

# PEPTIZATION RESISTANCE OF SELECTED SAMPLES OF KAOLINITIC, MONTMORILLONITIC, AND ILLITIC CLAY MATERIALS

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## ABSTRACT

Variations in the peptization resistance of selected samples of clay mineralogical materials toward alkaline dispersing agents are discussed from a quantitative point of view.

Clay samples, collected from South Carolina, Wyoming, Illinois, New Mexico, South Wales, Great Britain and Cornwall, England were subjected to the action of solutions of Calgon ("sodium hexametaphosphate"), ammonia, sodium hydroxide, sodium carbonate, sodium pyrophosphate, and "sodium lignosulfonate." The resulting apparent dispersion, in each case, was expressed as a function of the employed concentration and chemical nature of the dispersing agent. Pipette analysis and Oden balance techniques at constant temperature were used to measure the degree of dispersion. All clay samples employed were identified as to type by X-ray diffraction, chemical analysis, thermal analysis, and electron microscopy.

All samples examined exhibited a maximum in apparent dispersion (suspension stability) at a specific concentration of dispersing agent. Such maximum was followed by a sudden decrease in apparent dispersion, *i.e.*, flocculation, at higher concentrations of dispersing agent. Concentrations of dispersing agent were varied in steps of one part per thousand. One hundred and twenty experimental runs were made on each type of material examined. Differences in the degree of apparent dispersion attained by use of different dispersing agents were expressed in terms of a threshold concentration which altered "equivalent diameter" one tenth of a phi unit. Among dispersing agents employed, "sodium lignosulfonate" was found to be least selective of clay mineral type in its peptizing action.

An equation for the calculation of a "peptization resistance factor" is presented. Results obtained by application of this equation indicate that differences in the response of the same clay material to different alkaline dispersing agents may be attributed, in part, to differences in degree of peptization achieved by "threshold mechanisms" of peptization and by "adjustment mechanisms" along the peptization path. Such equation may have future value in the differentiation of marine and terrestrial clay deposits.

## INTRODUCTION

The stability of aqueous suspensions of kaolinitic, illitic, and montmorillonitic clay materials may be increased or decreased by the modification of the suspension medium with alkaline chemical agents. The direction of the change in such stability is apparently governed by the specific mineralogical, chemical, particulate, and concentration characteristics of the resultant clay-electrolytic solution system.

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Such clay suspensions are characterized by a great preponderance of surface area of clay to volume of clay (Hauser, 1951). Consequently, any variation in the surface activities of the clay micelles, toward and in association with the electrolytic ionic components and the liquid medium, will influence the stability of the suspension. Differences in such surface response of clay materials collected from natural deposits may well arise, in part, as a direct consequence of the variation of physical and chemical influences associated with the environments of deposition.

The research results reported herein are representative of the preliminary information that has thus far been gained from a quantitative investigation of the relative resistance of aqueous clay suspensions toward efforts to increase their stability by the addition of alkaline chemical agents. In particular, the stability modifications which arise as a consequence of differences in clay specie, or which result from variations in the concentration and chemical nature of the alkaline chemical agents, are discussed.

Some information relative to the influence of environments of deposition upon the stability characteristics of clay suspensions is also presented. More thorough treatment of the consequences of this influence and the specific discussion of the effect of variable clay concentrations upon the stability of clay-electrolytic solution suspensions are reserved for later publication.

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#### GENERAL DISCUSSION

##### *Peptization and Peptization Resistance*

The term *peptization* is employed herein to denote an increase in the stability of a clay suspension. Changes in stability are described as variations in the *peptization resistance of the suspension*. The original clay sample is assumed to have a dormant chemical characteristic called the *peptization resistance of the clay*, which acts as a partial control over the stability of the suspension.

The reference state for the peptization resistance measures is an aqueous (distilled water) suspension of the clay material concerned at a known weight concentration of clay material per liter of suspension.

A few remarks on the modes of interaction of colloidal entities are herein included for the benefit of the nonchemist.

From the classical colloid chemical point of view, an increase in stability that results from the disintegration of suspended agglomerates into primary particles of colloidal dimensions is often termed *peptization* (Weiser, 1949). However, for general understanding of the stability of a suspension of clay material in an electrolytic solution, it is somewhat more realistic and more convenient to describe the over-all effect of real or apparent physical dispersion, resulting from chemical influences, as *peptization*.

