-Al and Al-Mg replacement minus the excess positive charge due to the partial occupation of the vacant octahedrical position. It will be impossible to predict the b.e.c. on the basis of the chemical analysis but if both analysis and b.e.c. are known, the amount of Si and Al in tetrahedrical positions and the amount of Al and Mg (and possibly ferric ion) in octahedrical position may be calculated.

In Table II E the results of such a calculation are given for the parent material of the montmorillonite sols described in this chapter, having a b.e.c. of 87. For comparison the data for a French montmorillonite taken from the paper of Ross and Hendricks are also inserted in the Table. These data were calculated for a.b.e.c. of 70. Since a b.e.c. of about 70 instead of 87 is also found for our bentonite if the b.e.c. is determined by means of the method applied by Ross and Hendricks *) the calculation of the formula for our bentonite is also given for a b.e.c. of 70.

TABLE II E

		formula for montmorillonite: $(Al^{+++}_{a-y}Fe^{+++}_{b}Mg^{++}_{d})$ $(Al^{+++}_{y}Si^{++++}_{4-y})$ $X_x\ O_{10}\ (OH)_2$					
Sample	b.e.c.	octahedrical coordination			tetrahedrical coordination		exch. base
		a-y	b	d	y	4-y	x
Wyoming bentonite	75	1.53	0.19	0.27	0.065	3.39	0.32
French acc. to Ross	70	1.64	0.05	0.36	0.12	3.88	0.33
French	70	1.62	0.07	0.37	0.15	3.85	0.33
French	87	1.60	0.07	0.37	0.16	3.84	0.40
French if containing 5% quartz	70	1.63	0.075	0.40	0.27	3.73	0.35

The table shows that the sample analyzed by Ross et al. and our parent material give practically indentical results (compare the results for a different bentonite viz. a Wyoming bentonite given in the first line of the table). If it is assumed that 5% of quartz is present in the French bentonite the results of the calculation do not change appreciably (last line of table II E).

A comparison of the results for French bentonite, assuming either a b.e.c. of 70 or of 87 demonstrates that slight changes

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*) The method applied is conversion into hydrogen montmorillonite and subsequent potentiometric titration with NaOH. The result of the method is doubtful since the equilibrium pH is reached only very slowly, particularly in the neighbourhood of the end point.

in the substitutions would have a marked effect on the b.e.c. Since such slight changes in the lattice seem to occur on acid treatment when converting bentonite into hydrogen bentonite as shown by Mukherjee (7), this is another reason why the determination of the b.e.c. via hydrogen montmorillonite does not seem appropriate. Also for this reason we did not follow the common procedure for the preparation of Na or Ca montmorillonite via hydrogen montmorillonite and subsequent neutralization with NaOH or $Ca(OH)_2$, but we preferred the direct exchange with Na or Ca salts.

The theory of Ross and Hendricks does not take into account the possible presence of a fraction of the exchangeable ions at the edges of the micelles, where electroneutrality will also be disturbed owing to the disruption of the lattice sheets.
A.L. Johnson (8) takes the extreme opposite view; he assumes that the exchangeable ions are exclusively located at the edges. He shows that the b.e.c. calculated from the micelle dimensions agrees with the measured b.e.c. if the number of broken Si-O-Si bonds at the lateral surface is taken equal to the number of exchangeable cations. However, his determination of the micelle dimensions is, in our opinion, open to criticism: the electron micrographs published in his paper suggest that the dimensions of the plates are actually larger than those which are used in the calculations and which are derived from the equivalent spherical diameter according to Stokes' law. Therefore the lateral surface will actually be smaller and the number of broken bonds would only account for a fraction of the exchange capacity. Moreover, the presence of exchangeable ions between the lattice sheets is beyond doubt: their hydration explains the swelling of bentonite in water and their exchange with organic cations results in complexes with these cations which are located between the layers as inferred from X-ray analysis.

The location of a fraction of the exchangeable cations at the edges is usually assumed to explain the increase of the b.e.c. on grinding amounting to an increased lateral surface by breaking the thin plates. However, grinding may also cause lattice disturbances which may give rise to an increased charge deficiency and consequently an increased b.e.c. Moreover, the b.e.c. is not always observed to increase on grinding (compare (9)).

Finally a remark may be made about the mechanism of exchange. It is generally assumed that the exchanging ions penetrate between the layers. However, an alternative mechanism may be proposed, bearing in mind that the association of the layers to packets may be seen as a dynamic equilibrium as pointed out in this chapter. Then, the exchange can be supposed to take place at those surfaces of the layers which happen to be exposed to the liquid phase. The reaction would be complete as soon as all layers would have had their turn in the dissociation-association process. Particularly in the case of exchange with extremely large organic cations (see next section) the latter mechanism will be more likely, in our opinion. Moreover, if the assumption is made that the edges of the plates are positively charged, this charge would form a barrier for the cations to penetrate between the layers from the sides.

2. *Determination of the base exchange capacity of montmorillonite*

The following methods for the determination of the b.e.c. were applied:

i. exchange with an excess of NH_4Cl and determination of the final ammonium concentration in the equilibrium liquid;

ii. percolation of Ca montmorillonite with NaCl and determination of Ca in the percolate and percolation of Na montmorillonite with HCl and determination of Na in the percolate;

iii. a method based on the exchange with strongly adsorbed organic cations, which was newly developed. It is an extremely simple test tube method, which may be carried out with as little as 0.25 g of montmorillonite.

i. Ammonium chloride method

The well-known ammonium chloride method was carried out according to the instructions of Hofmann and Giese (10). A suspension of a weighed amount of clay is shaken with an excess of NH_4Cl. The b.e.c. of the clay is calculated from the decrease of the NH_4 concentration. The final NH_4 concentration is corrected for the amount of water adsorbed by the clay, which is derived from the increase of the Cl^- concentration of the equilibrium liquid.

Since a rather large amount of bentonite is required for this procedure it was only applied to the parent material of our sols. The results of duplicate tests were 100 and 103 or average 102 m.eq./100 g.

A general critical remark may be made concerning this method. Clay suspensions often show an alkaline reaction. On prolonged shaking of such an alkaline suspension with NH_4Cl some NH_4^+ may be removed as NH_3, which accumulates in the volume of air above the liquid in the shaking bottle. This amount gets lost before the determination of the final NH_4 concentration, resulting in too high a value of the b.e.c. In a blank test it was found that this does occur: on prolonged shaking of the same volume of an NH_4Cl

solution in a bottle of the same size and adjusting the pH to the same value as that for the clay-NH_4Cl suspension a decrease of the NH_4^+ content of the liquid was observed. Although the decrease amounted to only 1.63%, this has a considerable effect on the calculated b.e.c., the corrected value being 87 instead of 102.

This defect is avoided in the modification of the NH_4Cl method where the NH_4^+ content of the clay itself is measured after the exchange. For this procedure the NH_4^+-clay has to be washed but according to R.C. Mackenzie (11) there is no danger for the NH_4^+ to be removed from the clay if the washing is carried out with 80% alcohol.

ii. Percolation method

This method has been applied to both calcium and sodium montmorillonite. Ca montmorillonite was repeatedly leached with 1 N NaCl and the exchanged Ca ions were determined in the percolate. Na montmorillonite was repeatedly leached with 0.1 N HCl and the exchanged Na ions were determined in the percolate. The b.e.c. of Ca montmorillonite was found to be 94 and that of Na montmorillonite 106. The values were corrected for the amount of Ca and Na respectively in the intermicellar liquid of the sols.

iii. Lissolamine method (12)

The addition of successive small amounts of pure trimethylcetyl ammonium bromide (purified "Lissolamine A") to a dilute clay sol causes a gradual decrease in stability of the latter until the sol becomes completely flocculated; further addition of Lissolamine causes a reversal of this behaviour and the degree of peptization of the clay sol increases.

This phenomenon may be explained as follows: during the first additions of Lissolamine, quantitative base exchange takes place between the exchangeable cations of the clay and the strongly adsorbed cetyltrimethyl ammonium ions until all available negative exchange positions are filled by the latter.

As a result the lattice layer surface will become oleophilic, being covered by hydrocarbon chains and the stability of the sol will decrease.

On further addition of Lissolamine, association between the hydrocarbon chains already bound to the clay particle and the hydrocarbon chains of the freshly added Lissolamine would be expected to take place, the positive groups of the latter being directed towards the water phase. The micelle will thus obtain a positive charge and once again become peptized to some extent.

The sol will be in its least stable state when the number of Lissolamine ions added is equal to the number of exchangeable ions on the clay micelle. All negative spots will be neutralized at this point. Thus we should be able to calculate the base exchange capacity of the clay from the amount of Lissolamine necessary to achieve this minimum stability. However, this latter point cannot be distinguished with any degree of accuracy by visual means, since the sol is relatively unstable over a wide range of Lissolamine concentrations.

The following expedient offers a solution to this difficulty: At the stability minimum the micelle surface has become completely oleophilic, since it is covered with the hydrocarbon chains of the Lissolamine and no longer bears a negative charge. The positively charged edges on the other hand will not adsorb any organic cations, since their like charge precludes adsorption. Thus at the equivalence point the coated clay micelle will be simultaneously oleophilic (at the lattice surfaces) and hydrophilic (at the micelle edges). A micelle of this structure would be expected to act as an efficient emulsifier. Experimental verification of this hypothesis was readily obtained by shaking the sols, previously treated with increasing amounts of Lissolamine, with a paraffinic type of gas oil. A comparatively stable emulsion was indeed formed at a critical Lissolamine concentration. Values of the base exchange capacity of various montmorillonite suspensions calculated by utilizing this critical Lissolamine concentration for emulsification were found to be in good agreement with those obtained by other methods. This is shown in table II F.

TABLE II F

	base exchange capacity m.eq./100 g, determined by the		
sample	NH_4Cl method	Percolation method	Lissolamine method
French montmor.	87		86
Na montmor. sol		106	105
Ca montmor. sol		94	98 *)

*) It may be remarked that the figures are related to the weight of clay after drying at 105°C. Ca montmorillonite was found to retain more water of hydration at this temperature than Na montmorillonite. Compared with the weight after drying at 900°C, Ca montmorillonite retains 10.1% of water at 105°C and Na montmorillonite 6.4%, 5% of which is hydroxyl water. Correcting for the degree of hydration the values for Na and Ca montmorillonite will come closer together.

In Table II G some results of the Lissolamine method are compared with those for the NH_4Cl method for some raw clays.

TABLE II G

Origin of clay	base exchange capacity m.eq./100 g, determined by the	
	NH_4Cl method	Lissolamine method
Talang Djimar	34	35.9 ± 0.7
Badas	22	24.1 ± 1.1
Tjepu	31.5	31.7 ± 0.9
Nigeria	31	27 ± 0.5
Groningen	11.5	10 ± 2.5
Black China	13	13.3 ± 0.8
Tarakan	9	12 ± 1.0

If small increments of the organic base are used accurate results are obtained. For example, for Na montmorillonite a value of 105 ± 1 was found, which is in exact agreement with the value found with the percolation method. The Lissolamine method is much simpler and may be carried out with very small samples of clay, viz. 0.15 g. in the case of montmorillonite.

It was observed, however, that the presence of flocculating electrolytes will affect the determination: the presence of 20 m.eq./l of NaCl in a 0.25% sodium montmorillonite sol (or 47 grams of salt on 100 grams of clay) resulted in a b.e.c. which was high to the extent of 10%, whereas the addition of 5 m.eq./l of $FeCl_3$ (or 11 grams on 100 grams of clay) yielded a value which was low to the extent of 15%. On the other hand, the b.e.c. of a dialyzed calcium montmorillonite sol proved not to be affected by the addition of 10 m.eq./l of $CaCl_2$ to a 0.25% sol (22 grams on 100 grams of clay). In the case of strongly flocculated clays, therefore, the prior removal of electrolytes by washing on a collodion filter will be desirable for accurate work.

The procedure is as follows: In a series of test tubes 1.0 ml of a 1.5% clay suspension is treated with increasing amounts of a 1.0% solution of pure cetyltrimethyl ammonium bromide *), the final volume being made up to 6.0 ml with distilled water. After standing overnight the contents of the tubes are gently shaken with 5.0 ml portions of a paraffinic type gas oil **). The critical amount of bromide from which the b.e.c. is calculated is limited between a lower and an upper value calculated from the amounts of bromide present in the last demulsified and the first emulsified mixture.

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*) Possibly other cation active compounds which are available in a sufficiently pure state may be used as well.

**) In a few cases xylene was used instead of the gas oil, yielding identical results.

In a preliminary series the order of magnitude of the b.e.c. may be determined using large increments of the bromide. In a second series a more accurate value may be enclosed using increments of 0.01 ml of the bromide solution.

The b.e.c. is calculated from: b.e.c. = $\frac{1000 \cdot a}{b.\ 364}$ where a is the number of ml of 1.0% bromide solution at the critical concentration and b is the amount of clay in grams (364 is the mol.wt of the bromide).

Finally some additional information was obtained regarding the theoretical basis of the Lissolamine method.

The reversal of the charge of the sol was proved by cataphoresis; with an excess of Lissolamine, the micelles become positive.

The interlayer adsorption was proved by X-ray analysis. For equivalent exchange the basal spacing becomes 20.5 Å or ca 10 Å more than for dry bentonite although the diffraction pattern is rather vague. On addition of an excess of amine (equivalent with about 3 times the b.e.c.) the basal spacing becomes 39 Å and the diffraction pattern shows 16 sharp orders.

Jordan (13), who studied the adsorption of straight chain amine salts to bentonite, has shown that the basal spacing of the complex is ca 4 Å higher than for dry bentonite if the basal plane area covered by amine is smaller than 50% of the total area and ca 8 Å for a higher percentage covered. For equivalent exchange it may be calculated that amines up to C_{10} will occupy less than 50% of the surface area and those of higher chain length more than 50%. Jordan assumes that the chains between the layers lie flat, the thickness of 1 hydrocarbon chain being 4 Å. If the surface coverage is less than 50%, the organic molecules on the top surface of one lamina may fit into the gaps between those on the bottom surface of the lamina directly above it. Where the chains are longer and occupy more than 50% of the surface area, adjacent flakes will be unable to approach more closely than the thickness of two hydrocarbon chains or 8 Å. With the quaternary ammonium salts used in our work the presence of the three methyl groups at the end of the chains apparently prevents the layers to come closer than 2 x 5 Å instead of 8 Å (for the C_{18} chain the surface coverage will be higher than 50%). At higher Lissolamine concentrations more layers of amine will be adsorbed. Their orientation may be found from a Fourier analysis of the X-ray diagram.

It has been found from adsorption determinations that an amount of Lissolamine which is equivalent to the b.e.c. is indeed quantitatively adsorbed. The maximum adsorption capacity for Na montmorillonite was found to be about 2.4 times the b.e.c., adsorption being practically quantitative up to about 1.5 times the b.e.c.

The idea of the emulsification test was based on the general concept that finely divided materials will act as efficient emulsifiers if the particle surfaces are partly oleophilic and partly hydrophilic. Assuming that the exchangeable cations are exclusively located at the negative layer surfaces and not at the positive lateral surfaces, this condition would indeed be realized after complete exchange with organic cations. The layer surfaces would then have become oleophilic, whereas the lateral surface would remain hydrophilic. Although the success of the emulsification test could, mutatis mutandis, be considered a support for this assumption, it may certainly not be considered a definite proof, since only little is known as yet about the activity of small particles as emulsifying agents in connection with their surface conditions.

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CHAPTER 2

THE EFFECT OF SODIUM POLYMETAPHOSPHATE ON THE STABILITY OF FRENCH MONTMORILLONITE SOLS

Polymeric sodium metaphosphate as well as other phosphates are very effective deflocculants for muds. These compounds are known to form soluble complexes with calcium ions: they have a certain "calcium sequestering ability". Therefore, as mentioned in the introduction, their peptising effect might be attributed to an inactivation of the strongly flocculating calcium ions which will be present in most muds.

However, this may not be the whole truth. In addition, some other mechanism might contribute to their activity. Therefore, in the present investigation, their effect was first studied in the absence of calcium ions, using a dialyzed sodium montmorillonite sol. Subsequently the effect on calcium montmorillonite as well as the protection against the flocculating action of dissolved calcium salts was investigated.

A. POLYMERIC METAPHOSPHATE

One of the most commonly used phosphates in the treatment of drilling fluids is the water-soluble sodium metaphosphate which is usually referred to as "sodium hexametaphosphate" *). According to modern concepts these products are not hexameric but polymeric metaphosphates, containing 15-30 PO_3 groups depending on the method of manufacture (14).

W. Teichert et al. have shown that the complex formation ability with alkaline earth ions increases with the degree of polymerisation. The latter may even be calculated from the Ba-Na ratio in the soluble complex which is found from conductometric titration. Fig.II, 2 represents the result of such a titration of 20 ml 0.1 N sodium polymetaphosphate which was used in the present investigation with 1.0 N barium acetate. (The normality of the metaphosphate solution is based on the equivalent weight of the $NaPO_3$-group). The titration was carried out with the Philoscope at a frequency of 1000 cycles. Despite the addition of barium acetate,

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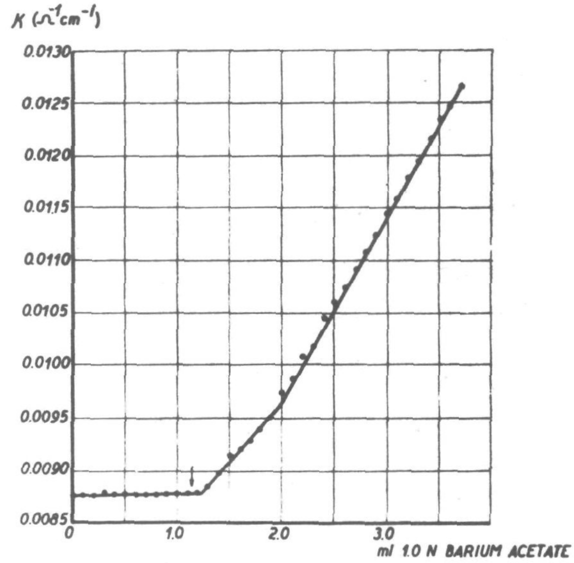
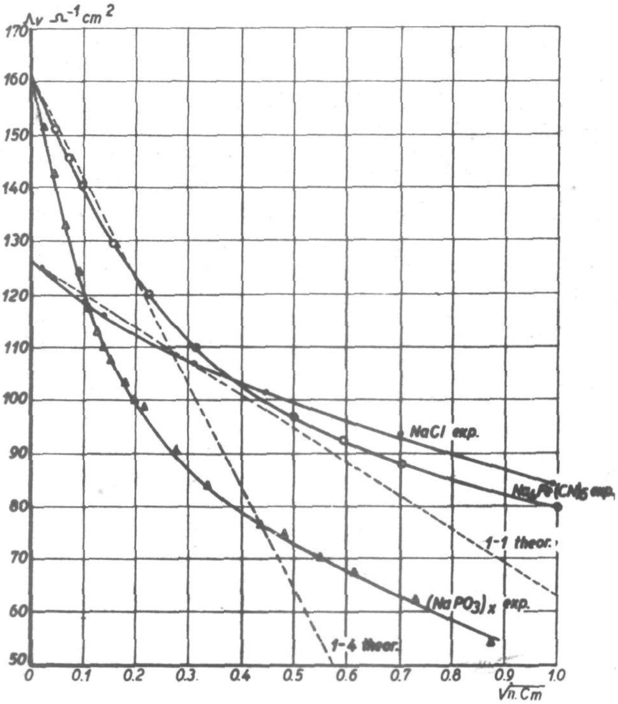
*) A commercial product marketed under the trade name "Calgon" was used in this investigation.



CONDUCTOMETRIC TITRATION OF 20 ml 0.1 N $(NaPO_3)_x$ SOLUTION WITH 1,0 N BARIUM ACETATE

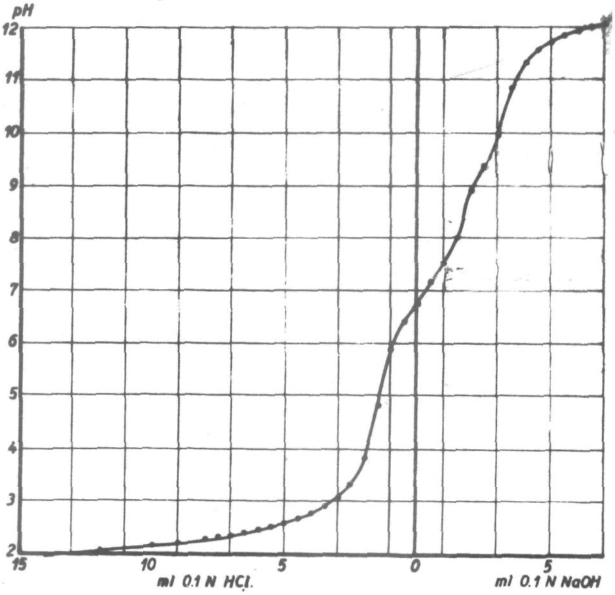
FIG. II, 2

the conductivity first remains practically the same, indicating the formation of a soluble complex. The inflection point at 1.2 ml barium acetate, from where a precipitate is formed, indicates that the soluble complex contains 12 equivalents of barium against 8 equivalents of sodium. From Teichert's formula, relating the barium-sodium ratio with the molecular weight, it is calculated that the degree of polymerisation of our product is about 30.
Owing to the presence of polymeric anions in the solution, the activity of the sodium ions may be expected to be rather low. This may be demonstrated by the dependence of the equivalent conductivity of the metaphosphate solutions on the concentration. In Fig. II, 3 the equivalent conductivity Λ_v of sodium polymetaphosphate solutions is plotted versus $\sqrt{n.c_m}$, where c_m = the molar concentration and n = the number of ions into which the salt is dissociated. For the polymeric metaphosphate the value of $n.c_m$ may be taken equal to the equivalent concentration c_a. According to the theory for strong electrolytes the Λ_v — $\sqrt{n.c_m}$ relation should be linear at low concentrations as indicated in the graph for a 1-1 valent and a 1-4 valent electrolyte (NaCl and $Na_4Fe(CN)_6$ respectively). The observed curves show the general character of the deviations from theory. Although the theoretical curve cannot



EQUIVALENT CONDUCTIVITIES OF A 1-1 AND 1-4 VALENT ELECTROLYTE, EXPERIMENTAL AND THEORETICAL CURVES $(NaPO_3)_x$ EXPERIMENTAL CURVE TEMPERATURE 25 °C

FIG. II, 3



POTENTIOMETRIC TITRATION OF 20 ml. 0.1 N $(NaPO_3)_x$ SOLUTION WITH 0.1 N NaOH AND 0.1 N HCl

FIG. II, 4

be calculated for a polymeric electrolyte, the low conductivities of the sodium polymetaphosphate solutions demonstrate the low activity of the sodium ions in these solutions.

Polymeric metaphosphates may be considered to be dehydrated orthophosphates: x H_3PO_4 - x H_2O = $(HPO_3)_x$. The sodium salts rehydrate very slowly when dissolved in water, forming ortho- and pyrophosphate. The progress of hydrolysis may be followed from potentiometric titration with both NaOH and HCl. Metaphosphoric acid being a strong acid-its titration curve is analogous to that of HCl-the slight acidity of the metaphosphate solutions should be attributed to the presence of products of hydrolysis viz. acid ortho and acid pyrophosphate. Fig.II, 4 shows the result of the titration of 20 ml 0.1 N sodium polymetaphosphate with 0.1 N NaOH and 0.1 N HCl, respectively. An exact quantitative interpretation of this curve should only be given from a comparison with the titration curves of known mixtures of the various phosphates, just as Teichert does in the case of the acids. However, the titration supplies a convenient check on the quality of a metaphosphate solution. In the investigation the solutions were no longer used than one or two weeks after preparation during which time their composition is practically constant. It is apparent from the titration curve that about 10% of the phosphates is present in the acid form.

B. STABILISATION OF SODIUM MONTMORILLONITE SOLS BY SODIUM POLYMETAPHOSPHATE (15)

Increasing amounts of sodium polymetaphosphate were added to a 0.25 % dialyzed sodium montmorillonite sol and the behaviour of the treated sols towards the action of NaCl was investigated.