An aqueous suspension of clay material is fundamentally different from a suspension of clay material in an electrolytic solution. After the addition of a chemical agent to an aqueous suspension of clay, the clay particle is no longer the same particle and the suspension is no longer the same system. These differences, chemical in essence, vary in degree if not in kind as the electrolyte and/or clay concentrations of the suspension system are varied. General understanding of such suspensions demands that consideration be given to the possible associations and relative orientations of the clay micelles, ionic constituents, and water molecules that form the statistical lattice structure of the whole suspension system.

Variations in the surface activities of the clay micelles will bring about different relative associations of all chemical entities in the suspension system and so modify the statistical lattice structure that the stability and other physical characteristics of the system are changed. Such alterations may become apparent due to different distributions of mass but are not necessarily dependent upon the disintegration of clay aggregates of micellar or coacervated types.

From a kinetic point of view, the settling of colloidal suspensions in a gravitational field is opposed by the osmotic pressure and the diffusion induced by Brownian movement. The "effective masses" of the settling units are dependent upon the viscosity of the system, the density of the dispersing medium, and the shapes and orientations of the settling entities. However, the surface characteristics of the primary clay particles and the chemical nature of the suspension system exercise control over the size and distribution of mass within the settling units and over the distribution of such units within the system.

The effective viscosity of the suspension is related to the distribution of the so-called electrostatic charges within the entire system. Such charge distribution influences the relative associations and relative orientations of the clay micelles, ionic constituents, and water molecules. That is to say, alterations in the zeta potentials within the system manifest themselves in changes in the viscosity of the system. This influence upon the stability of colloidal suspensions is often called the *electroviscous tension*.

The effective size of the settling units and the viscosity of the system are also functions of the degree of *lyophilic* character that the clay material displays. Of course, such categorical characterization of colloids is subject

to argument (Thomas, 1934) and the general classification of clays among colloids, in such classical sense, is also subject to debate (McBain, 1950). Nevertheless, the affinities of the dispersed clay for the dispersing medium, the reactions of the clay with the dispersing medium, and the resultant effects of such factors throughout the suspension system modify the stability of the system.

Ions located at the surface of the clay micelles are less chemically saturated than ions located in the interior of the clay micelles and the stability of a clay sol will depend upon the extent to which such surface ions can be solvated by or can react with the dispersing medium. In this regard, the probability of ionic exchange between the effective clay micelle and the dispersing medium at or near the surface of the micelle or at the solid-liquid interface must also be considered.

Theories of peptization and suspension stability have been advanced by Lottermoser (Zsigmondy, 1914), Mecklenberg (1912), von Weimarn (1914), Bancroft (1932), Hamaker (1937), Vervey (1948), van Olphen (1950) and others. For additional information, the reader is referred to the work of these investigators and to Freundlich (1932), Ostwald (1937), Bungenberg de Jong (1937), Langmuir (1938), and Thiessen (1942).

For our purposes, we say that such peptization of a clay material may result by adsorption of and reaction with distilled water and employ such an aqueous suspension as our peptization reference state. However, as previously indicated, the stability of clay-electrolytic solution suspensions may then be altered by varying the concentration of the electrolyte.

Solvation and coacervation (Bungenberg de Jong, 1937) play vital roles in the peptization and flocculation of clay materials. If we consider coacervates as colloid rich liquids which are not spontaneously birefringent, then settling entities (particularly in montmorillonite sols), which may often be settling assemblies of micelles in association with liquid, may be called "coacervates." Such a coacervate, a colloid-rich phase, is an association of micelles in which the points of contact are dynamic. It is a typical, but viscous liquid.

The states of coacervation, the distribution of mass and relative clay-liquid ratios within the coacervate, would be controlled by the chemical nature of the system as a whole and as a consequence bear close relation to the phenomenon of flocculation. Interesting and indicative evidence for the progressive changes in the states of coacervation of montmorillonite-electrolyte sols as the concentration of the electrolyte is varied should soon be ready for release. Such evidence has been gained from spectrophotometric and electron microscopy studies of montmorillonite sols. As flocculation of montmorillonite proceeds, the stability of the suspension approaches a minimum as the concentration of the electrolyte is gradually increased. If one visualizes the settling form of montmorillonite as a fluffy fibrous clay shell with interlocking or interpenetrating fibers surrounding an aqueous interior, then the gradual closing of such a shell (induced by the increasing

concentration of electrolyte with associated "squeezing out" of interior water) could decrease the stability of the suspension without change in the actual mass of montmorillonite per settling unit. That is to say, the density of the settling units may increase without an actual increase in clay mass per settling unit.