Fig.II, 5 represents the variations in *relative viscosity* of the original and the phosphate-treated sols on addition of NaCl.*) Addition of a small amount of salt to the original sol (curve marked "0 metaphosphate") results in a slight initial decrease in relative viscosity, which, on further addition of salt, is followed by a sharp rise of viscosity, indicating flocculation. (This effect was already mentioned in chapter 1, section D). Also when the metaphosphate is added to the original sol, a slight decrease in relative viscosity is observed first but on subsequent addition of salt to the treated sol the sharp rise in viscosity is largely suppressed, the more so as the quantity of the phosphate added is larger (compare the curves for 0.7-3.3-6.0 and 33.3 m.eq./l metaphosphate).

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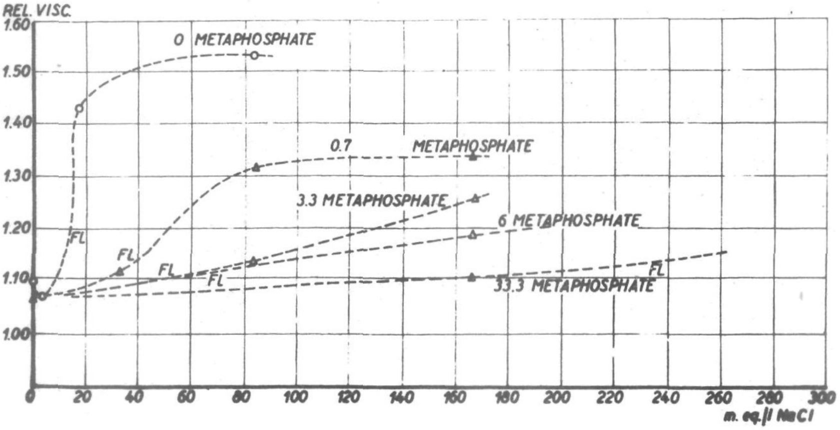
*) 17 m.eq/l of NaCl is equivalent to 0.1% wt of NaCl.
9.8 m.eq./l of sodium polymetaphosphate is equivalent to 0.1% wt.



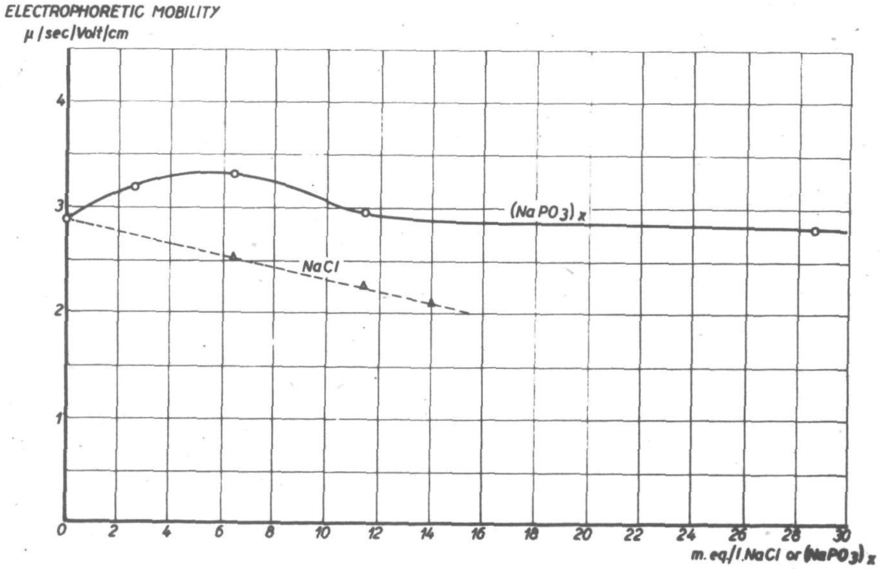
RELATIVE VISCOSITY CHANGES OF 0.25 % Na MONTMORILLONITE SOL ON ADDITION OF BOTH $(NaPO_3)_x$ AND NaCl

FIG. II, 5

Parallel to this effect on relative viscosity, the *flocculation value* of sodium montmorillonite towards NaCl is found to increase appreciably with increasing metaphosphate concentration as indicated by "FL" in Fig. II, 5. *This stabilizing effect of sodium-polymetaphosphate on sodium montmorillonite shows that the favourable effect of the metaphosphate is indeed not restricted to its calcium sequestering ability.*

In order to correlate the stabilisation phenomenon with the charge of the metaphosphate-treated sol micelles, the effect of the metaphosphate on the *electrophoretic mobility* (e.m.) of the sols was investigated, the results of which are presented in Fig. II, 6. For comparison also the effect of small amounts of salt has been included in the graph. On addition of salt the e.m. of the sol decreases gradually, whereas the addition of metaphosphate results in a distinct initial increase in e.m. On further addition of the phosphate the e.m. first decreases slightly, after which it remains constant at a value which is about equal to that of the original sol particles. Qualitatively, these results are in agreement with the observed stabilising effect of sodium polymetaphosphate.

Next, the variations in association tendency of the micelles in the presence of sodium metaphosphate or sodium chloride was studied by *ultramicroscopical counting* (compare chapter 1, section D). As expected the number of micelles decreases on addition of NaCl owing to flocculation. Paradoxally, however, also on addition of polymetaphosphate an increased association tendency is



ELECTROPHORETIC MOBILITY OF Na MONTMORILLONITE SOL TREATED WITH NaCl AND WITH $(NaPO_3)_x$ RESPECTIVELY
SOL CONCENTRATION 0.006 %

FIG. II, 6

observed, which at first sight seems inconsistent with the stabilising effect.

A possible explanation of the phenomena observed may be based on the hypothesis that the plate-like sol micelles bear a negative charge at the layer surface and a positive charge at the broken edges as set forth in the first chapter. Then the polyvalent metaphosphate anions may be assumed to be adsorbed to the positive edges of the micelles, resulting in a negative charge of the edges which is reflected in the increased negative electrophoretic mobility.

On the other hand, the negative double layer potential at the layer surfaces will gradually decrease owing to the Na ion concentration of the sodium metaphosphate solution, which accounts for the ultimate decrease in electrophoretic mobility. This decrease of the surface layer potential will also result in an increased tendency to parallel association of the sol micelles, or, in other words, in a "parallel flocculation", which may explain the decrease in the number of micelles. The observed viscosity behaviour ties in with this explanation: On addition of salt to the original sol, both the edge and surface double layer potentials decrease and the micelles will further associate - surface to surface and edge to edge links being formed too - into a network, displaying a rather high viscosity and thixotropy as well. If the metaphosphate is added first, creating a strong negative charge of the edges, the edge to edge association is largely prevented and no network is built up in this case. Consequently the viscosity remains low. The parallel association of the phosphate treated sol micelles, discussed above, even tends to lower the viscosity according to the Peterlin-Burgers equation.

The effect of sodium polymetaphosphate on sodium montmorillonite may therefore be attributed to the charging of the edges of the thin crystal plates of the sol by adsorbed polymetaphosphate anions which prevents the formation of a gel-like network, even in the presence of rather large amounts of a flocculating electrolyte.

In Table II H the various phases of micelle association are indicated together with the data observed.

TABLE II H

THE EFFECT OF SODIUM POLYMETAPHOSPHATE ON THE PROPERTIES OF SODIUM MONTMORILLONITE SOLS

properties	conc. sodium polymetaphosphate(m.eq./1		
	0	6.5	28.5
electrophoretic mobility μ/sec./Volt/cm	2.9	3.3	2.8
relative viscosity of 0.246% sol	1.10	1.07	1.07
$N_o \times 10^{-12}$ (N_o = number of particles pro 1 ml of 1½% sol)	1.90		1.50
flocculation value NaCl (m.eq./1)	15	80	230
micelle association primarily:	edge to surface	surface to surface	

The above tentative explanations are supported by the results of adsorption capacity determinations for sodium polymetaphosphate to sodium montmorillonite.

A sodium montmorillonite sol containing a known amount of sodium polymetaphosphate was subjected to ultrafiltration and the metaphosphate concentration in the ultrafiltrate was determined from which the amount of metaphosphate adsorbed by the montmorillonite was calculated.

The metaphosphate concentration was measured by means of a sensitive colorimetric method (16). Since this method is only valid for orthophosphates, the polymetaphosphate was first converted into orthophosphate by hydrolysis with acid.

Ultrafiltration was carried out on a fine sintered glass filter In a blank test with a metaphosphate solution containing 3 m.eq./l, the concentration of the phosphate in the ultrafiltrate was only 1½% low. The adsorption of the phosphate by the glass filter could therefore be considered negligible.

Evaporation of the filtrate during filtration was checked by measuring the increase in weight of a calcium chloride tube inserted between vacuum pump and flask. The concentration of the ultrafiltrate was corrected for evaporation losses.

It was assumed in the calculation that the phosphate does not change the degree of hydration of the montmorillonite. This assumption is supported by X ray investigation of wet pastes of phosphate-treated montmorillonite.

The adsorption capacity being calculated from the small difference of two relatively high concentrations, no high accuracy can be obtained.

The results of the adsorption capacity determinations are shown in Table II, I.

TABLE II, I

ADSORPTION CAPACITY OF SODIUM MONTMORILLONITE SOL FOR SODIUM POLYMETAPHOSPHATE

concentration Na montmorill. g/l	conc. Na polymetaphosphate added to sol m.eq./l	Na polymetaphosphate adsorbed m.eq./l	adsorption cap. of sol m.eq./100 g of clay
2.5	2.6	0.25 ± 0.05	10 ± 2
7.42	14.3	1.32 ± 0.28	18 ± 4
18.9	32.1	1.70 ± 0.65	9 ± 4

(10 ml of sol was used for each determination)

The order of magnitude of the adsorption capacity of Na montmorillonite for sodium polymetaphosphate is therefore about 14 m.eq./100 g of clay.

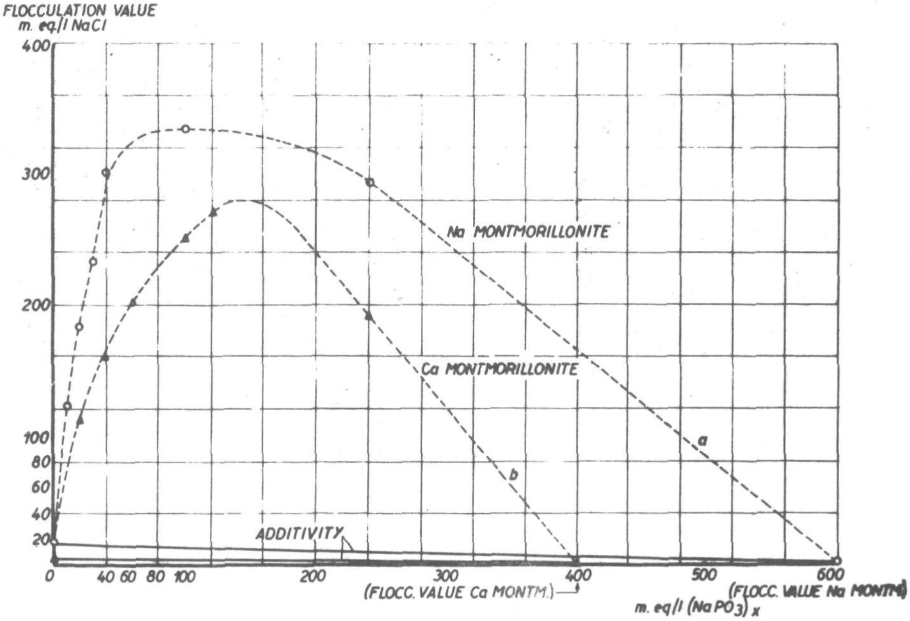
This adsorption capacity may be accounted for by the adsorption capacity of the lateral surface of the clay micelles if the following assumptions are made: there are three adsorption sites at each unit cell which is exposed at the lateral surface viz. two opposite the silica and one opposite the alumina sheet. Then for the most unfavourable choice of the micelle diameter, viz. 8000 Å an adsorption capacity of 14 m.eq./l of metaphosphate would imply that the flexible chains have contact with the edges at 4 to 5 points.

The alternative of edge adsorption viz surface adsorption of the anions is unlikely because of the repulsive negative charge of the layer surfaces. This view is supported by X ray diffraction diagrams of metaphosphate treated sodium montmorillonite after vacuum drying at 60°C: the observed layer spacing was found to be about 10 Å as in the case of the untreated sodium montmorillonite, leaving no space for phosphates in between the layers.

It may be remarked that there is a possibility for the particles to be linked by polymetaphosphate anions. Since the electron micrographs show that the diameter of the particles does not change on metaphosphate treatment the phosphate anions might stimulate the formation of piles of plates which are attached to the polymetaphosphate chain. This association will be promoted by the decreased repulsion between the flat surfaces due to the Na^+ ion concentration of the phosphate solution which was seen as the cause of the decrease of the number of particles. Analogous effects might occur on addition of protective colloids.

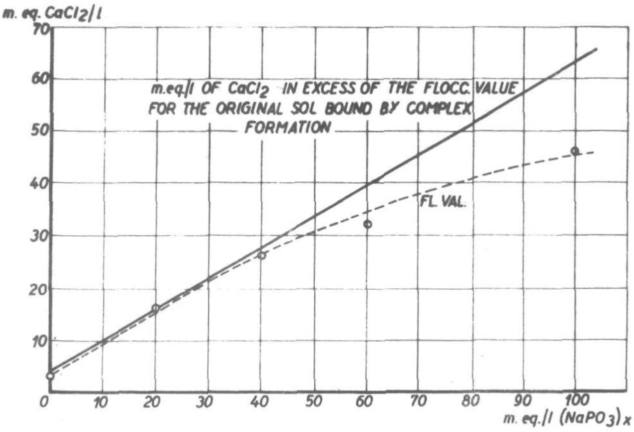
C "FLOCCULATION ANTAGONISM"

The stabilisation of sodium montmorillonite sols by sodium-polymetaphosphate was studied for a wider range of concentrations than discussed in section B, including the flocculation value for the phosphate itself, which was found to be as high as about 600 m.eq./l. Fig. II, 7, curve *a* shows the flocculation values of NaCl as a function of the amount of polymetaphosphate added. The curve clearly demonstrates the considerable antagonistic effect of phosphate and salt, by which is meant the deviation from additivity of the flocculation values of both electrolytes. This antagonism will be partly caused by the charging effect of the polymeric phosphate anions as pointed out in the preceding



FLOCCULATION ANTAGONISM WITH A MIXTURE OF $(NaPO_3)_x$ AND SALT (Na and Ca montmorillonite sols)

FIG. II, 7



INCREASED STABILITY OF Na MONTMORILLONITE TO $CaCl_2$, OWING TO THE ADDITION OF $(NaPO_3)_x$

FIG. II, 8

section. This effect may be called *"peptisation antagonism"*. A second contributing factor will be a so-called *ion antagonism* by which is meant the antagonistic effect which is due to the decrease in activity (and therefore in flocculating power) of the Na ions in the mixture containing the polyvalent metaphosphate anions (cf Vester 17). This is indeed another factor to be taken into account when explaining the stabilizing effect of polymetaphosphate. If in Fig. II, 7 the NaCl concentration should be replaced by Na ion activities the maxima of the curves would be lower and only the peptisation antagonism would remain. The valency of the polymetaphosphate anion being rather high the ion activities cannot be calculated. Unfortunately, therefore the relative importance of the ion antagonistic effect cannot be estimated. The extraordinarily high flocculation value of polymetaphosphate itself is, however, undoubtedly partly a result of the low activity of the sodium ions in the solutions of this salt.

D. EFFECT OF SODIUM POLYMETAPHOSPHATE ON CALCIUM MONTMORILLONITE SOLS

The flocculation antagonism of NaCl and sodium polymetaphosphate for a calcium montmorillonite sol is included in Fig. II, 7 curve b. The stability of the phosphate-treated calcium montmorillonite is somewhat less than that of the sodium montmorillonite sol. However, in view of the very low original salt stability of the calcium montmorillonite sol as compared with that of the sodium sol the antagonistic effect is still enormous, and at sufficiently high metaphosphate concentrations the stability of both sols is of the same order of magnitude. Qualitatively this result may be seen as a consequence of the conversion of the calcium montmorillonite sol into the more stable sodium form and simultaneous inactivation of the strongly flocculating calcium ions by the formation of soluble complexes with the polymetaphosphate anion.

E. PROTECTION AGAINST FLOCCULATION BY DISSOLVED CALCIUM SALTS

The flocculation value of sodium montmorillonite towards calcium salts is strongly increased on addition of sodium polymetaphosphate as is indicated by the dotted line in Fig. II, 8. At low concentrations of metaphosphate this can be quantitatively attributed to the inactivation of the calcium ions by the metaphosphate: the amounts of calcium (in excess of the flocculation values are identical at low metaphosphate concentrations, which demonstrates the importance of the calcium sequestering ability of the metaphosphate. At higher concentrations of metaphosphate the additional flocculating action of the sodium ions of the phosphate added will be responsible for the difference between observed and calculated values.

Note

No comparison has been made of the effect of the large variety of polymeric phosphates which have found technical application. Since the rehydration of these dehydrated orthophosphates to relatively inactive orthophosphate may depend on such factors as pH, temperature and presence of electrolytes, a study of the rehydration reactions would be a prerequisite for the investigation of the practical merits of these phosphates which is beyond the scope of this thesis. Some tentative experiments have shown that the stabilising effect of sodium pyrophosphate on both sodium and calcium montmorillonite is of the same order of magnitude as that for polymetaphosphate. The effect of sodium orthophosphate, which is indeed much lower, will be dealt with in the next section.

CHAPTER 3

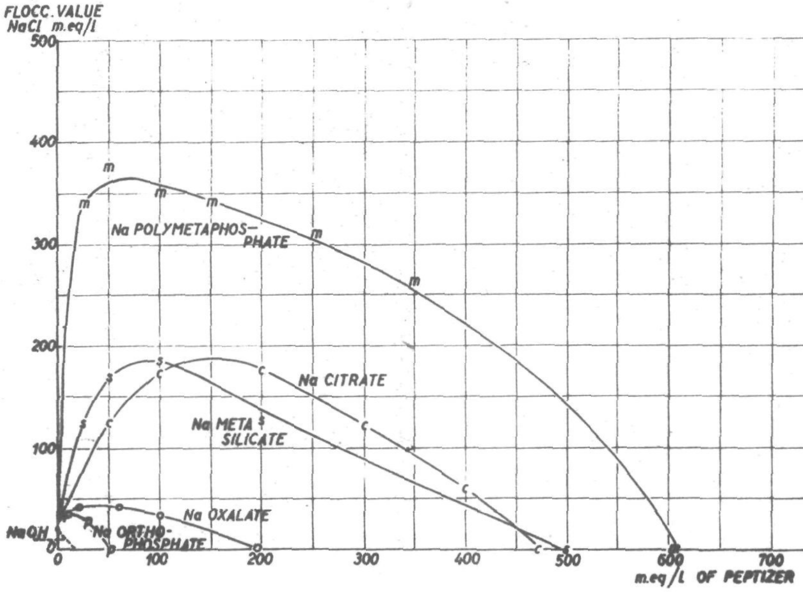
THE EFFECT OF SODIUM METASILICATE, OXALATE, CITRATE AND ORTHOPHOSPHATE ON FRENCH MONTMORILLONITE SOLS

This chapter deals with the effect of some additives for drilling fluids which are able to form precipitates with calcium ions. Their activity is sometimes attributed to a conversion of calcium clays into more stable sodium clays while simultaneously inactivating the strongly flocculating calcium ions by precipitation. Since it has been shown for polymeric phosphates that an inactivation of calcium ions accounts for only part of the stabilising effect, the activity of the calcium precipitating treating agents - like in the case of polymetaphosphate - was studied for sodium and calcium montmorillonite sols separately. The salts investigated are sodium metasilicate ("sil"), oxalate, citrate and orthophosphate.

A. EFFECT ON SODIUM MONTMORILLONITE SOLS

As described for polymetaphosphate, the flocculation antagonism for mixtures of NaCl and each of the four salts mentioned was determined, the results of which are represented in Fig.II,9. For comparison the data for polymetaphosphate have been included in the graph. The figure shows that both metasilicate and citrate have a reasonable antagonistic effect on sodium montmorillonite sols, which, however, amounts to only about half of the activity of the polymetaphosphate. Both oxalate and orthophosphate have a negligible effect.

As pointed out for polymetaphosphate, the total antagonism observed for metasilicate and citrate will partly consist of a peptisation and partly of an ion antagonism. Since the latter salts contain a di- and a trivalent anion, the total sodium ion activity in the mixtures with NaCl may actually be calculated. At the maximum of the metasilicate and citrate curve the total Na ion activity amounts to 145 and 162 mg ion/l respectively, whereas the blank sol is flocculated by 20 m.eq./l of NaCl corresponding with a Na ion activity of 17 mg ion/l. The ion antagonistic effect, therefore, does not account for the total antagonism which proves the presence of a definite peptisation antagonism.



FLOCCULATION OF Na MONTMORILLONITE SOLS WITH MIXTURES OF PEPTIZERS AND NaCl FIG. II.9

B. EFFECT ON CALCIUM MONTMORILLONITE SOLS

Contrary to polymetaphosphate which stabilises calcium montmorillonite, it was found that metasilicate and orthophosphate do not show any effect of this kind: calcium montmorillonite sols are already flocculated by ca 5 m.eq./l of these chemicals and although the flocculation value for sodium oxalate and citrate are higher (ca. 25 m.eq./l for oxalate and as high as 250 m.eq./l for citrate), their stabilising effect is negligible. Thus, contrary to general belief these salts are unable to stabilize calcium montmorillonite by conversion into sodium montmorillonite. Possibly the calcium salts of these anions are precipitated on the micelle surface proper, destroying the stabilising double layer.

Thus the peptisation effect of some of the chemicals investigated is limited to the sodium montmorillonite sols. A discussion of the peptisation mechanism in these systems will be given in Chapter VI after the collection of more information including the effect of alkali and of additional data for the effect of the various chemicals on a different montmorillonite.

* * * * * *

CHAPTER 4

THE EFFECT OF ALKALI ON FRENCH MONTMORILONITE SOLS

In the chemical treatment of muds it is common practice to try first whether addition of alkali improves the rheological properties of the mud. In some cases a thinning effect is indeed observed. This, however, does not apply to every mud, in many cases the reverse is true and the mud stiffens on addition of alkali, indicating flocculation of the clay. The reason for the different behaviour of various muds in this respect is not known. It may be either a matter of the different types of clay or of the type of exchangeable cations present in the mud. A third possibility is that foreign matter in the clays, for example humic acid, is neutralized by the alkali which might result in an improved stability owing to the action of the humate ions.

In this chapter the effect of alkali (NaOH of Na_2CO_3) on montmorillonite sols is discussed. Both H, Na and Ca montmorillonite sols have been investigated.

There are four possible ways in which alkalies may act as stabilizers for montmorillonite suspensions viz:

a. Hydroxyl ions have a peptization effect on the montmorillonite sol. This may be checked by studying the effect of NaOH on Na montmorillonite sols.
b. NaOH converts hydrogen clay into more stable sodium clay. In order to check this, the effect of NaOH on H-montmorillonite sols should be investigated.
c. Na_2CO_3 converts a calcium clay into a sodium clay and at the same time inactivates the strongly flocculating calcium ions by precipitation. This can be studied by investigating the system Na_2CO_3-calcium montmorillonite sol.
d. Na_2CO_3 renders ineffective any calcium ions dissolved in the intermicellar liquid. This may be checked by investigating the flocculation of Na montmorillonite with calcium chloride in the presence of various quantities of Na_2CO_3.

In the following paragraphs these possibilities will be dealt with.

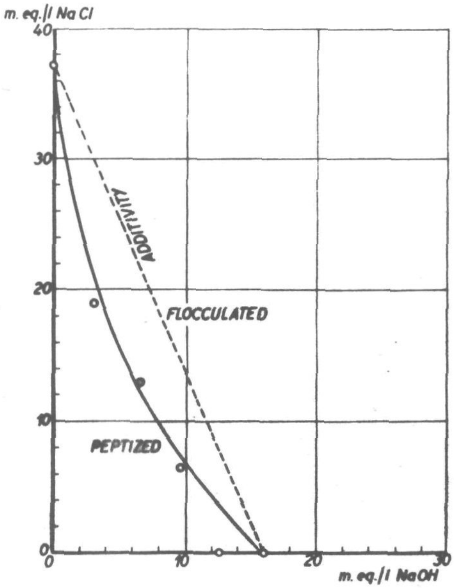


FIG. II, 10

FLOCCULATION OF 0.25 % Na MONTMORILLONITE SOL. WITH NaCl AND NaOH AND MIXTURES

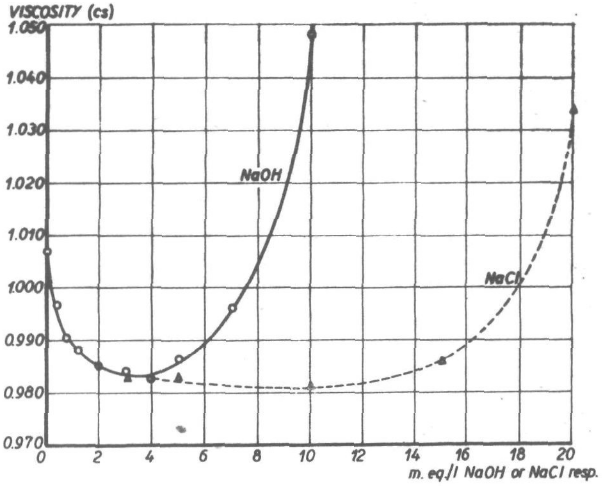


FIG. II, 11

VISCOSITY OF 0.25 % Na MONTMORILLONITE SOL. WITH INCREASING CONCENTRATIONS OF NaCl AND NaOH RESPECTIVELY

A. EFFECT OF NaOH ON SODIUM MONTMORILLONITE SOLS

The following flocculation values have been obtained for one of our sodium montmorillonite sols: NaCl 37 m.eq./l and NaOH 16 m.eq./l.

The order of magnitude of these flocculation values is primarily governed by the flocculating action of the monovalent cation Na, the net charge of the sols being negative. Apparently the presence of OH' causes a somewhat higher sensitivity of the sol towards the flocculating action of the Na ions.

This also appears from the results of flocculation experiments with mixtures of NaCl and NaOH, which is shown in Fig.II, 10. The observed deviation from additivity is called "sensibilization" which is the opposite of "antagonism" which has been described previously.

Also the effect of NaOH on the viscosity of the 0.25% sol at 25°C was measured and the results may be compared with those for NaCl by inspection of Fig.II, 11. The initial decrease of the viscosity on addition of NaCl which is followed by a sharp rise, indicating the beginning of flocculation *), has already been discussed in chapter 1. A curve of identical shape was obtained for NaOH. Although the action of NaOH is roughly comparable with that of NaCl the slight sensitization by the OH' is apparent from the more rapid increase of the viscosity on addition of NaOH.

It may be concluded therefore, that NaOH does not stabilize sodium montmorillonite sols; on the contrary, it sensitizes the sols slightly towards the flocculating action of sodium ions.

This effect of the hydroxyl ions will be more fully discussed in chapter 5.

B. EFFECT OF NaOH ON H-MONTMORILLONITE SOL

Hydrogen montmorillonite sol was prepared from sodium montmorillonite by base exchange with HCl, following an analogous

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*) The rise in viscosity is observed at electrolyte concentrations which are lower than the flocculation value determined according to the centrifuge method, the viscosity being a more sensitive criterion for detecting the initiation of flocculation.

procedure as described for the preparation of sodium and calcium montmorillonite.

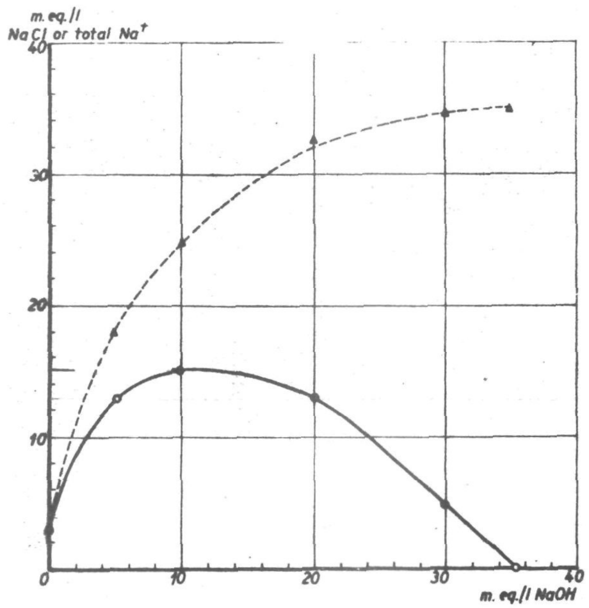
Hydrogen montmorillonite sol is rather unstable. The NaCl flocculation value for example is only about 3 m.eq./l.

The sol contains 50% more particles than the sodium montmorillonite sols of the same concentration. Its relative viscosity is about 8% lower. The micelle dimensions as calculated from both counting and viscosity data using the procedure described in chapter 1 are about 5500 Å for the diameter whereas the average thickness corresponds with that of a packet of about 8 layers. Since HCl treatment is known to remove some Al and Fe from the mineral it is conceivable that some of the plates are broken at the points where attack has taken place. This may account for the small diameter of the H montmorillonite particles in comparison with that of the sodium montmorillonite particles. The average association of the layers is higher than for sodium montmorillonite indicating a lower surface potential in H-montmorillonite.

The flocculation value of H-montmorillonite against NaOH is about 35 m.eq./l, thus much higher than that against NaCl, and of the order of magnitude of the Na^+ flocculation value for sodium montmorillonite. This can be seen as a consequence of a quantitative conversion of less stable H-montmorillonite into more stable Na montmorillonite by base exchange and simultaneous neutralization of the liberated hydrogen ions.

Fig. II, 12 shows the flocculation data with mixtures of NaOH and NaCl. The solid line shows the plot of the NaCl flocculation value as a function of the amount of NaOH added. The observed increase in stability may be seen as a result of neutralization on addition of NaOH. The dotted line shows the increase in total sodium ion stability against the amount of hydroxyl ions added. Since the sol concentration in the experiments was 0.25%, only 2.5 m.eq./l of NaOH is required for neutralization of exchangeable H. From this a sudden increase in the stability on addition of the first few milliequivalents of NaOH was rather expected instead of the gradual increase over a wide range of NaOH concentrations. This might be explained by the rather slow exchange reaction of H and Na, complete neutralization during the flocculation experiment being only achieved with a large excess of Na ions (compare chapter 1, section E where the time effect of the potentiometric titration of H montmorillonite with NaOH is mentioned).

It may be concluded, however, that neutralization of H montmorillonite by NaOH increases the salt stability, although not beyond that of Na montmorillonite.



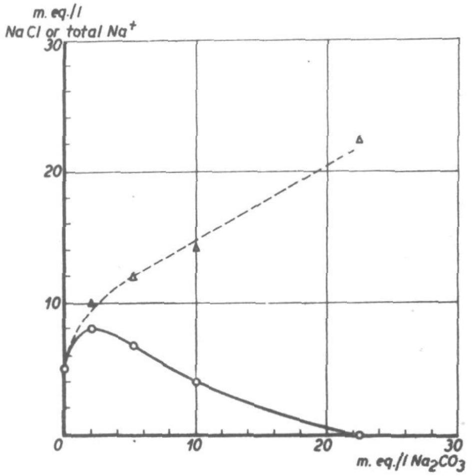
FLOCCULATION OF H MONTMORILLONITE SOL. WITH NaCl AND NaOH FIG. II, 12

C. EFFECT OF Na_2CO_3 ON CALCIUM MONTMORILLONITE SOLS

The following flocculation values for a calcium montmorillonite sol have been observed:
NaCl: 5 m.eq./l; NaOH: 6 m.eq./l; Na_2CO_3: 23 m.eq./l.

The values for both NaCl and NaOH are thus much lower than those for sodium montmorillonite, the Na_2CO_3 value, however, is of the same order as that for monovalent cations for sodium montmorillonite. This may be interpreted as a conversion of calcium montmorillonite into more stable sodium montmorillonite and simultaneous inactivation of the liberated calcium ions by precipitation. As a result essentially the flocculation value of sodium montmorillonite towards sodium ions will be measured.

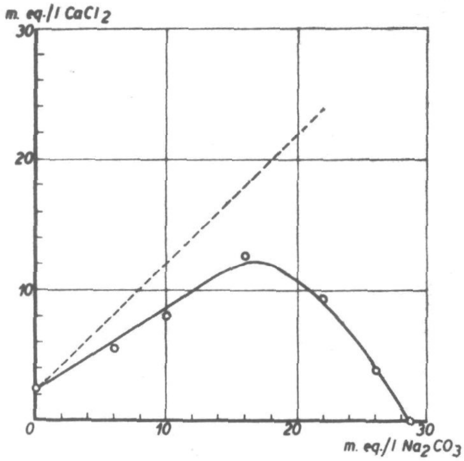
Fig.II, 13 shows the flocculation of calcium montmorillonite with mixtures of NaCl and Na_2CO_3. The solid line is the plot of the NaCl flocculation value as a function of the amount of carbonate added, the dotted line shows the effect of carbonate on the total sodium ion flocculation value. Again the gradual increase of the Na^+ stability suggests a gradual completion of the exchange reaction with increasing excess of sodium carbonate.



FLOCCULATION OF CALCIUM MONTMORILLONITE SOL. WITH NaCl AND Na_2CO_3

FIG. II, 13

8250-19-B$_4$



FLOCCULATION OF Na MONTMORILLONITE SOL. WITH MIXTURES OF $CaCl_2$ AND Na_2CO_3

FIG. II, 14

8250-20-B$_4$

D. FLOCCULATION OF Na-MONTMORILLONITE BY CALCIUM IONS AND ITS PREVENTION BY ADDITION OF SODIUM CARBONATE

Fig.II, 14 shows the flocculation values of Na montmorillonite towards $CaCl_2$ as a function of the amount of Na_2CO_3 previously added to the sol. The increase of the flocculation values due to sodium carbonate addition may be ascribed to the inactivation of strongly flocculating calcium ions by precipitation of $CaCO_3$. This would result in a flocculation curve indicated by the dotted line in the figure. However, the addition of Na_2CO_3 implies the addition of sodium ions, which also have a certain flocculating power although less than the calcium ions. As a result an optimum effect of the carbonate is reached at about 16 m.eq./l Na_2CO_3, where the sol just remains stable at a concentration of 10 m.eq./l of $CaCl_2$ (about 0.05% wt). On further addition of carbonate the flocculating action of the sodium ions which are unavoidably added, makes itself felt and at a concentration of about 30 m.eq./l the system is flocculated by sodium carbonate alone. This is known as overtreatment.

Reviewing the four possible stabilization mechanisms mentioned above we may conclude:

sub a. Hydroxyl ions have no peptizing effect on sodium montmorillonite micelles.

sub b, c and d. Both hydrogen and calcium montmorillonite are stabilized to some extent bij NaOH or Na_2CO_3, respectively due to conversion into Na montmorillonite and simultaneous inactivation of the liberated H^+ or Ca^{++} respectively. The carbonate also will render ineffective any calcium ions present in the intermicellar liquid. However, the maximum stability obtained never exceeds that of sodium montmorillonite against Na ions. This stability being rather low, the effect of alkali is only small in comparison with that of additives with peptizing anions like polymetaphosphate.

CHAPTER 5

MONTMORILLONITE SOLS FROM WYOMING BENTONITE

The study of montmorillonite sols described in the previous chapters was limited to those prepared from one type of bentonite only. Part of the work has now been repeated with sols prepared from a different bentonite viz. a Wyoming bentonite, in order to check to what extent the phenomena observed in one individual case might be considered characteristic of montmorillonite sols in general.

A. PREPARATION OF THE SOLS

Both a sodium and a calcium montmorillonite sol were prepared from Wyoming bentonite following the procedure described in chapter 1 which includes the removal of material of a particle size > 2μ equivalent spherical diameter.

In addition, an extremely fine particle size fraction *) of the sodium form was obtained by fractionation in a supercentrifuge. Part of this fraction was converted into calcium montmorillonite by repeated exchange with $CaCl_2$ and dialysis.

The following notations of the various sols will be used in this and the following chapters:

WB = Wyoming bentonite (raw)
WB-Na = its sodium form as dialyzed sol
WB-Na-ff = fine fraction of the same
WB-Ca = its calcium form as dialyzed sol
WB-Ca-ff = fine fraction of the same, prepared from WB-Na-ff
FB = French bentonite used so far (raw)
FB-Na = its sodium form as dialyzed sol
FB-Ca = its calcium form as dialyzed sol.

B. APPEARANCE OF THE SOLS, PARTICLE SIZE AND SHAPE

The observations on the appearance of the various sols are collected in Table II, I.

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*) Kindly supplied by Shell Oil Cy, Houston E & P Laboratories.

TABLE II.I

APPEARANCE OF VARIOUS MONTMORILLONITE SOLS

Observation of:	WB-Na	WB-Na-ff	WB-CA	WB-Ca-ff	FB-Na	FB-Ca
Tyndall light	greenish	greenish	milky	milky	milky	milky
transmitted light	brownish	brownish	brownish	brownish	brownish	brownish
ultramicroscope	diffuse	diffuse	submicrons	submicrons	submicrons	submicrons
sedimentation	none	none	slow	slow	none	slow
rheological prop.						
of 1% sol	viscous	viscous	liquid	liquid	liquid	liquid
of 3% sol	gel				liquid	

The most striking differences between the WB-Na and the previously studied FB-Na sols are the transparency and the high viscosity of the WB-Na sols as compared with the milky appearance and the water-like fluidity of the FB-Na sols.

Instead of distinct submicrons as observed in the ultramicroscope in FB-Na sols, the WB-Na sols show only a diffuse Tyndall cone.

The WB-Ca sols, however, are coarser than the WB-Na sols, even those prepared from the fine fraction sodium bentonite. Their appearance and ultramicroscopical picture are not too different from that of the FB-Ca sols. The presence of calcium apparently results in a higher degree of association as compared with the WB-Na sols.

The determination of the micelle dimensions from relative viscosity and counting data (compare chapter 1) is only possible for the WB-Ca sols, counting being impossible in the case of the WB-Na sols. For WB-Ca sols the relative viscosity was found to be 1.086 for a 0.25% sol and the number of particles for 1 cc of 1.5% sol: 2.0×10^{12} (counted in a dilution 1:1000). From these data the average radius may be calculated at 4650 Å and the axis ratio for the dry micelle at 225. Thus the average calculated height for the dry micelle will be 41 Å. These data are of the same order as found for the FB-Ca sols (and FB-Na sols as well).

If the average radius of the WB-Na micelles is assumed to be the same as for WB-Ca micelles, the average thickness of the WB-Na micelles may also be calculated, the axis ratio being known from the relative viscosity. In the region of proportionality of relative viscosity and sol concentration, the relative viscosity of a 0.25% WB-Na sol was found to be 1.21, from which an axis ratio of 545 for the dry micelle is calculated. Thus an average micelle thickness of 17 Å is obtained which is much smaller than for the calcium sols.

A further check on the calculation of the micelle dimensions was obtained from electron micrographs. Photographs 1 a, b, c and d show some typical electron transmission micrographs of the different sols together with one shadow cast picture. The crystallites appear to be much more perfect than those of the French montmorillonite. The micelle edges are curled *), which is clearly demonstrated by the shadow cast pictures. This effect is also the cause of the black borderlines of the micelles in the transmission micrographs. Unfortunately this invalidates the shadow cast technique for the estimation of the micelle thickness from the shadow length. A relative estimate may, however, be given by comparing the transparency of the WB-Na and WB-Ca micelles in the transmission micrographs. Although both are extremely thin, the Ca form seems to have thicker micelles than the sodium form. The variable transparency and the relief on the micelles in the shadow cast pictures suggests that the thickness of the plates is variable although shrinking effects may contribute to the apparent inhomogeneity. If the thickness is indeed variable it is conceivable that some plates may easily break at the regions of smallest thickness. In fact, this may have caused the apparent small diameter in the FB-Na micrographs and the increase of the number of micelles on evaporation as described in chapter 1.

Although the shape of the micelles often appears to deviate from the disc shape - a number of oblong particles are observed - the order of magnitude of the above calculated average diameter (ca 9000 Å) is certainly not far from the truth.

When preparing the electron micrographs the supporting film was positively charged by means of Lissolamine adsorption in order to fix the negative particles separately on the film before removing the last traces of water of the sol droplet. In the case of negative sols an excellent separation of the particles is usually obtained by this technique (18) and the formation of agglomerates of sol particles on evaporation of the droplet of sol is avoided. The method was indeed successful in the case of calcium

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*) This was also observed by Mlle Mathieu-Sicaud, Communication at the Groupe des Argiles Francais, 1949 and by Miss Marjorie Mac.Ewen, Communication at the Clay Minerals Group of the Mineralogical Soc. 1950.

Fig. II. 1a 20.000 x

WB-Na

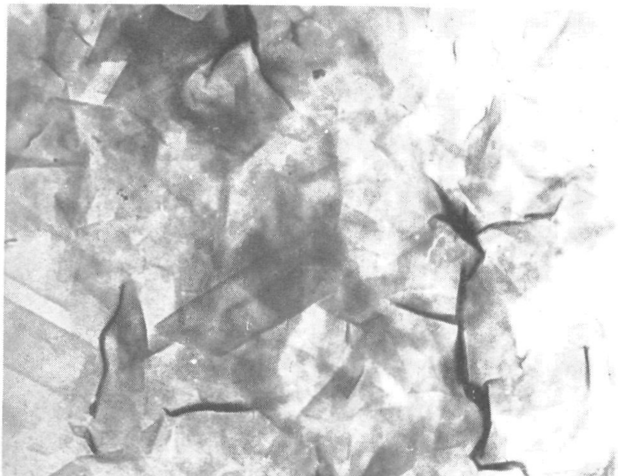


Fig. II. 1b 20.000 x

WB-Na-ff

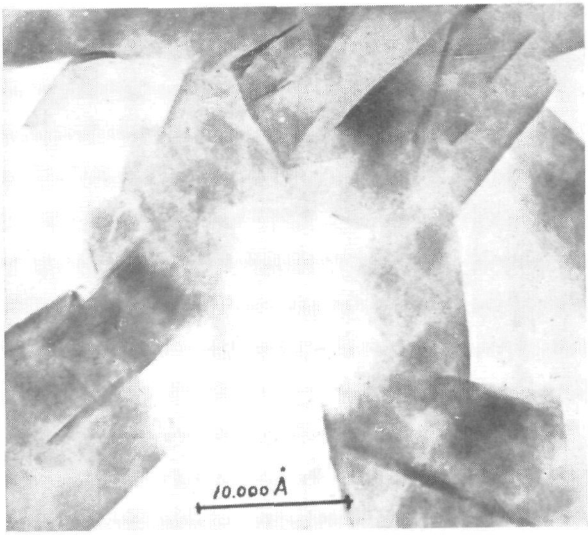


Fig. II, 1c 20.000 x

WB Ca-ff

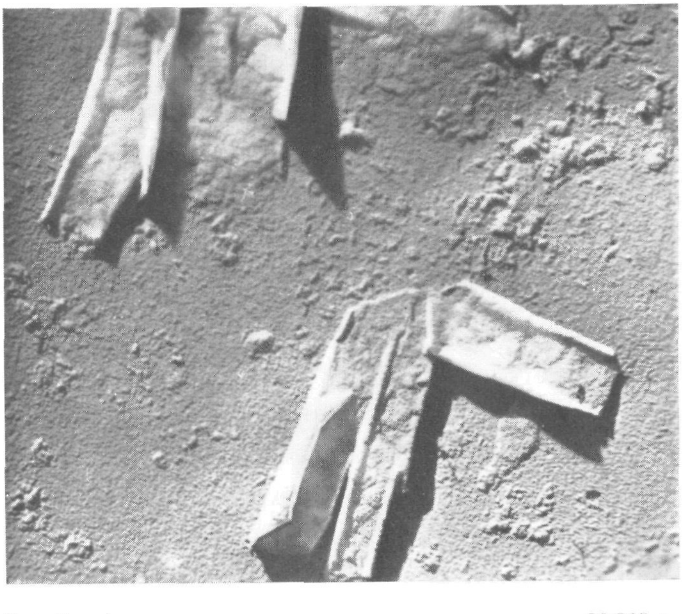


Fig. II, 1d 20.000 x

WB-Ca-ff
shadow casted

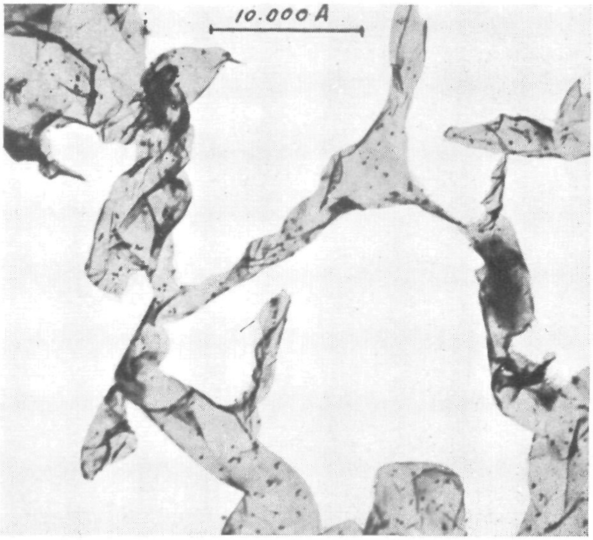


Fig. II. 2a 20.000 x

WB–Na
supporting film removed

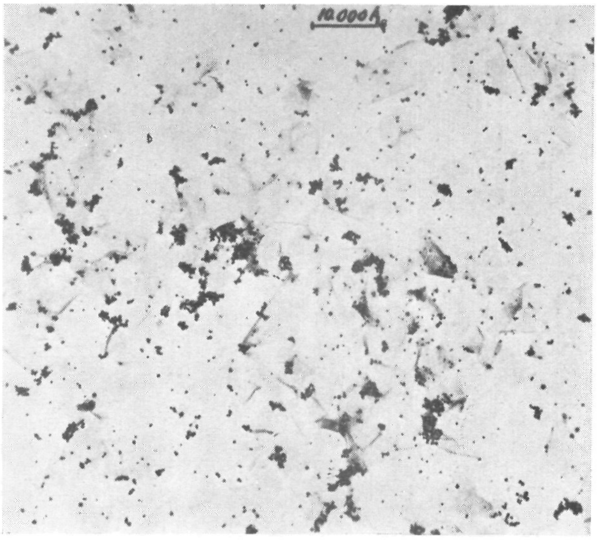


Fig. II. 2b 10.000 x

WB–Na–ff
gold adsorption

bentonite; in the sodium bentonite agglomerates are still present. The micrographs give the impression of collapsed structures. This would be in line with the assumption of an edge-to-surface association of the micelles in a sodium bentonite sol, owing to the opposed charges, as pointed out earlier. By accident the coherent structure of the micelles in a WB-Na sol was beautifully shown when the supporting collodion film broke during the electron microscopical observations: photograph 2a shows that the clay structure remained intact. The vagueness of part of the micelles building this structure demonstrates its three-dimensional character.

The latter picture was taken when studying the gold adsorption to the clay micelles. In chapter 1 the preferential adsorption of negative gold particles to the edges of kaolinite particles as observed by Thiessen was mentioned as a support for the positive edge hypothesis since the electrical conditions at the edges of kaolinite micelles might be considered analogous to those at the montmorillonite micelle edges. Thiessen's results could easily be reproduced in the case of kaolinite, but not for the French montmorillonite sols because of the rather vague micrographs obtained for these sols. A better chance was offered in the case of the WB-Na sols, which give much better micrographs. The result of the gold adsorption experiment is shown in photograph 2b. and, although the photographs are not as striking as those for kaolinite, there seems to be a preference for the gold particles to be adsorbed to the edges.