When the dispersion of clay material by distilled water is used as the reference state, greater dispersion or greater suspension stability in the presence of electrolytes may be considered either a consequence of an altered distribution of charge on the particle with associated alteration in the state of solvation or a consequence of an increase in the electroviscous tension. Such increase in dispersion, real or apparent, would be thermodynamically reversible only if chemical reaction did not induce an irreversible alteration within the adsorption layer of the clay. The resistance of the suspension to such increase would be measured by the rate of increase in dispersion as the concentration of the electrolyte is varied. This *peptization resistance of the suspension* may be a function only of the electrolyte concentration level or a function of both the degree of dispersion of the clay entities and the electrolyte concentration level.

If additional dispersion, relative to distilled water, occurs by concentration of the anion of an alkaline peptizing agent at the broken edges of the clay lattice, by increasing the solvation of the surface of the micelle due to ion exchange, or by expanding the interlamellar distances of the dispersed unit, then such dispersion should reach a maximum at a specific concentration level of the electrolyte. Further increase in electrolyte concentration should either have no measurable effect or should initiate instability or flocculation of the suspension due to the redistribution of surface charge, repression of the double layer, and partial desolvation of the micelle or coacervate by the increase of cations added or exchanged, within the double layer. A combination of these effects would then influence the flocculation values.

In the general understanding of the peptization of clay materials, it may be helpful to the nonchemist to consider the idealized representation of peptization given in Figure 1. The association of primary particles in the system to form flocculates or particulate assemblies is critical to the stability of the system. Peptization, or increase in stability, may result from the loss of particles from such an assembly or from reorientation of the particles within the assembly. Such reorientation could decrease the effective densities of the particulate assemblies without an actual decrease in mass of clay per settling unit.

One typical illustration of the latter effect is shown as "secondary peptization" in Figure 1. Flocculates of this type could result from the unrolling of more equidimensional flocculates (containing the same number of primary particles) to form anisodimensional chains within the suspension system.

Ideal, or "ultimate," peptization would be realized by dissociation of the

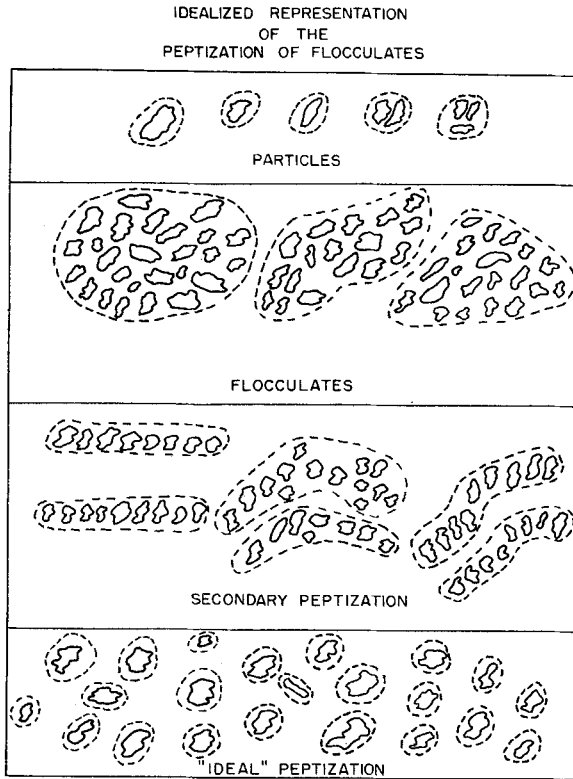


FIGURE 1. — Idealized representation of the peptization of flocculates.

particles within an assembly to the extent that each particle settles separately.

In other words, actual disintegration of primary particles is not essential to the realization of an increase in the stability of the suspension.

*Peptization Resistance of Suspension*

The *peptization resistance of the suspension*,  $P_{RS}$ , might be defined as follows:

$$(1) \quad P_{RS} = f(C, D)$$

wherein  $C$  = concentration of the added electrolyte and  $D$  is the measured degree of apparent dispersion of the clay solid, *i.e.*, is a measure of the stability of the system. In relation to the slope of a  $D$  versus  $C$  curve,

$$(2) \quad P_{RS}(C, D) = k \frac{dD}{dC}; \quad k = \text{experimental parameter}$$

and

$$(3) \int_{C_d}^{C_m} P_{RS}^1(C, D) dC = k_1 \int_{D_d}^{D_m} dD; \quad C_m, D_m = \text{maximum values.}$$

$$C_d, D_d = \text{distilled water values.}$$

If  $C$  and  $D$  are mutually dependent, then

$$(4) \int_{C_d}^{C_m} P_{RS}^1(C) dC = k_2 \int_{D_d}^{D_m} dD; \quad D = 1/d_a$$

$$d_a = \text{average "settling diameter" of particles}$$

Should  $C$  and  $D$  be linearly related, the resultant integrated form is

$$(5) \quad P_{RS}^1 = k_3 \frac{(D_m - D_d)}{(C_m - C_d)}$$

The  $P_{RS}^1$  values in expressions (3), (4), (5) would not be truly indicative of the relative peptization resistances of suspensions to different electrolyte peptizing agents unless the threshold values of electrolyte concentration and degree of clay dispersion were the same.