C. BASE EXCHANGE CAPACITY

The b.e.c. of raw Wyoming bentonite was found to be ca 75 (the lissolamine method yields 73, the ammonium chloride method 78). For the dialyzed Na and Ca bentonite sols ca 96 was found (lissolamine and percolation method). These values are of the usual order of magnitude for bentonites.

The bentonite formula calculated from both chemical analysis and b.e.c. which was reported earlier (Table II E of chapter 1) suggests that the degree of substitution in the silica sheet is smaller for Wyoming than for French bentonite. Thus the Wyoming bentonite should be considered a more perfect montmorillonite. This difference might explain the smaller degree of association of the WB-Na crystal layers as compared with those of FB-Na: The counter ions in the FB-Na layers will be more firmly bound since the distance of the centres of negative charge to the surface is smaller. This would involve the accumulation of a higher percentage of the counter ions at the surface and thus a steeper potential drop in the double layer, amounting to a smaller repulsion between two crystal layers.

D. SOL STABILITY AND CHARGE DISTRIBUTION ON THE MICELLES

The flocculation values for WB-Na and WB-Ca with various salts were determined by means of the centrifuge technique. With the sodium sols the critical concentration where flocs are becoming visible does not show up as a rapid increase of the sediment volume since the flocs are too light to settle properly. Therefore the flocculated appearance of the suspension after centrifuging was taken as a criterion for the flocculation value. The following values in m.eq./1 were found (between brackets the corresponding values for a FB-Na sol):

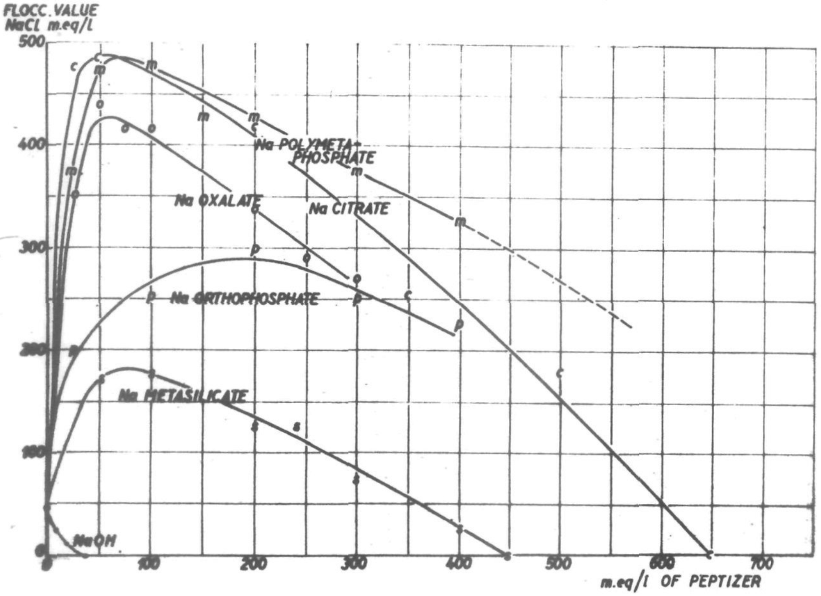
Na sols: NaCl 40-50 (17-20); $CaCl_2$ 3-4 (2-3); Na_2SO_4 50-60 (14-15)
Ca sols: NaCl 2-3 (2-3); $CaCl_2$ 0.5-1.0 (0.8-1.0).

The somewhat higher stability of the WB-Na sols as compared with that of the FB-Na sols might be due to the more favourable charge distribution on the lattice layer surfaces as inferred from the lower degree of association of the WB-Na sols.

When discussing the charge distribution on the montmorillonite micelles in chapter 1 the presence of a positive charge at the edges was considered a real possibility. Some supports for this hypothesis were mentioned and the anomalous decrease of the relative viscosity of the 0.25% sols on addition of a small amount of a flocculating electrolyte has been interpreted as a decrease of the positive edge-negative layer surface attraction forces. Analogous results were obtained for WB-Na sols as shown in figure II, 15.

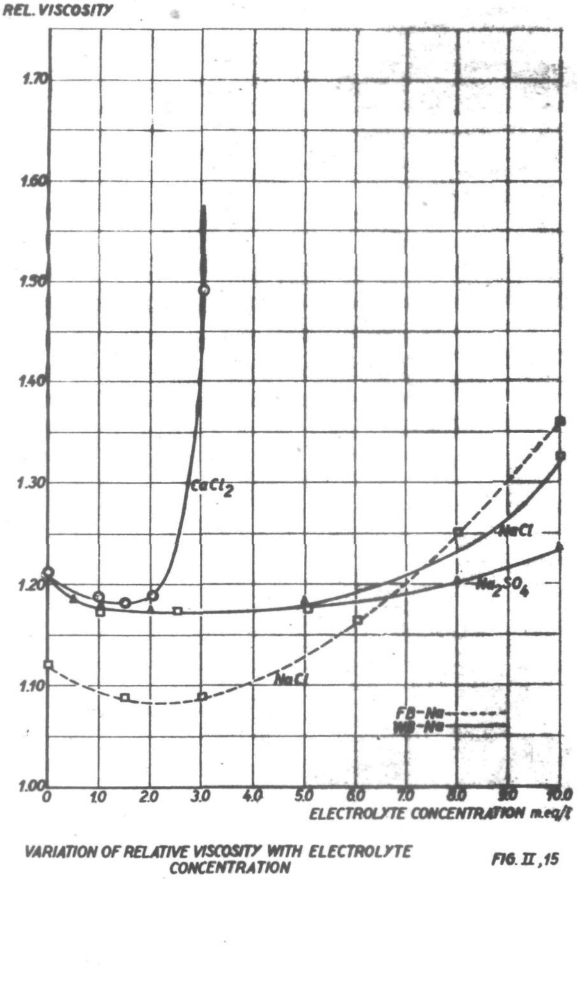
It has been pointed out earlier that this viscosity effect could also be explained by parallel association of the plates (decreasing shape factor!) or by a small electroviscous effect. Generally speaking the interpretation of the viscosity behaviour of these suspensions is rather involved and its conclusive force regarding structure formation in the suspensions is not too strong.

A more direct indication of structure formation is the development of rigidity in a dialyzed WB-Na sol at a clay concentration as low as 3%. Probably because of the smaller particles



FLOCCULATION OF WB-Na SOL WITH MIXTURES OF PEPTIZERS AND NaCl

FIG. II.16



VARIATION OF RELATIVE VISCOSITY WITH ELECTROLYTE CONCENTRATION

FIG. II,15

in the WB-Na sols a rigid system is obtained at a much lower concentration than in the case of FB-Na sols.

In order to further substantiate the view that the structure formation in the dialyzed sol is a result of positive edge-negative layer surface association, the effect of the addition of flocculating electrolytes on the yield stress of these concentrated sols has been determined (19). Since the addition of small amounts of NaCl will gradually reduce both double layer potentials of the micelles, the attractive force between the unlike charges will decrease, which would result in a smaller yield stress. On addition of more salt, flocculation will occur: then the Van der Waals attraction forces will prevail and the micelles will associate again - edge to edge, edge to surface and surface to surface - giving rise to an increased yield stress.

This expected behaviour was indeed confirmed by the experiment. The yield stress of the suspensions was determined by means of the modified Stormer viscometer. The determination was carried out both immediately after stirring of the suspension and after a period of rest of 30 minutes in order to measure the thixotropic change of the yield stress. The results are collected in Table II K.

TABLE II K

YIELD STRESS OF 3% DIALYZED W.B. SODIUM MONTMORILLONITE GEL ON ADDITION OF FLOCCULATING SALT. (MAXIMUM AMOUNT ADDED: 1 ml OF SALT SOLUTION TO 50 ml OF GEL)

Salt concentration (m.eq./l) in the sol	initial yield stress dynes/cm^2			yield stress after 30' dynes/cm^2		
	NaCl	Na_2SO_4	$CaCl_2$	NaCl	Na_2SO_4	$CaCl_2$
0	80	80	80	80	80	80
0.2	30	45	40	30	45	40
0.5	20	10	20	20	10	20
1.0	10	3	10	10	3	10
1.5	5	0	5	5	0	5
2.0	0	3	5	0	3	5
3.0	5	3	0	10	3	5
5.0	7	3	0	15	10	12
10	7	5	25	100	100	175
15	50	20	200	210	130	310
20	140	70	270	250	190	390

Without going into the slightly different behaviour of the three individual salts, the general effect is a decrease of the yield stress on addition of small amounts of salt followed by an increase when a flocculating amount of salt is present. The difference in thixotropic behaviour between the systems at low concentrations of salt and in the flocculated condition is striking: the first instantaneously set to a gel after stirring, whereas the flocculated systems show slow stiffening to even higher yield stresses.

These observations on the thixotropy may be seen as a further support of the interpretation given: the micelle association due to the unlike charges on layer and edge surfaces may indeed be expected to be instantaneous, whereas the association in the flocculated system, which is a result of the comparatively weak Van der Waals attraction forces, should be rather slow.

E. RESPONSE TOWARDS CHEMICAL TREATMENT

In fig. II, 16 the NaCl flocculation values for 0.25% WB-Na sols are plotted as a function of the amounts of various peptizers added. Analogous curves have been presented previously (fig. II, 9) for FB-Na sols.

Comparing the effects of the various peptizers on WB-Na and FB-Na sols, it is seen that the highly antagonistic effect of $(NaPO_3)_x$ and the moderate effect of sil are similar. Furthermore the slight sensibilization by NaOH is observed in both cases. The following differences are, however, observed: For FB-Na sols the effect of citrate is moderate, like that of sil, but for WB-Na sols it is equally strong as for $(NaPO_3)_x$. A further difference between the two sols is the high activity of oxalate and orthophosphate in the case of WB-Na sols as compared with the practically negligible effect of these chemicals on FB-Na sols.

A more detailed theory of the peptization mechanism should account for these individual characteristics of the two bentonites. Such a theory will be discussed in a subsequent chapter.

Finally it may be mentioned that the behaviour of WB-Ca sols towards polymetaphosphate and metasilicate is comparable with that of the FB-Na sols: calgon stabilizes the WB-Ca sols to the same extent as the sodium sols whereas a small amount of metasilicate flocculates the calcium sol.

* * * * * * *

CHAPTER 6

MODEL SOLS FOR MONTMORILLONITE - THE PEPTIZATION MECHANISM

A. INTRODUCTION OF MODEL SOLS

At the present stage of the investigation into the mechanism of chemical treatment of montmorillonite sols a new element has been introduced viz. the study of some model sols. The electrical conditions at the micelle surfaces in these sols will be considered as a possible model for the conditions at the lateral surface of the montmorillonite micelles.

In previous chapters it was assumed that montmorillonite micelles may have a dualistic character. The surface of the flat micelles will undoubtedly bear a negative charge which is due to isomorphous replacement in the lattice, the exchangeable cations being the counter ions. At the edges of the plates, on the other hand, a local positive charge due to the disruption of the octahedrical alumina sheets is a likely possibility in view of the fact that alumina sols are positively charged in a neutral medium.

The assumption of a positive edge charge, which is strongly supported by the results of rigidity measurements as discussed in chapter 5, proved to be a fruitful working hypothesis. On this basis the peptization of montmorillonite sols by various chemicals might be attributed to the adsorption of the di- or polyvalent anions of these chemicals to the positive spots at the edges resulting in a negative charge. The play of chemical treatment is thus supposed to be enacted at the lateral surface of the micelles. Thanks to the relatively small lateral surface area of the micelles the treating chemicals are already active in very small concentrations as compared with the high percentage of clay in muds.

In order to further substantiate our hypothesis, due consideration should be given to the electrical conditions at the edges in view of the fact that the stability conditions at the positive edges have been found to be less favourable than after a reversal of the charge due to anion adsorption. For polyvalent anions an increased charge density is conceivable (compare chapter 2), but in the case of divalent anions the occupation of one positive spot per anion would only result in an equal negative charge. The best line of attack seems to be to draw an analogy between the conditions at the lateral clay surface and that at the surface of simpler sol micelles viz. of both an alumina and a silica sol.

If the assumption holds that the broken Al-O-OH sheets are positively charged, an alumina sol may be considered a model for that part of the micelle. Consequently alumina and montmorillonite sols may show an analogous behaviour towards chemical treating agents.

Silica sols, on the other hand, might offer a model for the situation at the broken silica sheets. Despite their negative charge there is yet a possibility for certain anions to have a stabilizing effect on this part of the edges, as they might act as potential determining ions like iodine ions for negative silver iodide sols. In that case these anions should fit into the silica sheet lattice, which is possibly the case for metaphosphate and metasilicate anions. This possibility, which was not discussed in the earlier chapters should also be considered. It may be studied by investigating the behaviour of silica sols e.g. quartz sols towards chemical treating agents. As mentioned earlier there is, however, a third possibility: the simultaneous presence of positive and negative charges at the broken alumina and silica sheets respectively does not seem to present a very satisfactory picture for the following reason: In the intermicellar liquid of a montmorillonite sol traces of Al ions are present, which are likely to act as the potential determining ions for the broken alumina sheets. Now a negative silica sol can be shown to become positively charged if minute amounts of aluminium ions are present in the intermicellar liquid. Therefore it will certainly be possible that not only the broken alumina sheets but also the broken silica sheets are positively charged.

If so, the micelle surface of a silica sol which is positively charged by aluminium may be expected to present an adequate model for the situation at the broken silica sheets.

In view of these considerations the study of the behaviour of the model sols alumina, silica and positive silica towards the chemical treating agents may throw some light on the electrical conditions prevailing at the montmorillonite micelle edges.

Preparation and properties of alumina and silica sols

Alumina sols were prepared according to Ostwald by addition of ammonia to an $AlCl_3$ solution until a pH of about 5 is reached.

After dialysis of the alumina suspension peptization is achieved by boiling, resulting in a slightly acidic sol (pH: 5-6).

Silica sols were prepared by dispersing finely ground quartz in distilled water. The quartz had first been washed with distilled water. A small particle size dispersion was obtained by sedimentation and decantation.

The sols are milky heterodisperse suspensions of submicronic particles. The alumina micelles are positively charged, which is inferred from their electrophoretic behaviour; the silica particles are negative.

The flocculation behaviour of the alumina sols was measured by means of the centrifugal technique. This technique failed in the case of the silica suspensions, the change in floc volume being small in comparison with the sediment volume of the stable suspension. For this sol the classical visual method had to be used.

Some flocculation values for both sols are reported in Table II L.

TABLE II L

FLOCCULATION VALUES FOR ALUMINA AND SILICA SOLS

Salt	Flocculation value m.eq./1 for alumina *)	silica**)
NaCl	20-25	50-75
Na_2SO_4	0.5-0.7	25-50
$CaCl_2$	25-30	1-2

*) centrifuge method, sol concentration: 0.25%

**) visual method, sol concentration: 0.12%
observed after 48 hours' standing.

B. ANALOGIES IN RESPONSE TO CHEMICAL TREATMENT BETWEEN MONTMORILLONITE AND MODEL SOLS - PEPTIZATION MECHANISM

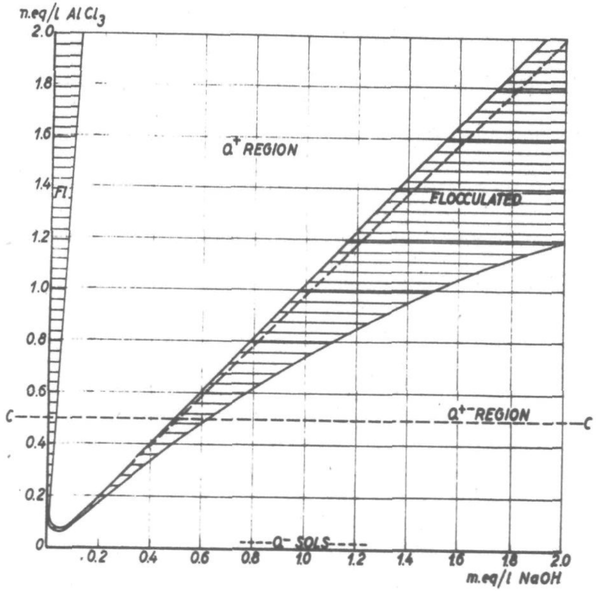
The effect of various peptizing agents on the salt flocculation of the model sols was determined. A rough inspection of the results has disclosed a certain similarity between the response to chemical treatment of model and montmorillonite sols. Where an antagonistic effect is noticed for montmorillonite sols, an analogous effect is observed in the case of some model sols. The slight sensibilization of montmorillonite sols by alkali is also found for model sols. This qualitative congruity pleads in favour of the value of the alumina and silica sols as models for montmorillonite. A detailed quantitative discussion of the stability conditions in these model sols may now offer the key to the mechanism of chemical treatment of montmorillonite sols.

The stability and charge conditions of quartz sols will be discussed first.

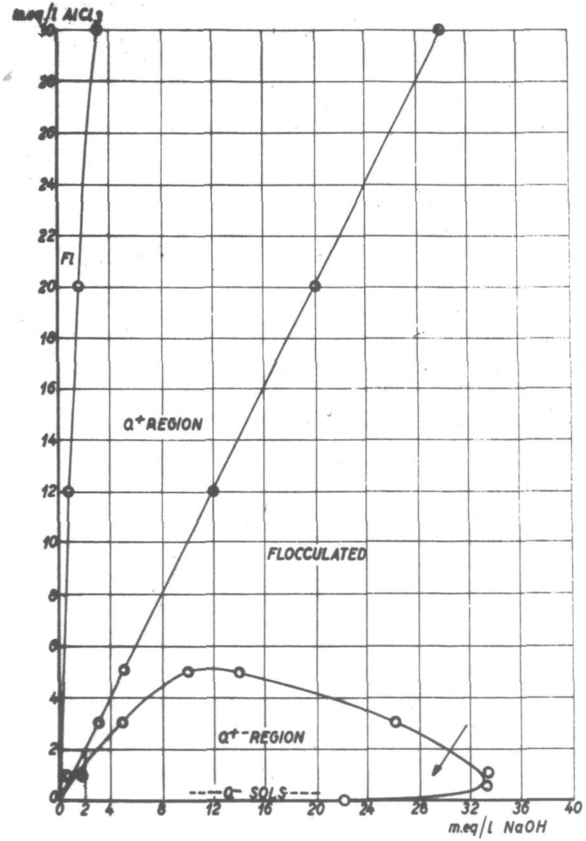
Troelstra (20) has stressed that the well-known charge reversal of negative sols by trivalent cations like Al^{+++} requires the presence of traces of alkali. Therefore he assumes that the adsorption of the product of hydrolysis of an aluminium salt, viz. $Al(OH)_3$, is responsible for the positive charge of the treated sols. On addition of more than an equivalent amount of alkali the sol again becomes negative.

Flocculation and electrophoresis experiments with $AlCl_3$--and NaOH-treated quartz sols confirm Troelstra's observations. The stability and charge conditions for this sol are presented in fig. II,17. For a dialyzed quartz sol the flocculation value for NaOH (22 m.eq./l) is marked on the abscissa and that for $AlCl_3$ on the ordinate (0.09 m.eq./l). That part of the figure which is marked by a dotted square near the origin is represented on a larger scale in fig. II,18. When following the horizontal line marked "c" in fig.II,18 in the direction of increasing NaOH concentration at the constant $AlCl_3$ concentration of 0.5 m.eq./l, it is seen that the originally flocculated sol is peptized by traces of alkali and remains stable up to an amount of alkali which is equivalent to the amount of $AlCl_3$ added (0.5 m.eq./l). In this region of stable sols the micelles proved to be positively charged. Then, on passing a narrow region of instability near the equivalence point, a stable sol is again obtained on further addition of NaOH, but now the sol proves to be negatively charged. These negative sols are finally flocculated by a larger excess of NaOH (see fig.II, 17).

By repeating the flocculation experiments with different concentrations of $AlCl_3$ the complete diagram of fig. II, 17 is obtained. With increasing concentrations of $AlCl_3$ the stability region of the positive sols widens proportionally but the region of stable negative sols becomes narrower, and no stable negative sol can be obtained with $AlCl_8$ concentrations beyond ca 5 m.eq./l.



ENLARGEMENT OF PART OF FIG.II,17 NEAR THE ORIGIN FIG. II,18



STABILITY AND CHARGE CONDITIONS OF QUARTZ SOLS ON ADDITION OF VARIOUS AMOUNTS OF $AlCl_3$ AND $NaOH$ FIG. II,17

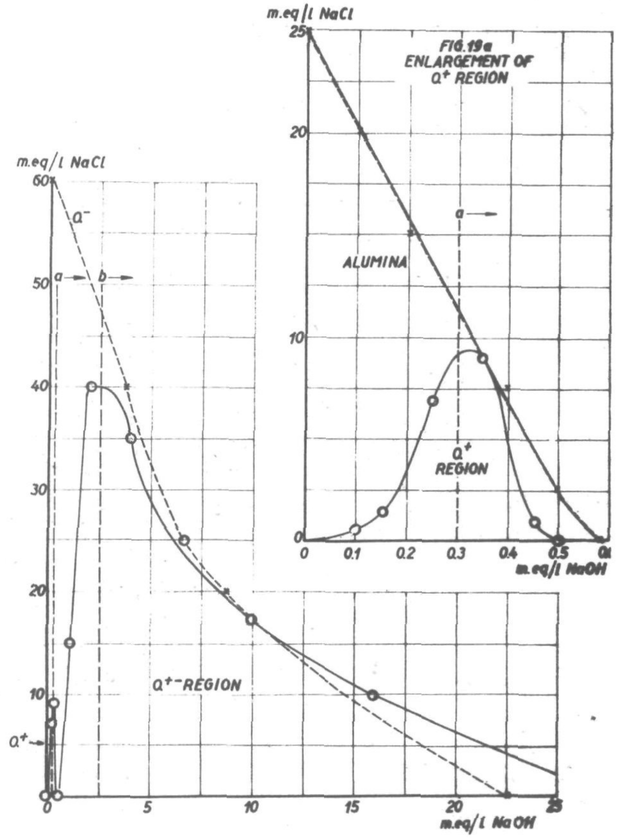
The use of the following notations may simplify the wording of the next paragraphs: the original-negative-quartz sols will be referred to as "Q^-" sols, those which are positively charged by $AlCl_3$ as "Q^+" sols and the negative sols obtained after the second reversal of the charge of the Q^+ sols as "Q^{+-}" sols. The stability regions of these different quartz sols are indicated in figs. II, 17 and 18.

The first question which may be raised is whether the micelles in the Q^{+-} and those in the original Q^-sols are identical or not; in other words, whether the aluminate anions formed on addition of an excess of NaOH to the $Al(OH)_3$-bearing positive sols will remain adsorbed to the quartz particles or become dissolved in the intermicellar liquid. Analytically this will be difficult to decide because of the small amounts of Al in the systems, but a comparison of the salt stability of the two sols may provide an answer to this question. In this respect, too, the salt stability of the Q^+ sols will be of interest.

Therefore, at a constant $AlCl_3$ concentration of 0.5 m.eq./l, the salt stability of the quartz sols was determined as a function of the NaOH concentration. The results are collected in fig. II, 19, which is thus valid for the systems indicated by the cross section "c" in fig. II, 17. Fig. II, 19a is a large-scale representation of part of fig. II, 19 in the neighbourhood of the origin.

The figures show that the salt stability of the Q^+ sols is lower than for the Q^{+-} sols. When shifting the ordinate in the diagram to the vertical line marked "a" (at the arbitrary NaOH concentration of 0.3 m.eq./l) the stability diagram of some arbitrary Q^+ sol towards NaCl/NaOH mixtures is obtained. Similarly the part of the graph located to the right of line "b" for a constant NaOH concentration of, say, 2.5 m.eq./l represents the stability conditions in an arbitrary Q^{+-} sol towards flocculation by mixtures of NaOH and NaCl.

These diagrams for a Q^+ and a Q^{+-} sol respectively may now be compared with those for either an alumina or an untreated quartz (Q^-) sol. Then it is seen that at low NaOH concentrations (in the Q^+ region) the behaviour of the Q^+ sols is very much analogous to the behaviour of alumina sols towards NaOH/NaCl mixtures (dotted line in fig. II, 19a). This suggests that aluminium hydroxide which, according to Troelstra, is adsorbed to the quartz, governs the stability conditions in the positive quartz sols.



STABILITY AND CHARGE CONDITIONS OF QUARTZ SOLS ON ADDITION OF NaCl AND NaOH

FIG. II, 19 and 19a

At higher NaOH concentrations, in the region of the Q^{+-} sols, the behaviour of the quartz sols is very much analogous to that of the Q^{-} sols (compare the dotted line in fig. II, 19), particularly with regard to the order of magnitude of the flocculation values and the slight sensibilization by NaOH. Yet the Q^{+-} sols may not be concluded to be identical with the Q^{-} sols, since they are slightly different with respect to their NaOH stability, as is demonstrated by the part of Fig. II, 17 marked with an arrow: if 0.5 m.eq./l of AlCl$_3$ is added to a Q^{-} sol containing, say, 15 m.eq./l NaOH, the additional amount of NaOH required to flocculate the sol increases from 7.5 m.eq./l for the Q^- sol to 18 m.eq./l for the Q^{+-} sol. This increase is too large to be explained as a removal of NaOH by $AlCl_3$ and must therefore be attributed to a certain stabilization of the quartz micelles by aluminate ions.

Following this comparative discussion of the model sols the flocculation behaviour of the montmorillonite sols may be analyzed. In the chapters 4 and 5 it has been shown that a slight sensibilization is observed of montmorillonite sols after alkali treatment. Further, the flocculation values for NaCl and NaOH are rather low. All this is very similar to the behaviour of quartz sols in the Q^{+-} region or in the original condition (Q^-). There is, however, no indication of a comparatively unstable region at low NaOH concentrations (the Q^+ region).

Returning to the discussion of the stability conditions of montmorillonite sols, these were assumed to be primarily governed by the double layer at the lateral surface of the micelles and the possibility has been stressed (see introduction) that the structure of this double layer might be analogous to that at the surface of a positively charged quartz micelle (Q^+ condition). If so, the lateral surface would cause a rather unstable condition of the dialyzed sol (as in the Q^+ sols), but on addition of NaOH it would become negative and thus the sol would become more stable (as in the Q^{+-} sol). The latter is indeed in line with the observations but, as was already said, the less stable region at low NaOH concentrations is not apparent in the experiments. At first sight it might therefore be concluded that the electrical condition at the lateral surfaces in the dialyzed sol is *not* the same as that at the surface of the Q^+ sol micelles, but rather of the Q^{+-} or even of the Q^- micelles. It is believed, however, that this conclusion of identical structure of negative quartz and lateral surface in the dialyzed sol is wrong, for the following reasons:

In the first place, that the region of low stability and the first flocculation point with small amounts of NaOH is lacking may well be a result of the presence of a second stability factor in the montmorillonite sols viz. the layer surface potential.

Furthermore, besides the various supports for the assumption of a positive edge potential, there are some even strong indications that this originally positive lateral surface charge is converted into a negative charge on addition of NaOH, just like the conversion of a Q^+ into a Q^{+-} sol.

This may be concluded from a comparison of the effect of NaOH and NaCl on the yield stress of dialyzed concentrated WB-Na sols. In continuation of the experiments described in chapter 5 the yield stress of 3% WB-Na sols (dialyzed) was determined after addition of increasing amounts of NaOH. The results are collected in table II, M together with the previously reported data for NaCl.

TABLE II M

EFFECT OF ALKALI AND OF SALT ON THE YIELD STRESS OF 3% DIALYZED WYOMING BENTONITE SOLS (SODIUM FORM)

Electrolyte concentration m.eq./l	Initial yield stress dynes/cm^2		Yield stress after 30' dynes/cm^2	
	NaCl	NaOH	NaCl	NaOH
0	80	80	80	80
0.2	30	55	30	55
0.5	20	40	20	40
1.0	10	25	10	25
1.5	5	15	5	15
2.0	0	10	0	10
3.0	5	0	10	0
5.0	7	0	15	0
10	7	0	100	0
15	50	0	210	0
20	140	0	250	0

The initial decrease of the yield stress on addition of NaCl up to a concentration of ca 3 m.eq./l has been attributed to a simultaneous decrease of the opposed double layer potentials on layer and lateral surfaces, resulting in a reduction of the electrical attraction between these surfaces. As soon as the double layer potentials have become so small that the micelles will associate due to the prevailing Van der Waals attraction forces, the thixotropic stiffening becomes very pronounced. In the case of NaOH, on the other hand, the initial decrease of the yield stress is not followed by a thixotropic stiffening: the 30' yield stress remains negligibly small up to NaOH concentrations which are near to the flocculation value. This may be explained by the assumption that the edges become negative with small amounts of NaOH. Thus edge-to-edge and edge-to-surface association of the micelles leading to the formation of rigid structures is avoided.

In this respect it is also interesting to note that the addition of NaOH to FB-Na sols does not result in a decrease of the electrophoretic mobility, as is the case on addition of NaCl. This may also be seen as a result of the conversion of the positive edge charge into a negative charge, which may compensate the effect of the decrease of the negative surface charge on the electrophoretic mobility.

Summarizing these observations the following interpretation of the behaviour of montmorillonite sols towards the flocculating action of mixtures of NaCl and NaOH may be offered: The salt stability of the dialyzed sol is mainly dictated by the stability of the surface double layer, which compensates the low stability of the lateral surface and even the further decrease of the stability at this point on addition of traces of NaOH. At higher NaOH concentrations the lateral surface which obtains the character of a Q^{+-} sol governs the stability of the montmorillonite sols: their behaviour is characterized by a sensibilization curve *).

Finally, the interpretation of the *effect of peptizers* on montmorillonite sols will be discussed.

The effect of chemical treating agents on montmorillonite sols may be analyzed from a comparative study of their activity towards the model sols. First the effect of polymetaphosphate may be discussed with reference to figure II, 20 where the salt flocculation values are plotted (as a function of the amount of phosphate added) for montmorillonite, alumina and quartz sols.

The response of a positive quartz sol, containing 0.5 m.eq/l $AlCl_3$ and 0.3 m.eq./l NaOH, to metaphosphate addition is represented in figure 20 c. The salt stability of the Q^+ sol is 10 m.eq./l, which is plotted on the ordinate. On addition of 0.1 m.eq./l of polymetaphosphate the sol is flocculated but becomes stable and negative on further addition of phosphate. The salt stability of the negative sol is rather high, maximum 250 m.eq./l. With more polymetaphosphate the salt stability decreases again and the quartz is finally flocculated with 160 m.eq./l of the phosphate. Qualitatively this behaviour of positive quartz sols is similar to that of alumina sols, as shown by fig.20 b. The positive alumina sol is flocculated with 0.1 m.eq./l of polymetaphosphate but becomes stable and negative on further addi-

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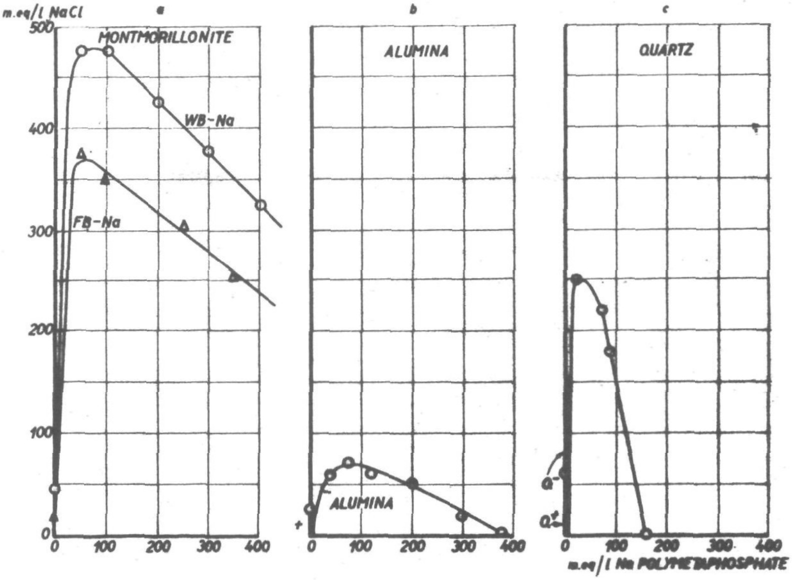
*) A further analogy between the montmorillonite and quartz sols with respect to alkali treatment is that neither montmorillonite sols nor quartz sols are flocculated with large amounts of ammonia.



STABILIZATION OF MONTMORILLONITE, ALUMINA AND QUARTZ SOLS TOWARDS NaCl BY Na POLYMETAPHOSPHATE

FIG. II, 20 a, b and c

tion of phosphate, exactly like the Q^+ sols. This is another support of the view that the stability of the Q^+ sols is governed by the adsorbed aluminium hydroxide.

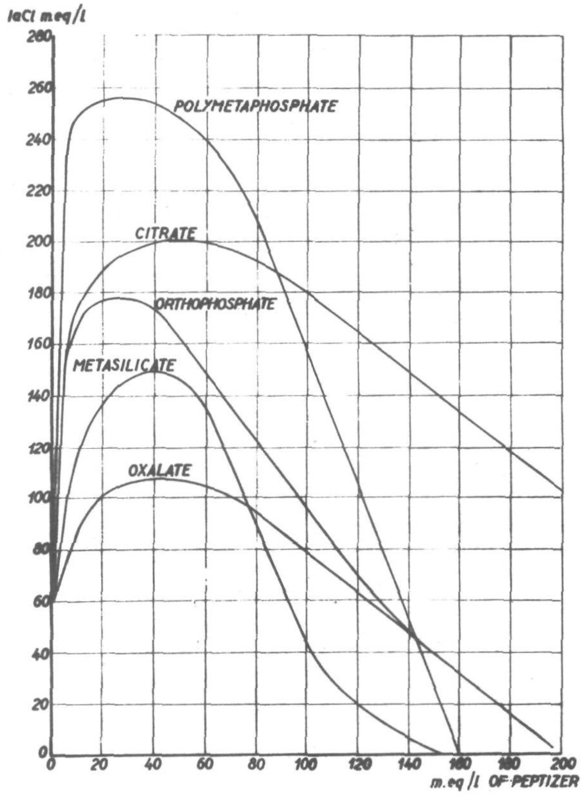
The conversion of the positive charge of alumina and positive quartz sols into a negative charge by polymetaphosphate may be seen as an adsorption of the polyvalent metaphosphate anions to the micelles by means of an aluminium ion link. This is conceivable since it can be shown from conductometric titration that aluminium ions form complex ions with the metaphosphate anion. The flocculation antagonism with polymetaphosphate and NaCl for montmorillonite sols and alumina or positive quartz sols is indeed very similar (compare fig. 20a) except for the lack of the first flocculation point at 0.1 m.eq./l of polymetaphosphate. Again, as discussed above in the case of NaOH, the point of zero charge at the lateral surface at 0.1 m.eq./l of polymetaphosphate may not show up in the experiments owing to the second stability factor in montmorillonite sols. Moreover, the behaviour of the rigid concentrated WB-Na sols towards peptizers is analogous to that towards NaOH: the initial decrease of the yield stress on addition of peptizers is also followed by a region of zero yield stress, which points to a charge reversal at the lateral surface. Furthermore, the increase of the electrophoretic mobility on addition of polymetaphosphate, which was discussed in chapter 2, points in the same direction.

Although the conclusive force of the observed analogies seems strong, another analogy has been observed which leaves room for a different interpretation of the peptization antagonism: There is a close congruity between the polymetaphosphate/NaCl flocculation curve for the Q^+ sol beyond the phosphate concentration where the quartz has become negative, and the curve for the originally negative quartz sol containing no aluminium (Q^- sol, fig. II, 20 C). This means that polymetaphosphate stabilizes these negative (Q^-) quartz sols. The observed antagonism may be partly an ion antagonism and partly a peptization antagonism. Therefore, polymetaphosphate anions may stabilize quartz sols without being linked to the micelle by aluminium thus acting as potential determining ions. Consequently the stabilization of the positive quartz sol may also be seen as a result of the dissolution of the adsorbed aluminium hydroxide in the intermicellar liquid by complex formation, leaving behind a negative quartz sol which is peptized by polymetaphosphate.

Returning to the montmorillonite micelle, possibly both explanations hold for the lateral surface: the aluminium link theory may be applicable to the broken octahedrical Al-O-OH sheets, whereas the stabilization of the broken silica sheets may be explained by removal of adsorbed alumina and subsequent stabilization of the exposed negative silica surface by polymetaphosphate. Then the montmorillonite stabilization may be seen as a superposition of the two effects.

Turning to other peptizers, their total effect on montmorillonite sols may be predicted from the separate effects on the broken octahedrical and tetrahedrical sheets which may be derived from their activity towards alumina and quartz sols respectively.

As in the case of polymetaphosphate, the stabilizing effect of sodium citrate, metasilicate, oxalate and orthophosphate on Q^+ sols is identical with that for Q^- sols in the region of peptizer



FLOCCULATION OF Q$^-$ SOLS WITH NaCl AND VARIOUS PEPTIZERS FIG. II, 21

concentrations where the positive quartz sol has been converted into a negative sol. Fig. II, 21 shows the flocculation curves for a Q$^-$ sol (or a converted Q$^+$ sol) for the various peptizers. The Q$^-$ sols being considered a model for the condition of the exposed silica sheets at the lateral surface at not too low concentrations of peptizer, the sequence of the activities of the various peptizers observed for quartz sols may equally apply to the silica part of the lateral surface. This sequence and the heights of the maxima (expressed in m.eq./l of salt) is the following:

> polymetaphosphate (260) > citrate (200) > orthophosphate (180) > metasilicate (150) > oxalate (110).

For the FB-Na sols, however, the following sequence and maximum salt stabilities are observed:

polymetaphosphate (375) > citrate = metasilicate (200)
> oxalate = orthophosphate (50).

The differences between the observed sequences for both sols may be a result of the different contributions to the total effect by the exposed octahedrical sheets. The latter contribution may be derived from the behaviour of alumina sols towards the various peptizers. As mentioned above, the conversion of positive alumina sols into more stable negative sols by polymetaphosphate makes it clear that for this peptizer both the broken silica and alumina sheets are stabilized, resulting in a large total effect. The opposite is found for oxalate and orthophosphate: these electrolytes are unable to peptize positive alumina sols to negative sols and this may be the reason for the small total effect on FB-Na sols, despite the stabilizing effect of these peptizers on the silica part of the lateral surface. Like polymetaphosphate, metasilicate does have a stabilizing effect on positive alumina sols, which are converted into negative sols, and this explains that metasilicate stabilizes FB-Na sols. That its activity on FB-Na is somewhat smaller than that of polymetaphosphate is readily explained by the lower activity on quartz sols, and thus on the silica part of the lateral surface.

Although citrate has no stabilizing effect on alumina sols either, it is more active on montmorillonite sols than orthophosphate, despite the fact that both peptizers have nearly the same effect on quartz sols.

Since the above explanation of the peptization mechanism of montmorillonite sols and various peptizers is quite general, it should equally apply to some other montmorillonite. However, in chapter 5 it has been shown that the response to chemical treatment is different for FB-Na and WB-Na sols. Thus the question arises how these individual characteristics of the FB-Na and WB-Na should be explained. In the case of the WB-Na sols the following sequence for the various peptizers was observed:

polymetaphosphate = citrate (475) > oxalate (425)
> orthophosphate (300) > metasilicate (175).

It could be shown that there is an important difference between the chemical compositions of the French and Wyoming bentonite: the latter contains about three times as much ferric ion in octahedrical position than the former (table II E of chapter 1). Therefore the broken octahedrical sheets in the WB-Na sols, to a certain extent, may display ferric hydroxide sol characteristics and the intermicellar liquid may contain more ferric ions than that of a FB-Na sol. Now, the previous discussions on the charge reversal of silica sols with NaOH or peptizers in the presence of aluminium ions apply with equal force to ferric ions. Therefore the response of the silica sheets to peptizers will be analogous for both FB-Na and WB-Na sols, but the response of the octahedrical sheets in the WB-Na sols may differ from that of the FB-Na sols, since the reaction of ferric hydroxide sols and aluminium hydroxide sols to peptizers is different. Contrary to the $Al(OH)_3$ sols, $Fe(OH)_3$ sols are converted into stable negative sols by *all* the peptizers mentioned above, thus including oxalate, orthophosphate and citrate and this may explain why in the case of WB-Na sols all peptizers have a reasonable effect. The resulting total effect seems to be governed by the stability conditions of the broken silica sheets: apart from oxalate the sequence of the peptizers for WB-Na sols is the same as that for quartz sols.

Semi-quantitatively speaking, therefore, the picture given is well balanced. It is thought, however, that the electrical conditions at the lateral surfaces of the montmorillonite micelles are too delicate to allow of a detailed quantitative interpretation.

Summarizing the above theories, the analogy study has resulted in a reduction of the more complicated problem of clay stability to the simpler one of the stability of quartz and alumina (ferric hydroxide) sols. This is, of course, only the first step to a complete analysis of the peptization mechanism of clays. The problem is now mainly replaced by the more general one of the response of silica and alumina sols towards chemical treating agents.

Incidentally, during the above discussions, some possible interpretations of the peptization mechanism in these sols were indicated. A more detailed account may be given below:

a. Peptization of quartz sols

The traces of aluminium or ferric hydroxide on the surface of the positive quartz sol particles (or the broken tetrahedrical silica sheets in montmorillonite) were assumed to be removed by the peptizers leaving behind a negative quartz sol, which is stabilized by the peptizers. The antagonistic effect of mixtures of these peptizers and NaCl on negative quartz sols may for the greater part be an ion antagonistic effect: this is suggested by the sequence of the activities of the various peptizers which was found to be polyvalent metaphosphate > trivalent citrate and orthophosphate > divalent metasilicate and oxalate. If the total sodium ion activities in the mixtures are calculated neglecting the ion dimensions, the ion antagonism does not account for the total antagonism: The sodium ion activity in the maxima of the curves still remains about twice as high as at the flocculation value for the untreated sol. Possibly, therefore, part of the antagonism should be attributed to a peptization antagonism.

b. Peptization of aluminium hydroxide or ferric hydroxide sols

The stabilization of aluminium and ferric hydroxide sols (or the broken octahedrical sheets in montmorillonite) was seen as a conversion of these positive sols into more stable negative sols by anion adsorption via an Al or Fe ion link. This point of view should be defined more precisely. Apart from the flocculation experiments in alumina sols in the presence of polymetaphosphate which have been described earlier (fig. II, 20 b), the following experiments were carried out with freshly precipitated alumina for all peptizers under discussion. A solution of 10 m.eq./l of $AlCl_3$ was boiled for ½ h with 9 m.eq./l of NaOH. The precipitate of aluminium hydroxide obtained appeared to become peptized on addition of traces of all peptizers, but it is again flocculated by less than 1 m.eq./l of these chemicals. At still higher concentrations the hydroxide is again peptized by metasilicate and polymetaphosphate, but not by oxalate, citrate or orthophosphate. For metasilicate the second peptization is observed around 7 m.eq./l, but this is already followed by a second flocculation around 15 m.eq./l. For polymetaphosphate the second peptization range is much wider, viz. from 0.3 to 350 m.eq./l.

In the case of freshly prepared ferric hydroxide (using the same procedure as described above for alumina) a second peptization range is observed for all peptizers. The ranges are:

10-50 m.eq./l	for orthophosphate
20-50 m.eq./l	for oxalate
3-300 m.eq./l	for metasilicate

5 to more than 500 m.eq./l for citrate and
1 to more than 500 m.eq./l for polymetaphosphate.

This remarkable behaviour may be interpreted on the basis of the following assumption: (example: aluminium hydroxide and metasilicate)

i. with the first traces of metasilicate the hydroxide becomes negative and stable by adsorption of the anion to the surface by means of an Al link forming a double layer, which may be represented by the formula:

$$(Al_2O_3,H_2O)\ Al\text{-}SiO_3^-\ Na^+$$

ii. with more metasilicate, aluminium metasilicate is formed, which is insufficiently dissociated to form a stabilizing double layer and the hydroxide is flocculated.

iii. the aluminium metasilicate at the micelle surface is peptized by an excess of metasilicate anions, acting as potential-determining ions and the sol is peptized for the second time.

iv. with a large excess of metasilicate the sol is again flocculated, mainly due to the increasing sodium ion concentration.

An analogous interpretation may be given for the other peptizers. Their effectivity would, according to this interpretation, depend on the ability of their anions to act as potential-determining ions for the aluminium salts.

These suggestions regarding the mechanism of the response of aluminium or ferric hydroxide and quartz sols to chemical treating agents are in part speculative. A full account of the stability conditions can only be expected from an extensive fundamental investigation of these sols.

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CHAPTER 7

THE PEPTISATION OF MONTMORILLONITE BY TANNINS

On the basis of the analysis of the peptisation of montmorillonite by a number of salts as described in the preceding chapter it may now be attempted to solve the problem of the mechanism of tannin treatment.

A. TYPES OF TANNIN-TREATED MUDS

Tannins are widely used for the treatment of muds. Several types of tannin-containing muds may be distinguished:

i. Muds to which a small amount, a few tenths per cent, of a tannin is added in alkaline solution. Some other conventional treating chemical, e.g. sil, is often added simultaneously (21).

ii. So-called red muds, containing a relatively high percentage of quebracho tannin (0.5-2%) in strongly alkaline solution (22).

iii. Lime red muds, which are red muds to which solid lime has been added (23).

    The red muds are known to stiffen at elevated temperatures, which limits their applicability to medium depth operations. It has recently been discovered that this effect of heating can be avoided by subsequent lime treatment. Therefore it has become common practive to convert the red mud to a lime red mud at a certain critical depth.
    A feature of both red muds and lime red muds is that they have formation-conserving properties.

iv. Acidified muds containing tanning agents (24). This is a less common type, which will not be discussed here.

B. SEARCH FOR A MODEL COMPOUND FOR TANNINS

The study of the mechanism of the effects of tannins on clay suspensions, and particularly of the paradoxical beneficial effect of subsequent lime treatment, offers a rather complex problem.

In the first place, the composition and structure of natural tannins like quebracho extract are not known with certainty. Therefore we preferred first to investigate the effect of a simpler model compound. Since the tannins are polyphenolic compounds the model substance should be a phenol exhibiting an analogous effect on clay suspensions.

Another complicating factor is the sensitivity towards oxidation, which is common to both tannins and phenols. In the search for a model phenol, therefore, the activity of phenols and natural tannins should be compared while under nitrogen, - so as to avoid oxidation - and when exposed to the air.

1. *Tannin-alkali treatment*

The liquefaction of concentrated clay suspensions being the primary effect of treating chemicals like alkaline tannin solutions, the choice of a model phenol was guided by observations of their activity in this respect.

The liquefaction of bentonite suspensions by alkaline tannin treatment appears to be mainly a matter of decreased thixotropy: the thixotropic stiffening is much slower for the treated than for the original suspension (in practice this amounts to an appreciable decrease in Bingham yield stress of the system). Therefore the ratio of the setting times of treated and original suspension may be considered a suitable criterion for a comparative study of the effectiveness of various tannins and model phenols. The determination of the setting times can be carried out very conveniently by means of the Freundlich reversed tube method, using 5% bentonite suspensions (FB). Since the setting time of the original suspension was found to be 45'', a setting time ratio of 1000 indicates a setting time of about 12 hours for the treated suspension.