Relative resistance to peptization would be more realistically measured from the points at which electrostatic charge distribution and solvation conditions permit initiation of peptization. Such threshold electrolyte concentration levels would be a function of the characteristics of the selected peptizing agents but would not necessarily be integral parts of the real rates of resistance to peptization even though they might influence such rates. The threshold adjustment may also include an apparent flocculation stage. The *peptization resistance of the suspensions* after threshold conditions are realized might be represented, relative to equations (3), (4), (5), as follows:

$$(6) \quad \int_{C_e}^{C_m} P_{RS}(C, D) dC = k_1 \int_{D_e}^{D_m} dD$$

$$(7) \quad \int_{C_e}^{C_m} P_{RS}(C) dC = k_2 \int_{D_e}^{D_m} dD$$

$$(8) \quad P_{RS} = k_3 \frac{(D_m - D_e)}{(C_m - C_e)}$$

wherein  $D_e$  and  $C_e$  represent the threshold conditions.  $C_e$  would be that electrolyte concentration at which an experimentally detectable increase in dispersion ( $D_e - D_d$ ) is realized. Such threshold values would be difficult to define experimentally but calculations of  $P_{RS}$  upon the basis of  $C_e$  values representing the same initial increase in dispersion should be relatively indicative.

*Peptization Resistance of Clay Material*

It is useful to assume that the clay solid, before subjection to chemical alteration in a suspension, has a dormant resistance to the dispersal attack of any particular peptizing agent. Such *peptization resistance of the clay material*,  $P_{RC}$ , is considered to be single valued and would be measured by the slope of a linear  $C, D$  form between the point at which peptization is initiated and the point at which peptization becomes maximum. Such linear form would not necessarily be the slope of a line drawn between the experimentally measured  $C_e$  and  $C_m$  but would be a modification of that slope. This modification might be expressed as the product of the  $C_e, C_m$  slope and a multiplicand  $k$  (see Fig. 2).

(a) 
$$P_{RC} = k \frac{dD}{dC} = \text{constant}$$

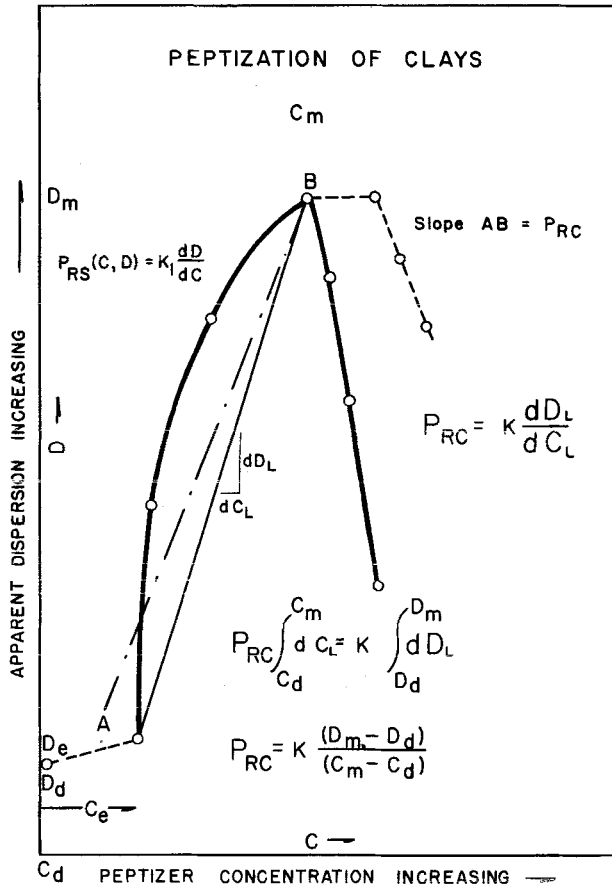


FIGURE 2.— Peptization of clays.