In fig. II, 22 the activity of various compounds in terms of setting time ratios are plotted for three tannin-phenol concentrations and various amounts of NaOH (expressed as equivalent ratios of tannin: NaOH). Data are given for a) quebracho, b) the cold water soluble fraction of quebracho*) (= the ether extract

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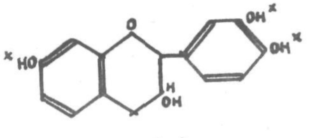
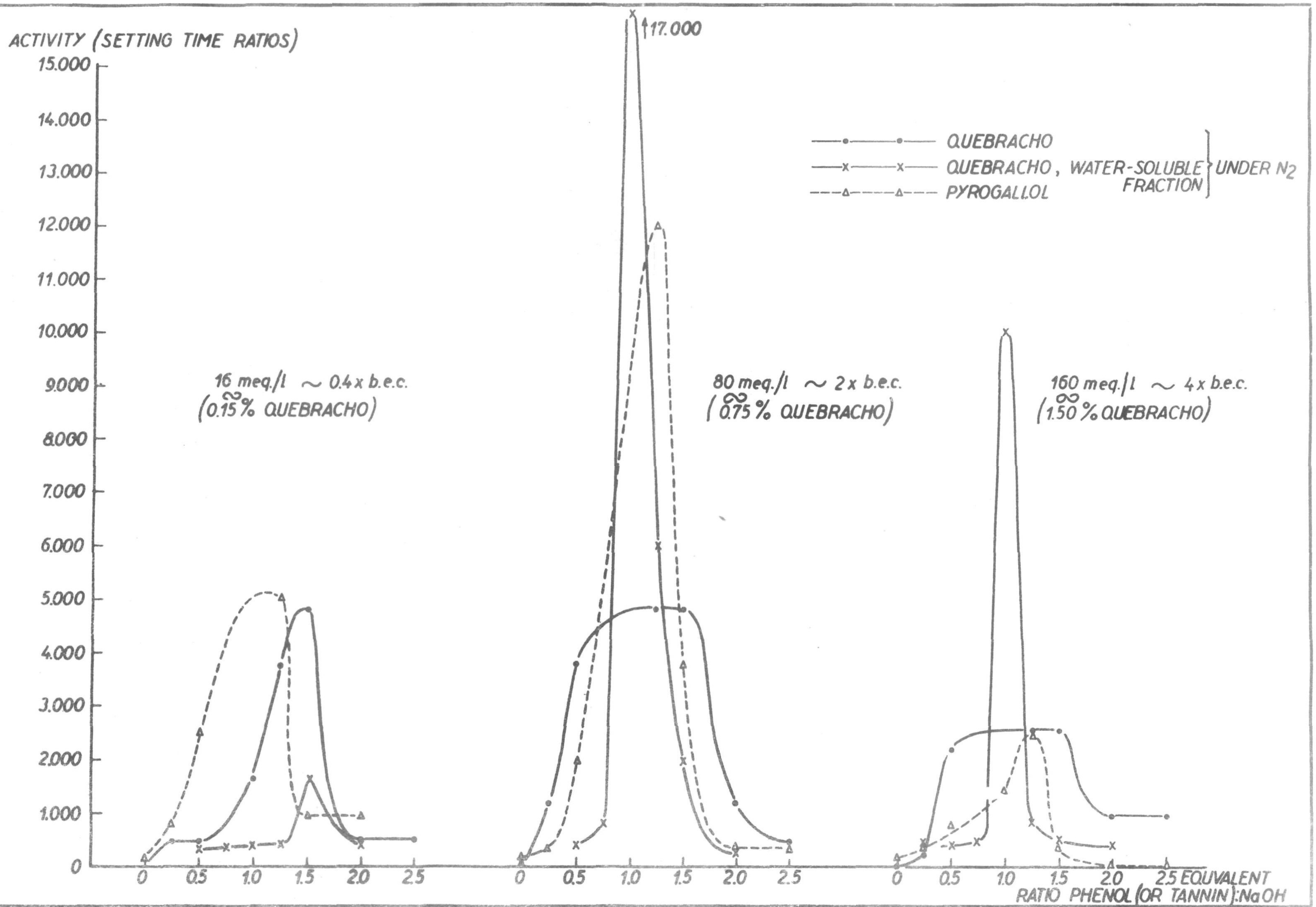
*) According to Freudenberg, quebracho is a condensation product of the catechin:



The three phenolic OH groups $^{(x)}$ are not affected by the condensation. Thus the equivalent weight of quebracho may be taken at 1/3 of the monomeric molecular weight.
The equivalent weight of the water-soluble fraction of quebrancho could be checked by conductometric titration of a calcium hydroxide solution with a strong quebracho solution.



ACTIVITY OF PHENOL (OR TANNIN) + Na OH ON 5% BENTONITE SUSPENSIONS

FIG. II, 22

which contains the low molecular weight condensation products only) and for c) pyrogallol (1,2,3-oxybenzene).

The experiments were carried out under nitrogen.

Fig. II, 22 shows that under these conditions the optimum activity of quebracho amounts to about 5000. (For comparison it may be mentioned that the optimum activity of Na metaphosphate is about 1300). The optimum ratio between quebracho and NaOH covers a rather wilde range (0.5-1.5).

A more pronounced effect is noticed for the cold water soluble fraction of quebracho. Although the effectiveness at low concentrations is small, its optimum activity at higher concentrations is as great as 17,000. The optimum quebracho:NaOH ratio is much more critical in this case (about 1).

The behaviour of the systems treated with the triphenolic compound pyrogallol is very much analogous to that of systems treated with the water soluble fraction of quebracho, although the maximum effect is somewhat smaller. The optimum occurs at the same tannin concentration: 80 m.eq./l (for quebracho 80 m.eq./l corresponds with a wt. concentration of about 3/4%).

The results are valid when oxidation is excluded. When exposed to the air the activities are much smaller, amounting to 200-400 for quebracho and to 100 only for pyrogallol.

The following phenols have been found to be inactive: phenol, resorcinol and hydroquinone and the trivalent symmetrical phenol phloroglucinol. "Ordinary" tannin and gallic acid are less active than quebracho: under nitrogen their optimum activity was found to be 1000-1700.

Alkaline pyrogallol may thus be concluded to be a suitable model compound when investigating the effect of tannins on montmorillonite sols, provided that oxidation is avoided in the experiments.

2. *Lime-tannin treatment*

Additional experiments were carried out in order to check whether bentonite suspensions containing pyrogallol or any other simple phenolic compound show the same sensitivity towards the addition of lime as tannin-treated bentonite.

The activity of various phenols and tannins in the presence of alkali and lime was tested by comparing the thixotropic stiffening time of a treated bentonite suspension with that of the original suspension. It was found that the addition of lime greatly enhanced the activity of the tannins in this respect. Suspensions of bentonite which are treated with sufficient quebracho, NaOH and lime no longer stiffen, even after several months' storage. Therefore no figure was given for the stiffening time ratio but the activity of the chemicals was judged from their ability to produce permanent liquefaction.

The lime treatment was carried out by heating the suspensions containing tannin or phenol with lime for 20 minutes at 70°C either under nitrogen or exposed to the air. The results are summarized in table II N. The bentonite concentration was again 5%. The relative concentrations of the various chemicals are expressed in equivalent ratios. The state of suspension after three months' storage is indicated as solid (s), liquid (l) and semi-liquid (sl).

The concentration of all phenols mentioned in table II N was 160 m.eq./l, the concentration of the other compounds are given as fractions of the phenol concentration which is taken as unity.

TABLE II N

EFFECT OF LIME TREATMENT

Tannin or phenol	conc.	conc. NaOH	concentration of $Ca(OH)_2$						in N_2 or air
			0	0.38	0.76	1.06	1.52	2.28	
quebracho	1.0	0.05	s	s	s	s	s	s	N_2
		0.55	s	s	l	sl	s	s	N_2
		1.05	s	s	l	sl	s	s	N_2
		1.55	s	s	l	sl	sl	s	N_2
		1.05	s	s	s	l	l	sl	air
gambir	1.0	1.00	s	s	sl	l	sl	s	N_2
		1.00	s	s	s	l	l	l	air
pyrogallol	1.0	1.00	s	s	s	sl	l	s	N_2
		1.00	s	s	s	s	s	s	air
tannin	1.0	1.00	s	s	sl	l	sl	s	N_2
		1.00	s	s	s	s	s	s	air
gallic acid	1.0	1.00	s	s	s	l	sl	s	N_2
		1.00	s	s	s	s	s	s	air

In addition to the results mentioned in the table the following phenols were found to be inactive: phenol, hydroquinone, resorcinol, pyrocatechol and phloroglucinol.

The results show that the effect of pyrogallol under nitrogen is comparable with that of the tannins investigated, although the optimum lime content is different for various compounds. When exposed to the air only gambir and quebracho remain active, the optimum lime content is, however, shifted to a higher value. The activity of tannin and gallic acid as well as that of pyrogallol disappears on oxidation.

Considering the results obtained with this still limited number of natural tannins and phenols, the activity of phenolic compounds on mud both in combination with alkali and alkali + lime, seems to be limited to those containing at least 3 phenolic OH groups, two of which should be adjacent.

It may be concluded that also for the study of lime red mud behaviour, pyrogallol will be a suitable model compound.

C. BEHAVIOUR OF RED MUDS AND LIME RED MUDS FROM BENTONITE

The most essential features of red mud and lime red mud behaviour may be summarized as follows:

Alkaline tannin treatment of a bentonite suspension results in a certain liquefaction as shown by an increased thixotropic stiffening time, whereas the addition of lime to this system results in permanent liquefaction.

Moreover, the effect of alkaline tannin treatment is partly eliminated by heating, whereas the rheological properties of the limed systems are not impaired.

In the following table (II,0) these facts are demonstrated by yield stress determinations with the modified Stormer viscometer.

TABLE II 0

YIELD STRESSES OF BENTONITE SUSPENSIONS AFTER TANNIN TREATMENT

Treatment of 5% bentonite suspension			c not heated h heated for 16 h at 70°C	initial yield stress dynes/cm^2	30 min. yield stress dynes/cm^2
quebracho m.eq./l	NaOH m.eq/l	$Ca(OH)_2$ m.eq/l			
-	-	-	c	21	45
			h	29	31
100	200	-	c	4	14
			h	11	40
100	200	285	c	4	4
			h	3	3

These are the main facts requiring an explanation from a colloid chemical point of view. In the next section the mechanism of alkaline tannin treatment will be dealt with, using pyrogallol as a model. In view of the pronounced effect of calcium on the properties of these systems, the presence of calcium had to be carefully avoided; thus, sodium montmorillonite sols were used.

Finally the mechanism of the effect of lime on the tannin or pyrogallol treated systems will be discussed.

D. THE MECHANISM OF TANNIN-ALKALI TREATMENT

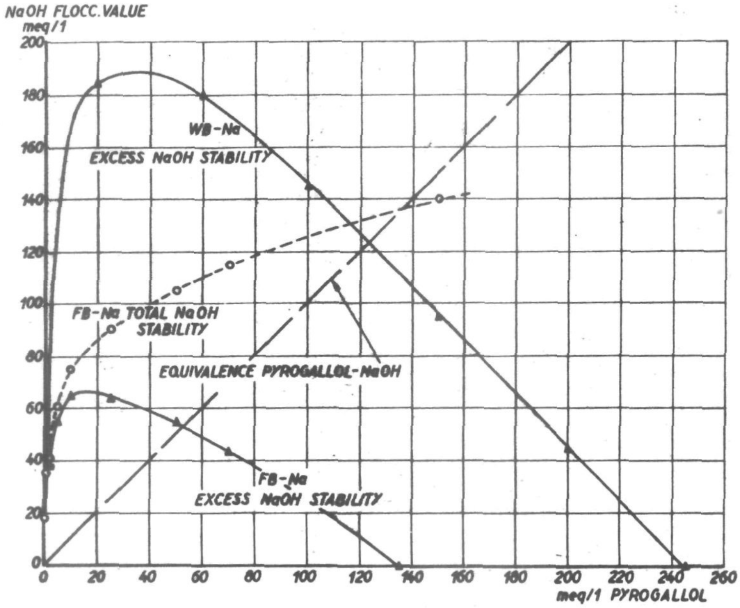
First the stability conditions in FB-Na and WB-Na sols were studied as a function of the pyrogallol or quebracho content.

In order to avoid oxidation during the flocculation experiments with the centrifuge, they were carried out under oxygen-free nitrogen, which is particularly important when working with pyrogallol in alkaline solution. A convenient technique, suggested by G.K. Jones, was used: the centrifuge tubes are closed with rubber caps and the liquids are supplied under nitrogen pressure from a burette, the tap of which is drawn out in a sharp point piercing the cap like an injection needle. The tubes are rinsed beforehand with oxygen-free nitrogen in the same way.

Fig. II, 23 shows the NaOH flocculation value for both FB-Na and WB-Na sols as a function of the amount of pyrogallol added. The dotted line for FB-Na refers to the total NaOH stability, the solid lines for both FB-Na and WB-Na refer to the excess of NaOH over the amount required for complete pyrogallate formation, in other words they refer to the NaOH stability as a function of the amount of sodium pyrogallate added to the sol.

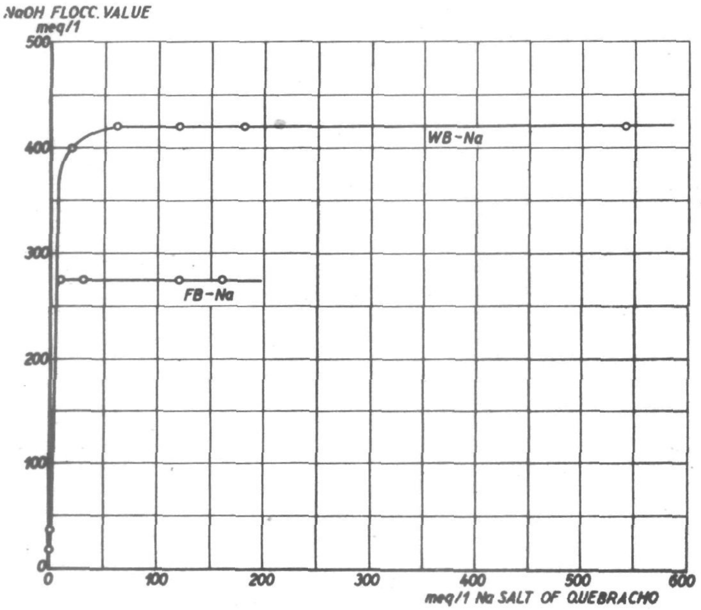
With pyrogallol alone no flocculation is observed. The flocculation value towards *sodium pyrogallate* for the two sols are ca 135 and 245 m.eq./1, respectively. The pyrogallate appears to stabilize the sols with respect to flocculation by NaOH: the solid lines show a certain antagonistic effect indicating peptisation of the sol by pyrogallate, although part of the effect will be due to ion antagonism.

Fig.II, 24 shows the results of analogous experiments, using quebracho instead of pyrogallol. The same trends as observed in the case of pyrogallol are found, but the antagonistic effect is much larger than for pyrogallate, whilst the sols are not flocculated by large amounts of quebrachate.



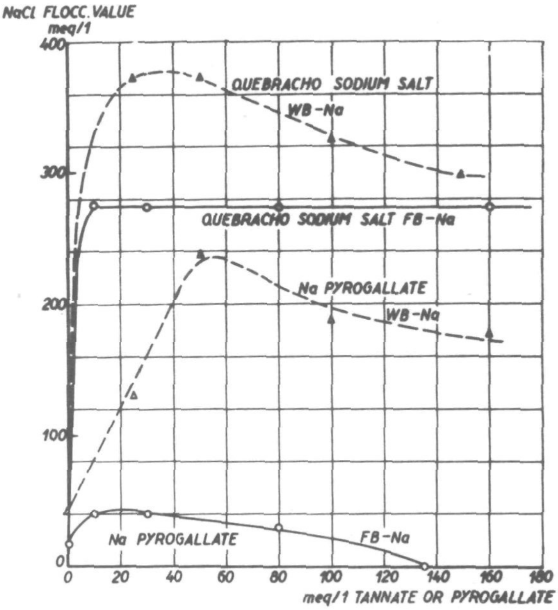
STABILISATION OF Na MONTMORILLONITE SOLS BY PYROGALLOL TOWARDS FLOCCULATION BY NaOH

FIG II, 23



STABILISATION OF Na MONTMORILLONITE SOLS BY QUEBRACHO-SODIUM SALT TOWARDS FLOCCULATION BY NaOH

FIG II, 24



STABILISATION OF FB-Na AND WB-Na MONTMORILLONITE SOLS TOWARDS FLOCCULATION BY NaCl BY PYROGALLATE OR QUEBRACHO Na SALT

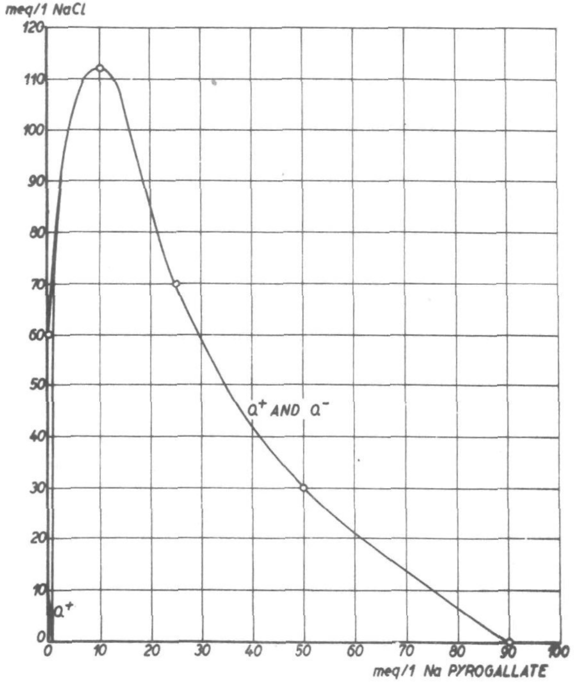
FIG II, 25

Fig. II, 25 gives some NaCl flocculation values for FB-Na sols after peptisation with various amounts of pyrogallate and quebrachate. It is seen from these graphs that the salt flocculation values of the treated systems are of the same order as the NaOH flocculation values. Also the antagonism pyrogallate-NaCl is much smaller than that of quebrachate-NaCl.

Qualitatively the observed stabilisation is well in line with the favourable effect of alkaline tannin treatment on concentrated suspensions as could be expected from previous experience with other chemicals. Quantitatively an exact parallelism is lacking between the stability conditions in the dilute sodium montmorillonite sols and the thixotropic behaviour of the concentrated raw bentonite suspensions after treatment (see under B 1). In the latter systems an optimum effect was observed at a tannin or phenol concentration of ca 80 m.eq./l, but in the dilute sols there is no indication of any optimum stability at this concentration. It should be borne in mind, however, that the raw bentonite contains calcium. Therefore, to some extent the systems may show lime red mud behaviour which may be responsible for the observed discrepancy between the results in the concentrated raw bentonite suspension and in the dilute purified sodium montmorillonite sols. This interpretation is supported by the fact that with concentrated WB-Na sols which enable the study of thixotropic effects, the optimum concentration of tannin for maximum stiffening time is found to be of the order of 16 m.eq./l of tannate.

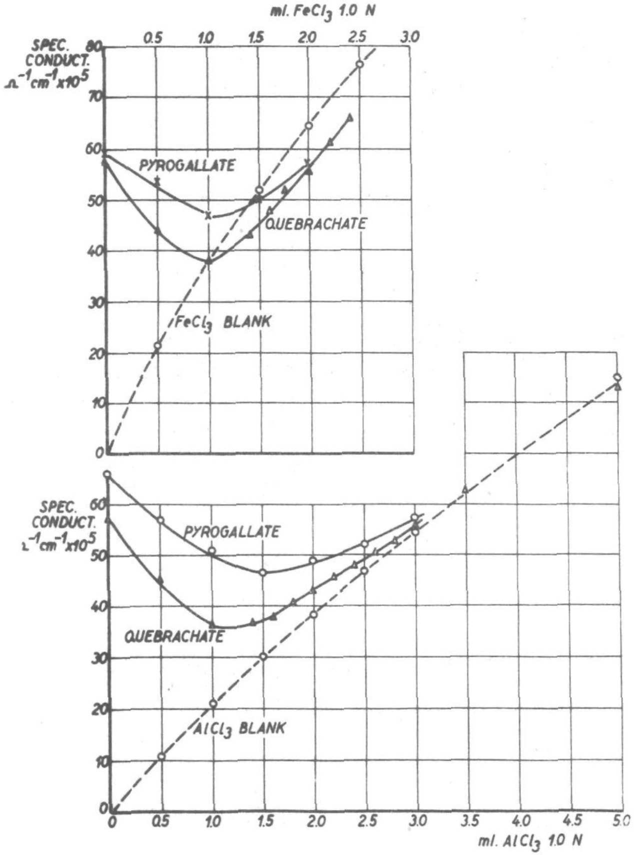
In chapter VI, dealing with the analogies between the flocculation of montmorillonite and some model sols, the peptisation mechanism was analyzed as the combined action of the various peptisers on both the broken tetrahedrical silica and octahedrical alumina or ferric hydroxide sheets at the lateral surface of the clay particles. The chemicals which stabilize both alumina or ferric hydroxide sols and quartz sols are found to be the best peptisers for montmorillonite. The same was found to apply to the peptiser Na pyrogallate or quebrachate. The stabilising effect of pyrogallate on both positive and negative quartz sols is demonstrated by Fig. II, 26. Again the peptiser converts the positive quartz sol Q^+ into a negative sol which is in turn peptised by pyrogallate like the original negative quartz sol Q^-. The activity of pyrogallate is of the order of that of oxalate. Unfortunately the dark colour of quebrachate prevented the determination of the effect on quartz sols where flocculation must be detected visually. Furthermore pyrogallate is able to peptise aluminum and ferric hydroxide. The "second peptisation range" (compare chapter 6) is 2-150 m.eq./l for aluminum hydroxide and from 1 to more than 500 m.eq./l for ferric hydroxide. The same applies to quebrachate, its stabilisation range for both aluminum and ferric hydroxide sols seems to be even wider than in the case of pyrogallate. The assumption that the peptiser anion is linked to the octahedrical sheets by means of an aluminum or ferric ion may equally apply to pyrogallate and quebrachate, since it can be shown from conductometric titration that these compounds are able to form complexes with these cations (see Fig. II, 27).

It is interesting to compare the effect of pyrogallate with that of the symmetrical trioxybenzene, phloroglucinol, which was found to be inactive on bentonite suspensions (section B-1). It was observed that phloroglucinolate is unable to stabilise aluminum, ferric hydroxide or quartz sols and this is in accordance with its lacking activity on montmorillonite sols.



STABILISATION OF Q^+ AND Q^- SOLS BY* Na PYROGALLATE

FIG II, 26



CONDUCTOMETRIC TITRATION OF 50 ml 0.05 N Na PYROGALLATE AND Na QUEBRACHATE WITH 1.0 N $AlCl_3$ OR $FeCl_3$

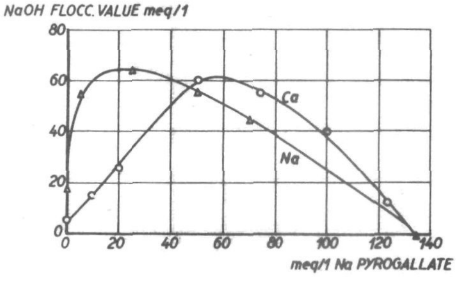
FIG II, 27

Finally the quantitative differences between the activity of pyrogallate and quebrachate may - in analogy with polymetaphosphate - be ascribed to a larger ion antagonistic effect and probably to a larger charging effect on the octahedrical sheets by the high molecular poly condensed quebrachate.

E. THE MECHANISM OF LIME-TANNIN TREATMENT

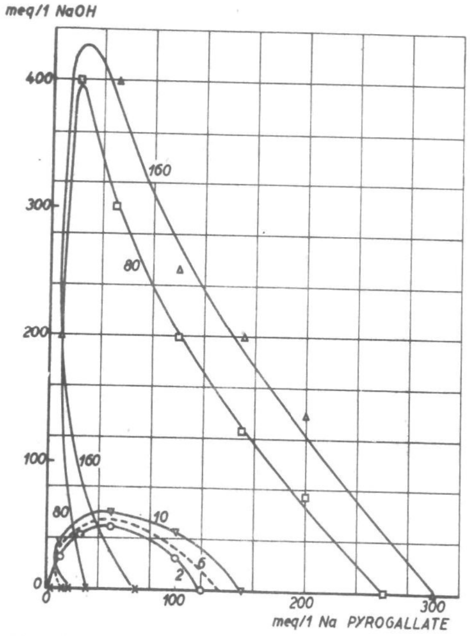
Finally the effect of the addition of lime to the tannate-treated systems will be considered. First, the response of sodium montmorillonite and calcium montmorillonite sols to pyrogallate addition was compared. The pyrogallate-NaOH flocculation curves for both sols are shown in fig.II, 28. The stabilising effect of pyrogallate appears to be of the same order of magnitude for both sols but the optimum in the curve is shifted to a higher pyrogallate concentration for calcium montmorillonite with respect to that for sodium montmorillonite (ca 60 m.eq./l as compared with ca 20 m.eq./l). This is in line with the observation that for raw bentonite the optimum activity of pyrogallate on the stiffening time is around 80 m.eq./l (see under B-1). When discussing the relation between the stability conditions in sodium montmorillonite and the rheological behaviour of raw bentonite suspensions the position of the optimum for the latter was already tentatively attributed to the presence of calcium in the raw bentonite.

Next the flocculation in pyrogallate-treated sodium montorillonite sols was investigated in the presence of various mounts of lime. The results are shown in fig.II, 29 where the aOH flocculation values are plotted versus the amount of pyroallate added for sols containing 2, 6, 10, 80 and 160 m.eq./l of a$(OH)_2$ respectively.



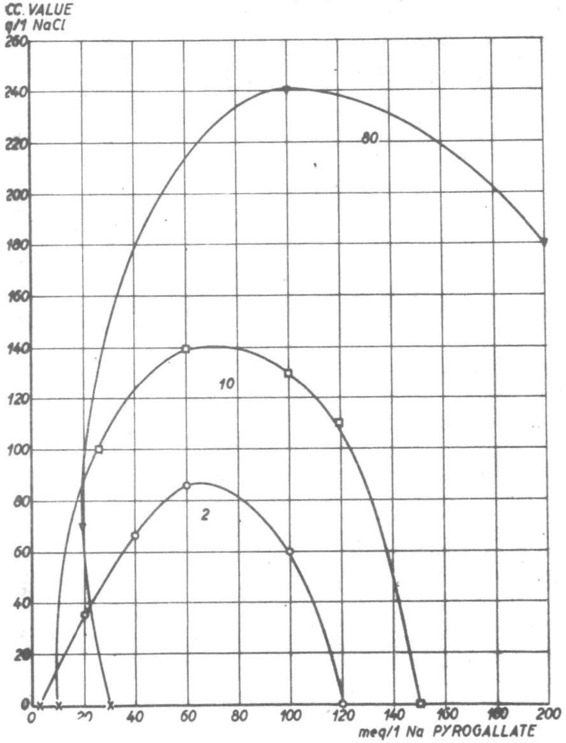
FLOCCULATION ANTAGONISM NaOH-Na PYROGALLATE FOR Ca AND Na MONTMORILLONITE SOLS

FIG II, 28



NaOH FLOCCULATION VALUES FOR Na MONTMORILLONITE AS A FUNCTION OF THE Na PYROGALLATE CONCENTRATION FOR DIFFERENT LIME CONTENTS

FIG II. 29



NaCl FLOCCULATION VALUES FOR FB-Na SOLS AS A FUNCTION OF THE Na PYROGALLATE CONCENTRATION AT DIFFERENT LIME CONTENTS

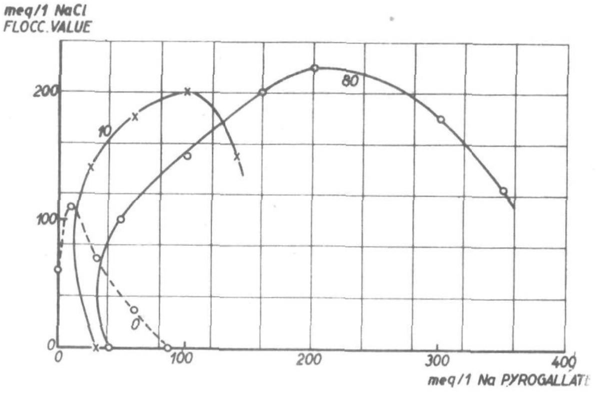
FIG II, 30

The curve for 2 m.eq./l of lime shows a close resemblance to that for a calcium montmorillonite sol without lime (compare fig. II, 28). The latter system contains about the same amount of calcium viz. about 2.5 m.eq./l of exchangeable calcium, the sol concentration being 2.5 g/l and the b.e.c. about 100 m.eq./100 g. A difference between the two flocculation curves is that the lime-treated system is only stable beyond a pyrogallate concentration of about 2 m.eq./l.

With increasing lime content the minimum amount of pyrogallate required to obtain a stable system increases as indicated by the points marked "x" in Fig.II, 29. Yet the stability region becomes wider and higher and particularly between 10 and 80 m.eq./l of lime a substantial increase in the stability is observed. Thus, in accordance with the favourable effect of lime treatment observed in practice, the stabilising effect of pyrogallate is greatly enhanced if a sufficient amount of lime is present. An analogous effect is observed with regard to the salt stability although the shape of the stability curves is a little different (Fig.II,30).

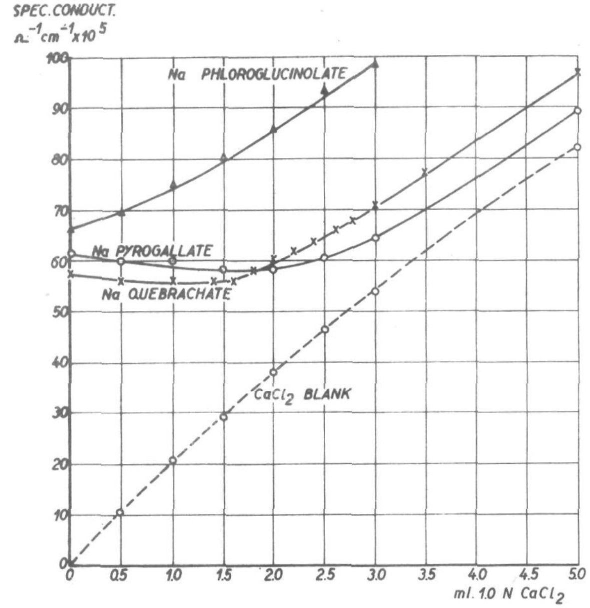
Since the study of model sols has been very helpful in the interpretation of the stabilisation mechanism in the case of a variety of peptisers, also the effect of pyrogallate in the presence of lime was investigated for both alumina and quartz sols. It was found that lime does not increase the stability of pyrogallate-treated alumina sols, but a pronounced effect was observed in the case of quartz sols. Fig.II, 31 shows the salt flocculation curves for a Q^- sol as a function of the amount of pyrogallate added for a lime content of 10 and 80 m.eq./l respectively. For comparison the curve for the lime-free system (marked 0) is included. Except for the small region of very low pyrogallate concentrations, it is immaterial whether the flocculation values are determined for Q^- or Q^+ sols, the latter being converted into a negative sol by pyrogallate and lime. The graphs demonstrate that the stability of the pyrogallate-containing sols is appreciably increased by the addition of lime, which the quartz sols have in common with the montmorillonite sols.

As a consequence of this analogous behaviour of both sols, the effect of lime-pyrogallate treatment on montmorillonite may be assumed to result from a stabilisation at the broken silica sheets at the lateral surface. This stabilisation may be a result of a very effective adsorption and charging effect of the pyrogallate anions. Possibly they are linked to the silica surface by means of calcium. Some supporting evidence for this point of view is offered by the following observations:



NaOH FLOCCULATION VALUES FOR QUARTZ SOLS AS A FUNCTION OF THE Na PYROGALLATE CONCENTRATION FOR DIFFERENT LIME CONTENTS.

FIG. II, 31



CONDUCTOMETRIC TITRATION OF 50 ml. 0.05 N TANNATE SOLUTIONS WITH $CaCl_2$

FIG II, 32

i. Pyrogallate takes up calcium in its anion by complex formation. This is inferred from conductometric titration of Na pyrogallate with $CaCl_2$ as represented in Fig.II, 32.

ii. The same applies to quebracho which is also an efficient peptiser in the presence of lime. On the other hand, a phenol which does not form a calcium complex, viz. phloroglucinolate (see Fig.II, 31) is observed to be inactive in the presence of lime (compare section B-2).

iii. The voluminous precipitate of calcium silicate obtained by mixing a sodium silicate and a calcium hydroxide solution e.g. in a concentration of 10 m.eq./l, is readily peptised to a hydrophobic sol with say 100 m.eq./l of pyrogallate. In this case too, pyrogallate adsorption by calcium linking seems to be the most likely explanation.

Summarizing, the peptisation of montmorillonite by pyrogallate-lime may well be ascribed to the adsorption of the complex pyrogallol-Ca anion to the lateral surface exposed silica sheets.

However, the possibility that pyrogallate anions are also linked with the flat layer surface by calcium may not be exluded a priori. Such an adsorption would result in an increased basal spacing of the dried clay due to the large organic ions between the layers. This spacing appeared, however, not to be different from that of untreated dry montmorillonite.*) Thus, a stabilisation at this part of the surface is improbable. It may rather be expected that owing to the high electrolyte concentration in these systems, the stability at the flat layer surfaces will decrease, any extra protection by adsorption being absent. This would result in an increased parallel association of the particles. An indication of such an effect was obtained when treating WB-Na sol with pyrogallate and with pyrogallate-lime respectively. With pyrogallate alone the sol shows a diffuse Tyndall cone in the ultramicroscope, just as the untreated sol which contains extremely thin particles (compare chapter V). On addition of lime, however, definite ultramicrons are observed which points to a growth of the particles. This may also explain the higher settling tendency of lime-treated muds as compared with red muds.

The remarkable resistance to heating of the limed systems as compared with those without lime, remains to be explained. This

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*) Note added in proof.
Also the adsorption capacity of montmorillonite for pyrogallol in the presence of lime viz. ca 7 m.eq./100 g. although higher than in the lime-free systems can be accounted for by the capacity of the lateral surface.

might be attributed to a smaller degree of desorption of the tannates when linked by calcium, but in the model systems thus far no difference of the effect of heating on the stability could be observed. On the other hand, in montmorillonite sols there is a possibility that the clay is partly decomposed on heating in the alkaline solutions. These decomposition products may have a flocculating action and the addition of lime might result in an inactivation of these products. A support for the possibility of an effect of this kind is the following: The alkali may attack the octahedrical sheets at the edges forming aluminate. If now sodium aluminate is added to a quebracho-containing bentonite suspension a considerable stiffening is observed in the *cold*. On subsequent addition of lime, still without heating, the suspension liquifies again.

Experimentally it will be difficult to differentiate between desorption and clay decomposition effects. The study of the latter would involve a thorough investigation of any changes in both composition and lattice structure by means of chemical and X ray methods. This is, however, beyond the scope of this thesis.

It may be concluded from the work described in this chapter that, essentially, a satisfactory explanation of the peptisation mechanism of tannates could be given. The key was offered by the study of the stability conditions in model systems. Admittedly, the composition of such systems e.g. those consisting of quartz, aluminium-chloride, alkali and lime and salt is far removed from that of a lime-treated red mud, but the substitution of the complicated systems of actual practice by more simple ones seems to be the only way of attack. This is but the first step in the interpretation of lime red mud behaviour. Further work will be required to study the optimum ratios of tannin, alkali and lime, the heating effect and also the well known formation conserving properties of these muds. In this investigation, when extrapolating any results obtained for pyrogallate containing systems to actual red muds, the effects of the colloidal character of the high molecular weight condensation products in quebracho should also be given due consideration.

* * * * * *

PART II

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PART III

THE RELATION OF COLLOID CHEMICAL STABILITY AND RHEOLOGICAL BEHAVIOUR OF MONTMORILLONITE SUSPENSIONS

SUMMARY

In part I it has been shown that chemical treatment mainly affects the Bingham yield stress of muds. In part II the addition of chemicals has been found to increase the stability of dilute clay sols as judged from their salt flocculation values. In the present part the relation between the rheological and the stabilising effect is discussed on a quantitative basis. Simultaneously the plastering behaviour is given attention.

A rough parallellism is observed between the salt flocculation values of dilute suspensions and the effect of salt on Bingham yield stress and filter loss for sil, quebracho and polymetaphosphate-treated concentrated suspensions. An increase of the flocculation value on addition of these chemicals goes parallel with an increased resistance of rheological and plastering quality against the detrimental effects of salt contamination.

Although a constant quantitative relation of general validity is lacking, it is concluded that the determination of the flocculation values in dilute suspensions may be considered a useful guide in choosing the most appropriate chemicals as well as the required dose for a given mud.

* * * * * *

INTRODUCTION

In part I it has been shown that the addition of either salt or treating chemicals to clay suspensions mainly results in an increase or a decrease, respectively, of the Bingham yield stress, the variation of the differential viscosity being comparatively small.

It was proved in part II that treating chemicals have a stabilising effect on montmorillonite sols. The peptisation mechanism was seen as the result of an increase of the repulsive potential at the lateral surface of the clay particles which prevents edge to edge association and thus the formation of a network, displaying a yield stress in more concentrated systems.

This demonstrates a qualitative agreement between the results of both investigations. The quantitative relation between colloid chemical stability and rheological behaviour will be discussed in this part.

In order to obtain a well differentiated picture a comparison will be made between the amount of salt which just flocculates a dilute French bentonite suspension after treatment with various amounts of peptiser and the amount of salt which just eliminates the favourable effect of a peptiser on the Bingham yield stress of a concentrated French bentonite suspension.

When carrying out this program involving the preparation and testing of a large number of suspensions containing various amounts of salt and peptiser, another property of practical importance has been studied at the same time, viz. the plastering behaviour of the treated suspensions. (vide the introduction page 1).

This property was measured by means of a standard test consisting of the determination of the filtrate loss, when filtering the suspension under standard conditions of pressure difference, filtering area and medium and filtering time. The results are reported as "cc filtrate loss A.P.I." The lower the filtrate loss the better the plastering properties are. (A.P.I.-RP29, May'50)

Since chemical treatment of clay suspensions usually improves their plastering behaviour a correlation may be expected to exist between the flocculation value of dilute suspensions and the filtrate loss of concentrated suspensions. As described above for the rheological properties, simultaneously the salt flocculation values for treated dilute suspensions will be compared with the amount of salt, which eliminates the favourable effect of a peptiser on the filtrate loss of the concentrated suspensions.

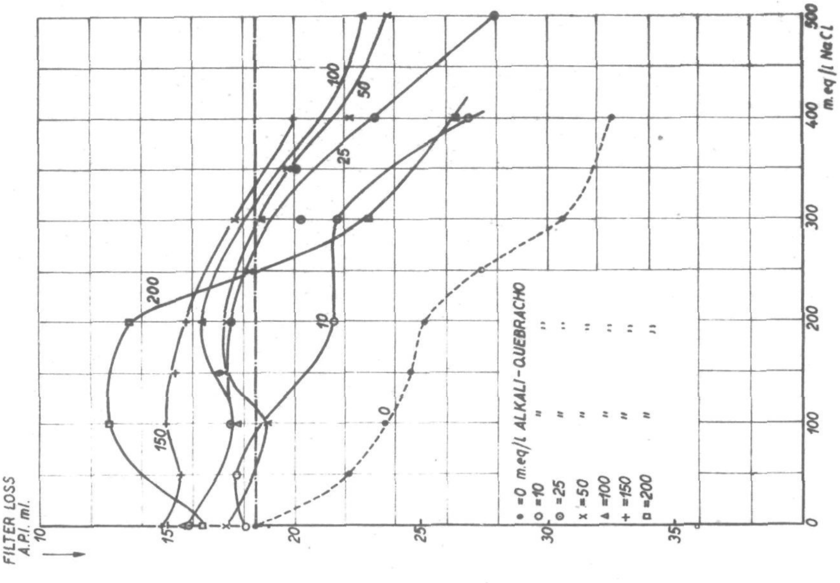
A rather stiff suspension containing about 6% of French bentonite was prepared. This suspension was thoroughly mixed with varying amounts of peptiser and the effect of increasing amounts of NaCl on these treated suspensions was investigated. In all cases the final bentonite concentration after addition of peptiser and salt solution was adjusted to 5.7% by adding water. The rheological and plastering properties of these suspensions were measured after 3 weeks' storage. At the same time the flocculation antagonism curve was determined by means of the centrifuge method.

The experiments have been carried out with three different chemicals viz. Na quebrachate, metasilicate and polymetaphosphate. The results are collected in the figures III, 1-7 incl.

A. EFFECT OF Na QUEBRACHATE

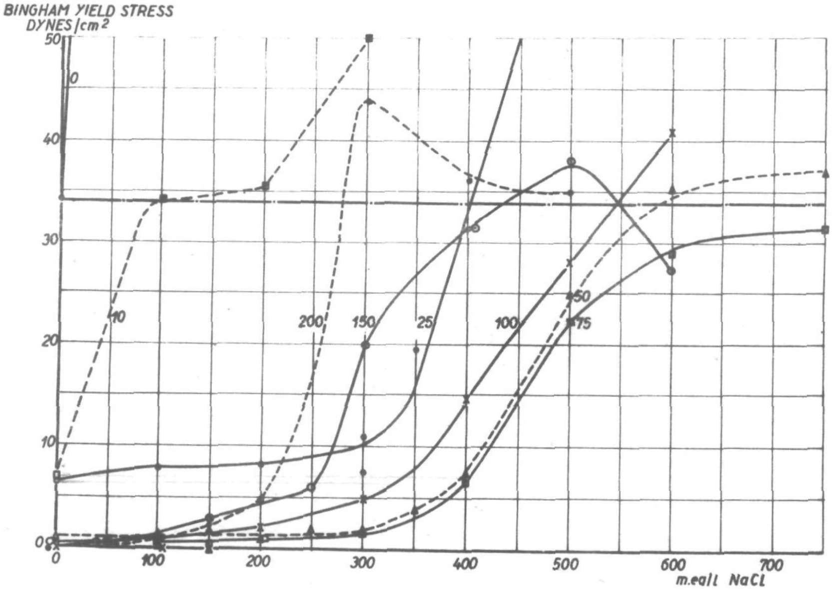
Fig. III, 1 shows the effect of alkali-quebracho (eq. ratio) and NaCl on the Bingham yield stress τ_B of the 5.7% French bentonite suspensions. The curve marked "0" in fig. III, 1 is a plot of τ_B versus the amount of salt added to the original suspension. (In fig. III, 4 the full curve is drawn in the graph for sil). The yield stress of the salt containing suspensions is higher than that of the original. Analogous curves are drawn for quebrachate treated suspensions, the amounts being indicated on the curves in m.eq./l.

The addition of quebrachate to the original suspension results in a large decrease of τ_B but on subsequent addition of salt the yield stress increases again. Now, the amount of salt which just compensates the favourable effect of the quebrachate on the blank suspension, will be considered a measure of the activity of the amount of quebrachate added. In fig. III, 3 these compensating salt concentrations are plotted as a function of the amount of quebrachate in the system. (the curve of constant yield stress indicated τ_B = 34 dynes/cm^2) In addition a second curve of constant yield stress marked τ_B = 10 dynes/cm^2 is included in the graph. This curve represents the amounts of salt which may be taken up by the treated suspension before the yield stress passes the value of 10 dynes/cm^2 as a function of the amount of quebrachate added.



EFFECT OF VARIOUS AMOUNTS OF ALKALI-QUEBRACHO AND NaCl ON THE A.P.I. FILTER LOSS OF A 5.7% FRENCH BENTONITE SUSPENSION

FIG. III, 2



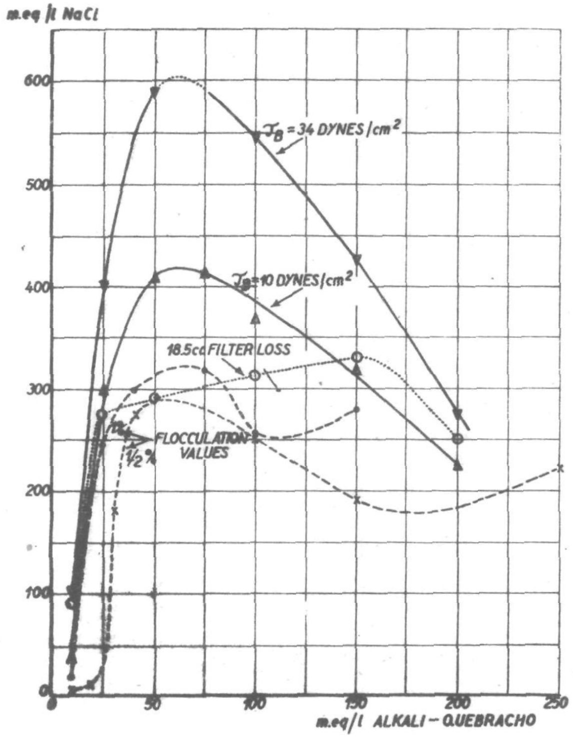
EFFECT OF VARIOUS AMOUNTS OF ALKALI-QUEBRACHO AND NaCl ON THE BINGHAM-YIELD STRESS OF A 5.7% FRENCH BENTONITE SUSPENSION

FIG. III, 1

The maximum "activity" of quebrachate may be read from the graph: in the region of 50-100 m.eq./l of quebrachate the best suspensions are obtained with regard to the sensitivity of the Bingham yield stress to salt contamination. An enormous effect is obtained on addition of the first 50 m.eq./l but there is no sense in further addition of quebrachate aiming at a further improval of the rheological behaviour: with an excess the reverse effect is obtained which is known as over-treatment.

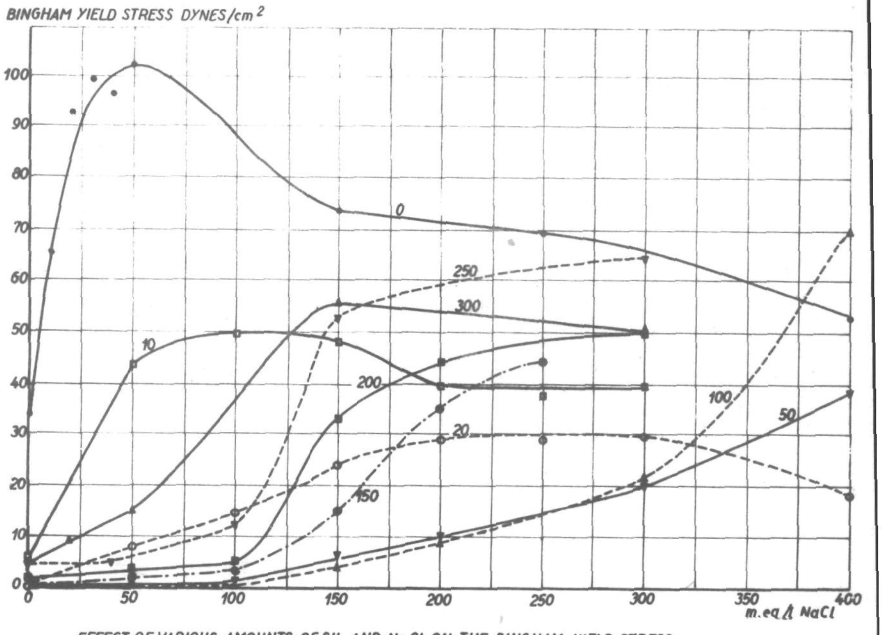
The dotted curves in fig. III, 3 show the salt flocculation values of dilute suspensions, determined by the centrifuge technique at a final sol concentration of 0.5 and 1%, respectively. A comparison of these curves with those for constant yield stresses demonstrates a parallellism between the stability of the dilute sols and the rheological properties of more concentrated suspensions:
The sharp rise of the flocculation value on addition of the first 30-40 m.eq./l of quebrachate and the position of the maximum in the flocculation curve are indicative for the rheological behaviour of the concentrated suspensions. In the region of 0.25-2.0% the sol concentration has no marked effect on either the position or the height of the maximum in the flocculation curve. The difference in height of the flocculation curves and those of constant yield stress will be a matter of the arbitrary character of the flocculation experiment and the choice of the yield stress which should be considered an indication that the system is in the first phase of floc formation.

In fig. III, 2 the effect on the plastering behaviour is presented. The A.P.I. filter loss is plotted versus the salt concentration for 5.7% bentonite suspensions after treatment with various amounts of quebrachate which are stated near the curves in m.eq./l. Owing to the low clay content as compared with that of muds in practice the filter losses are rather high. The figure shows, however, that quebrachate treatment improves the plastering properties of the suspensions. Subsequent addition of salt, however, cancels the improvement. The compensating amounts of salt may again be read from the graph, they are plotted as a function of the amount of quebracho added in fig. III, 3 (curve.......) This curve also discloses a certain parallellism with the flocculation curves although at higher concentrations of quebrachate the filtration properties are somewhat better than would be expected from the flocculation curve. This may be due to a contribution of the colloidal fractions of quebracho to the total plastering effect.



FLOCCULATION VALUES AND CURVES OF CONSTANT BINGHAM-YIELD STRESS AND CONSTANT FILTER LOSS FOR AKALI – QUEBRACHO TREATED BENTONITE SUSPENSIONS

FIG. III, 3



EFFECT OF VARIOUS AMOUNTS OF SIL AND NaCl ON THE BINGHAM-YIELD STRESS OF A 5.7% FRENCH BENTONITE SUSPENSION

FIG. III, 4

Generally speaking, it may be concluded from these data that the stability conditions in dilute systems are indicative for the rheological and plastering quality of the concentrated systems.

B. EFFECT OF METASILICATE

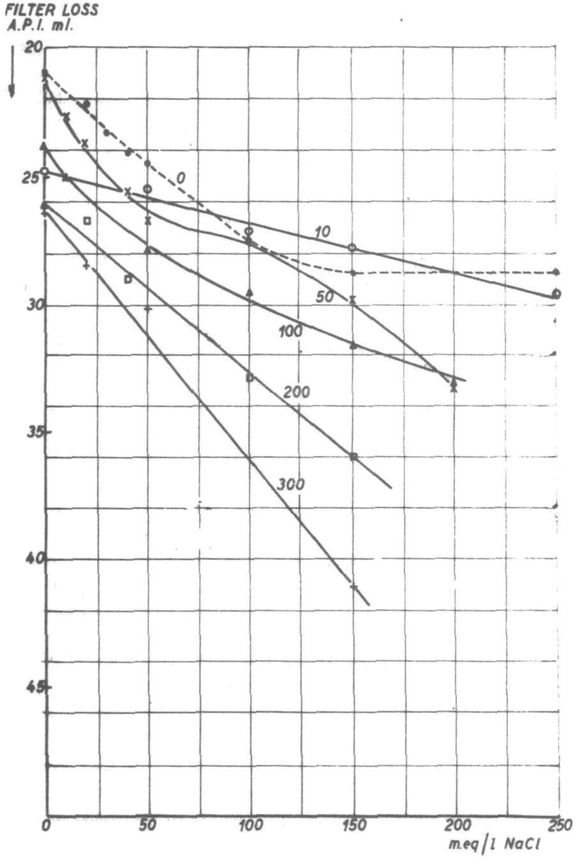
Figs. III, 4, 5 and 6 show analogous graphs for sil-treated bentonite. The effect of sil on the yield stress is comparable with that of quebracho although the sil-treated systems are more sensitive to subsequent addition of salt: the maximum compensating salt concentration is just below 400 m.eq./l for sil treatment against ca 600 m.eq./l for quebrachate. (fig. III, 6). This is in line with the lower salt flocculation values of the dilute suspensions in the case of sil as compared with quebrachate (dotted line in fig. III, 6) The region of maximum stability for sil is 40-200 m.eq./l, thus much wider than the region of maximum salt resistance from a rheological point of view which is only 50-100 m.eq./l. Thus, although a strict parallellism is lacking over the entire range of sil concentrations, the flocculation values are again indicative of the change in quality of the concentrated suspensions, particularly in that range of low sil concentrations which is of practical importance.

Fig. III, 5 is a collection of the filter loss data. The results show that unlike quebrachate, sil is unable to improve the plastering behaviour, on the contrary the filter losses increase on addition of sil. It is felt that this defect of sil treatment may be due to the presence of calcium in the bentonite, causing the formation of precipitates of calcium metasilicate on the particles which may impart the filtering properties without harming the rheological behaviour appreciably.

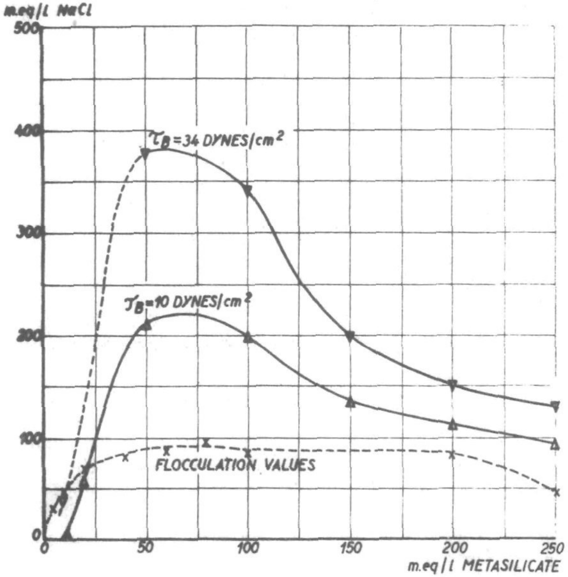
It may be remarked that the relation between filter cake permeability and the charge distribution on the particles constituting the cake is a problem which still requires thorough investigation. The results of the plastering experiments are only given here as a matter of general interest but a fundamental discussion is beyond the scope of this thesis.

C. EFFECT OF POLYMETAPHOSPHATE

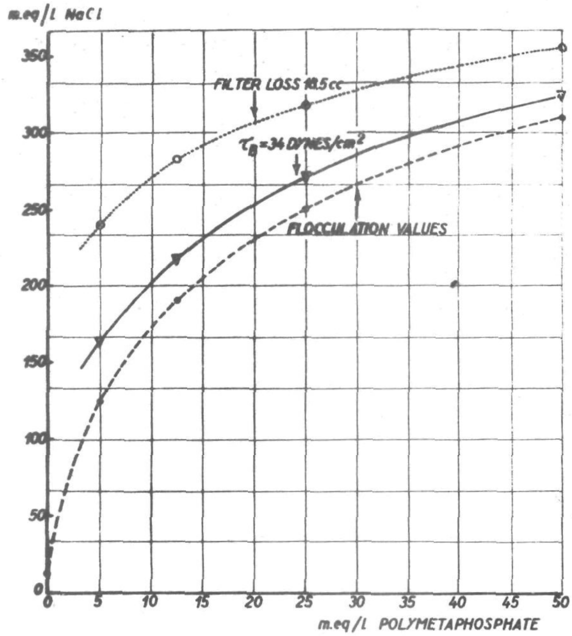
Fig. III, 7 shows the summarizing graph for the effect of polymetaphosphate in the small range of concentrations which are of practical interest (up to the maximum in the stability curve). The parallellism between flocculation values and the curves of



EFFECT OF VARIOUS AMOUNTS OF SIL AND NaCl ON THE A.P.I. FILTER LOSS OF A 5.7% FRENCH BENTONITE SUSPENSION FIG. III, 5



FLOCCULATION VALUES AND CURVES OF CONSTANT BINGHAM-YIELD STRESS FOR SIL-TREATED BENTONITE SUSPENSIONS FIG. III, 6



FLOCCULATION VALUES AND CURVES OF CONSTANT BINGHAM-YIELD STRESS AND CONSTANT FILTER LOSS FOR POLY-METAPHOSPHATE-TREATED BENTONITE SUSPENSIONS

FIG. III, 7

constant Bingham yield stress and constant filter loss is evident from the graph. The curve of constant yield stress is much closer to the flocculation curve than in the case of quebracho or sil treatment. Apparently there is not a quantitative relation of general validity, the various peptisers showing individual characteristics.

It may be remarked that the addition of the first 25 m.eq./l of polymetaphosphate has a marked effect on the stability and practical properties whereas the addition of a further 25 m.eq./l improves the mud to a much smaller extent. Thus a certain overdosing beyond 25 m.eq./l will not have a direct favourable effect. However, such an extra quantity may be useful for combating the detrimental effect of electrolytes which may be taken up in the course of the drilling operation, the more so as it has been found that a greater amount of phosphate will be required if the effect of salt contamination has to be remedied afterwards. It will be advantageous to keep the mud in the deflocculated state, flocculation being not completely reversible.

Although the number of peptisers investigated is still limited it is believed that a rough parallellism between flocculation values and rheological and plastering behaviour is the rule, such cases as a lacking effect of sil treatment on the plastering behaviour being rather exceptional.

It may be concluded that the determination of the flocculation conditions in muds will be an important guide for the mud chemist when choosing the most appropriate type of chemical treatment for a given mud.

* * * * * *

SAMENVATTING

Onder de boorspoelingen nemen de klei-waterspoelingen de belangrijkste plaats in. Zij worden gewoonlijk bereid uit in de nabijheid van de boorterreinen gedolven kleien, waardoor de eigenschappen van de spoelingen van plaats tot plaats zeer uiteenlopen. Daar de meeste kleien met electrolyten verontreinigd zijn verkeert een spoeling dikwijls in de gevlokte toestand. Een dergelijke gevlokte kleisuspensie is meestal zo dik dat zij niet met een behoorlijke snelheid in het boorgat rondgepompt kan worden. In de practijk heeft men nu gevonden dat sommige chemicaliën, in kleine hoeveelheid aan de spoeling toegevoegd, deze als bij toverslag in een dun vloeibare uitstekend verpompbare suspensie veranderen. Men stelde zich hierbij voor dat dergelijke chemicaliën de suspensie peptiseren, doch over het mechanisme van deze peptisatie had men slechts vage voorstellingen. Men begreep onvoldoende, hoe het komt dat verschillende spoelingen zo verschillend op diverse chemische behandelingen reageren of soms in het geheel niet reageren. Teneinde meer klaarheid in deze onoverzichtelijke, grotendeels op empirie berustende procedure der chemische spoelingbehandeling te verkrijgen, werd een colloidchemische studie van het mechanisme van de chemische peptisatie van kleisuspensies opgezet, welke het onderwerp vormt van het tweede gedeelte van dit proefschrift. In het eerste gedeelte wordt de verpompbaarheid zelve onder de loupe genomen en wordt deze kwantitatief in verband gebracht met de rheologische eigenschappen van de spoelingen. In het derde gedeelte wordt tenslotte nagegaan of er inderdaad een verband bestaat tussen de mate van peptisatie van een kleisuspensie en zijn rheologisch gedrag en verpompbaarheid.

(DEEL I) Een goede verpompbaarheid van de gebruikte spoeling is conditio sine qua non voor de boring. Met de bereikbare pompdrukken moet een minimum circulatiecapaciteit gehandhaafd kunnen worden waarbij het boorgereedschap afdoende gekoeld wordt en het boorgruis voldoende snel naar de oppervlakte meegevoerd wordt. Bij de diepere gaten welke men tegenwoordig boort is het pompprobleem weer sterk op de voorgrond gekomen. Teneinde te kunnen voorspellen welke capaciteit de spoelingpomp minstens zal moeten hebben moet men de dimensies van het circuit, het s.g. en de rheologische eigenschappen van de spoeling kennen. Het laatste eist een rheologische karakterisering aan de hand van viscosimetrische gegevens. Daarom wordt door analyse van de stroming in de verschillende gedeelten van het circuit eerst vastgesteld welke rheologische konstanten bekend moeten zijn voor de pompdrukberekening en bovendien, met het oog op het thixotrope karakter der meeste spoelingen, onder welke omstandigheden deze konstanten gemeten dienen te worden. Gebaseerd op de uitkomsten van deze analyse wordt een viscosimeter ontwikkeld waarmede inderdaad die gegevens bepaald kunnen worden welke voor het verpompingsprobleem van belang geacht moeten worden. Met behulp van dit instrument werd een aantal spoelingen voor en na chemische behandeling onderzocht. Het bleek dat onder de in het circuit heersende omstandigheden de kleispoelingen zich hetzij als een Newtonse vloeistof, hetzij als een zgn. Bingham plastisch systeem gedragen. Voorts bleek dat het effect van chemische behandeling voornamelijk neerkomt op een verlaging van de Bingham vloeigrens terwijl de differentiele viscositeit van het systeem niet of in onbetekende mate verandert. Dit verklaart een verlaging van de pompdruk in het gebied van laminaire stroming waar de pompdruk in de eerste plaats door de Bingham vloeigrens bepaald wordt. In het turbulent gebied weet men echter niet nauwkeurig in hoeverre de pompdrukken door de vloeigrens beinvloed worden daar in de literatuur geen gelijktijdige metingen van pompdrukken en vloeigrens bekend zijn. Daarom werd een aantal experimenten op semitechnische schaal en een enkele proef in de praktijk uitgevoerd. Hieruit bleek, dat weliswaar de drukverliezen in het turbulente gebied groter zijn dan men op grond van de differentiele viscositeit alleen verwachten zou maar voor spoelingen met ongeveer gelijke differentiele viscositeit kon geen invloed van een toenemende vloeigrens geconstateerd worden waarbij het onderzoek zich uitstrekte tot de voor spoelingen reeds tamelijk hoge waarde van 150 dynes/cm^2. Wel wordt het overgangspunt van laminaire naar turbulente stroming met toenemende vloeigrens naar hogere circulatiesnelheden verschoven. Zo zijn er gebieden van circulatiesnelheden aan te geven waarin de spoeling met de hoogste vloeigrens gemakkelijker verpompbaar is dan die met de lagere omdat de eerste in het laminaire gebied en de laatste reeds in het turbulente gebied ligt.

(DEEL II) In het tweede gedeelte wordt de stabiliteit van kleisuspensies bestudeerd. Een representant van het type der montmorilloniet kleien werd als onderzoekingsobject gekozen en hiervan werden zuivere natrium en calcium montmorilloniet solen bereid. Met behulp van vlokkingsproeven kon aangetoond worden dat de gebruikelijke chemicaliën voor de spoelingbehandeling inderdaad een stabiliserend effect op deze solen hebben: de vlokkingswaarde tegen bijvoorbeeld NaCl, die voor de zuivere solen betrekkelijk laag is, neemt aanmerkelijk toe bij toevoeging van kleine hoeveelheden van deze chemicaliën. Getracht werd nu met de ons ter beschikking staande middelen het mechanisme van deze peptisatie te analyseren. Een sluitende interpretatie kon verkregen worden door de uitkomsten van Röntgen analyse, electronenmicroscopie, electroforese en adsorptiemetingen alsmede viscometrie en ultramicroscopische deeltjes tellingen te combineren. Het vruchtbaarste bleek hierbij de introductie van de studie van enkele model solen nl. aluminium oxyde en kwarts solen. De electrische dubbellaag aan het oppervlak van de micellen van deze solen mag tot op zekere hoogte representatief geacht worden voor die welke op bepaalde delen van het oppervlak van de klei micellen voorkomen. Het resultaat van dit onderzoek kan als volgt samengevat worden:

De montmorilloniet micellen zijn zeer dunne ultramicroscopische plaatjes. Het platte oppervlak van deze plaatjes draagt een negatieve lading welke de ~~uit~~verwisselbare cationen als tegenionen heeft. De electrische structuur van de randen is echter geheel verschillend: hier zijn de tetraëdrische silicaatlagen en de octaëdrische aluminiumoxyde lagen afgebroken en de hieraan gevormde electrische dubbellagen mogen verwacht worden overeenkomst te vertonen met die van kwarts en aluminiumoxyde sol deeltjes. De laatste zijn positief en hoewel de kwartsdeeltjes negatief zijn is het bekend dat zij door sporen aluminium en hydroxyl ionen omgeladen worden en aangezien in de evenwichtsvloeistof van een kleisol deze ionen zeker aanwezig zijn, is het waarschijnlijk dat niet alleen de gebroken aluminiumoxyde lagen in de klei maar ook de gebroken silicaatlagen positief zijn. Een aantal verschijnselen pleit voor de hypothese dat het kleideeltje inderdaad een dualistisch karakter heeft en dat, hoewel de netto kataforetische lading negatief is, de randen positief zijn.

Wat de stabiliteit betreft, deze schijnt in het gedialyseerde sol voornamelijk door de dubbellaag op de platte vlakken bepaald te worden. Deze is betrekkelijk gering en wordt eerder tegengewerkt door de situatie aan de kanten dan gesteund. De stabiliteitsverhoging door de bij de spoelingbehandeling gebruikelijke chemicaliën echter, speelt zich waarschijnlijk geheel af aan de randen: zij laden de randen om, waardoor deze in een aanmerkelijk stabielere negatieve conditie komen, analoog aan de door ons geconstateerde omlading van een aluminiumoxyde en positief kwarts sol met deze chemicaliën. Tot op zekere hoogte kan zelfs het effect van een peptisator op montmorilloniet kwantitatief gezien worden als een superpositie van zijn effecten op de twee model solen.

Door deze interpretatie is het probleem van de kleistabiliteit gereduceerd tot het meer algemene probleem van de stabilisering van aluminiumoxyde en kwarts solen, waarvan enkele aspecten besproken worden.

De gegeven interpretatie werd getoetst voor natriumphosphaten, metasilicaat, oxalaat, citraat en alkalie. Laatstgenoemde heeft geen stabiliserend effect op montmorilloniet en evenmin op de model solen, het heeft integendeel een gering sensibiliserend effect op beide. Bovendien werden twee verschillende montmorillonieten bestudeerd en enkele individuele verschillen in de responsie op chemische behandeling konden toegeschreven worden aan het verschil in ferri-ionengehalte van de octaëderlaag. Het is daarom waarschijnlijk dat een bentoniet met een hoog ferrigehalte aan de randen meer het karakter van een ferrihydroxyde sol vertoont dat enigszins anders op de diverse peptisatoren reageert dan een aluminiumoxyde sol.

Tenslotte bleken de beschouwingen ook te gelden voor behandeling met een looistof in alkalisch milieu. Ter vermijding van de complicatie van de slecht gedefinieerde structuur van vele natuurlijke looistoffen werden deze in het onderzoek vervangen door een goed gedefinieerd meerwaardig phenol dat dezelfde effecten op kleisuspensies vertoont als de looistoffen nl. pyrogallol. Voorts kon ook een verklaring van het merkwaardige gunstige effect van kalk op tanninen bevattende spoelingen gegeven worden toen bleek dat een geheel analoog effect bij kwarts solen optreedt. Deze stabilisatie speelt zich blijkbaar ook aan de randen en in het bijzonder aan de gebroken silicaatlagen af, waarbij de tannaationen vermoedelijk door middel van calcium met het silica-oppervlak verbonden worden aangezien tannaationen met calcium complexen vormen. Ook hierbij speelt het platte oppervlak geen rol van betekenis.

Juist doordat de chemische behandeling zich geheel aan de randen zou afspelen waarvan het oppervlak slechts een fractie van het totale micel oppervlak is, ontplooien de chemicaliën hun activiteit in zulke geringe concentraties in vergelijking met de kleiconcentratie.

Het sterke opladen der randen door de peptisatoren zou de rand tegen randassociatie van de deeltjes kunnen voorkomen welke juist aanleiding zou geven tot de vorming van een netwerk met een hoge vloeigrens. Zo wordt het dus begrijpelijk dat het juist de vloeigrens is welke door chemische behandeling verlaagd wordt zoals in het eerste gedeelte geconstateerd was.

(DEEL III) In het derde gedeelte wordt dan tenslotte het kwantitatieve verband bestudeerd tussen vloeigrensverlaging en colloidchemische stabilisering van bentonietsuspensies. Inderdaad kon een zeker parallelisme geconstateerd worden tussen de stabiliteit van met chemicaliën behandelde verdunde solen tegen vlokking met NaCl en de hoeveelheid zout welke het gunstige effect van een bepaalde hoeveelheid peptisator op de vloeigrens van een geconcentreerde suspensie weer teniet doet.

Op deze wijze kon dus de analyse van de ladingsdistributie op een ultramicroscopisch kleideeltje gekoppeld worden met de pompdruk welke nodig is om een honderd kubieke meter spoeling per uur in een boorgat rond te pompen.

* * * * * *

STELLINGEN

1. De randen van de plaatvormige kristallijne micellen in een neutraal montmorilloniet sol dragen een positieve lading.

2. De mening van Johnson, dat de uitwisselbare kationen in montmorilloniet uitsluitend aan de randen van de deeltjes voorkomen volgt niet overtuigend uit zijn waarnemingen en houdt geen stand tegen Röntgen analyse van preparaten verkregen door ionenuitwisseling met kation actieve stoffen.

   Johnson, A.L.; J.Am.Cer.Soc. 1949, **32**, 210
   Jordan, J.W.; J.Phys.Coll.Chem. 1949, **53**, 294
   1950, **54**, 1196

3. De studie in organisch milieu van de afstanden der lagen van bentoniet na adsorptie van aminen van verschillende ketenlengte kan een belangrijk hulpmiddel zijn voor de interpretatie van de stabilisatie van water-in-olie-emulsies door oppervlakte actieve stoffen.

4. De studie van het electroviskeus effect in twee dimensies in stelsels welke oppervlakte actieve ketenmicellen bevatten, gecombineerd met druk-oppervlakte metingen, waaruit het per ketenmicel ingenomen oppervlak berekend kan worden, kan bijdragen tot interpretatie van het electroviskeus effect in het algemeen.

5. Het falen der „ringanalyse" volgens Waterman cs. bij toepassing op tot nu toe gesynthetiseerde koolwaterstoffen houdt geen principiële veroordeling van de methode in; het bewijst slechts dat deze koolwaterstoffen, ofschoon zij in de destillaatfracties, welke uit ruwe olie bereid worden voor kunnen komen, niet representatief zijn voor deze fracties.

   K.van Nes and H.A.van Westen: „Aspects of the Constitution of Mineral Oils" Chapters III and IV (1951)
   R.E.Hersh, M.R.Fenske, E.R.Booser and E.F.Koch; J.Inst.Petroleum **36** (1950) 624-668.

6. Bij de meting van het vochtgehalte van stoffen door bepaling van het in dioxaan opgenomen water door middel van de diëlectrische constante van het mengsel, kan extractie door destillatie vervangen worden, zodat de methode ook toegepast kan worden op stoffen welke met dioxaan mengbare componenten bevatten.

   L.Ebert, Z.Angew.Chem. **47** (1934), 312

7. In de toegepaste viscometrie wordt dikwijls verzuimd te analyseren, welke rheologische gegevens voor het praktijkprobleem van belang zijn.

8. De veronderstelling, dat een polymetaphosphaatoplossing flexibele ketenmoleculen bevat geeft een aantrekkelijker verklaring van het vermogen calcium in complexe ionen te binden dan die welke gebaseerd is op de door Teichert voorgestelde molecuul structuur.

   W.Teichert; Acta Chemica Scandinavica 2(1948),225,414
   3(1949), 72

9. Afzetting van paraffine op een koude wand uit een daarlangs stromende verzadigde oplossing wordt in de eerste plaats bepaald door de adhesie van de kristallisatiekernen aan het wandmateriaal.

10. De "yield stress"-verlaging veroorzaakt door de aanwezigheid van enkele mol procenten vetzuur in een calcium zeep gel in minerale olie moet toegeschreven worden aan een verandering van zowel de micelvorm als van de micelassociatie.

11. Voor de ontwikkeling van kogellagervetten welke bij temperaturen boven ca.100°C toegepast moeten worden is afwezigheid van gelatinering bij verhitting een belangrijker criterium dan het druppelpunt.

    N.V.De Bataafsche Petroleum Maatschappij (uitvinder: H.van Olphen) Ned.Octrooi 65.126.

12. De toepassing van autoclaven tijdens de zogenaamde uitroerfase verheft de kalkvetbereiding van kunst tot kunde.

13. De bewuste toepassing van de resultaten der psychoanalyse in scheppende literaire arbeid verlaagt het schrijven van kunst tot kunde.

14. De mening van Maria Montessori, dat de discipline in een volgens haar systeem geleide schoolklasse bepaald wordt door de bezigheid met het materiaal, waarbij de leidster op de achtergrond blijft, houdt geen stand tegen psychoanalytische beschouwing van het ontstaan van discipline in een groep.

    E.Buxbaum; Z.f.Psychoan.Padagogik 6 (1932), 324

15. Bij psychotechnische selectie van researchpersoneel verdient het aanbeveling „tests" in te schakelen waarmede een inzicht verworven wordt in aard en sterkte der afweermechanismen van de proefpersoon.