Such single value of  $P_{RC}$  would apply only to the dormant resistance of a specific clay sample toward a specific chemical peptizing agent. The  $P_{RC}$  of a clay mixture would be a statistically weighted average of the  $P_{RC}$  values of the individual components.  $P_{RC}$  would not represent the changing slope of an experimental  $C, D$  form, but would govern, in part, the shape of the experimental form by predetermining  $C_m$ . Only in the case of a linear experimental form would  $P_{RC}$  and  $P_{RS}$  approach the same value.

In integrated form,

$$(b) \quad P_{RC} = k \frac{(D_m - D_e)}{(C_m - C_e)}$$

This theory requires the parameter  $k$  to be dependent upon  $P_{RS}$  such that  $k = \theta(C, D) P_{RS}$ . Experimental determination of the form of  $\theta(C, D)$  would require an absolute determination of the point of the initiation of peptization. Such determination is not experimentally feasible. Consequently the selection of a useful single valued measure of the *peptization resistance of the clay sample* requires the adoption of a modification of the  $P_{RC}$  concept.

#### *Peptization Resistance Factors*

The area under a  $D, C$  curve is also a measure of the peptization resistance of the suspension. Such area may be conveniently called the *peptization resistance factor of the suspension*,  $P_{RS}^f$ . It may be evaluated by numerical graphical integration if the dependence of  $D$  upon  $C$  cannot

be expressed in a form convenient for the evaluation of  $\int_{C_e}^{C_m} D(C) dC$ .

However, such  $P_{RS}^f$  values for the same clay material exposed to a series of different alkaline peptizing agents might be adjusted to a single value if the relative peptization resistances differ only in degree and not in kind. Such single value would be a peptization resistance factor representing the typical behavior of the selected clay material to such alkaline agents. If the relative threshold adjustments prior to initiation of peptization are considered measures of the action of mechanisms that bring about the apparent differences in degree of resistance, then the area from  $C_e$  to  $C_m$  may be considered a multiple of the threshold area. Then

$$(9) \quad P_{RS}^f = k_4 \frac{\int_{C_e}^{C_m} D(C) dC}{\int_{C_a}^{C_e} D(C) dC}$$

wherein  $k_d$  may be considered as the reciprocal of the over-all fractional change in  $D$  from  $C_e$  to  $C_m$ .

In a similar way, a *peptization resistance factor of the clay material*,  $P_{RC}^f$ , may be derived by expressing  $(D_m - D_e)$ , and  $(C_m - C_e)$  in fractional relation to  $(D_e - D_d)$  and  $(C_e - C_d)$ , respectively. Such factor can be expressed in the following form:

$$(c) \quad P_{RC}^f = k_c \frac{C_m (D_m - D_e)}{C_e (D_e - D_d)}$$

The parameter  $k_c$  would require expression in terms of the experimental  $C, D$  curve. A choice of such expression that would give a single value of  $P_{RC}^f$  for the exposure of the same clay material to a series of alkaline agents would be a requirement for the application of the  $P_{RC}^f$  concept.

Additional justification would be supplied if the  $P_{RC}^f$  values for different clay materials relatively paralleled  $P_{RS}^f$  values for these materials.

Further, if the application of the peptization resistance factor concept to two different sets of materials led to single values for the first set and variable values for the second set, then the sets would be fundamentally different in kind of response to peptizing influences over the  $C_e$  to  $C_m$  range. The response of the second set would not then be governed by the threshold mechanisms to the same extent as the first set.

In other words, differentiation of fundamental chemical differences in clay materials might be realized in some cases by application of the peptization resistance factor concept.

## EXPERIMENTAL DISCUSSION

### *Materials*

The clay materials employed in these investigations consisted of samples from both terrestrial and marine sources and samples treated in the laboratory with several electrolytic solutions, including artificial sea water (Lyman and Fleming, 1940).

The kaolinitic clays studied included material from Bath, South Carolina, Macon, Georgia and Cornwall, England. The illitic clay materials represent deposits near Fithian, Illinois and in South Wales, Great Britain. The montmorillonitic clays include materials from Upton, Wyoming, Polkville, Mississippi and College Station, Texas.

In addition, montmorillonitic-illitic material from Gallup, New Mexico and clay materials from Brazos River, Texas, Atchafalaya Bay, Louisiana and the Gulf of Mexico were examined.

All materials studied were examined to determine clay mineral composition by X-ray diffraction, thermal analysis, chemical analysis, and electron microscopy. Base exchange capacities for some of the materials were also determined by the method of Coffman (1946). Apparent densities of the samples were determined by pycnometer method.

Complete analytical data for all samples studied is not given herein. However, representative data for the reference kaolinitic, montmorillonitic, and illitic clay specimens (upon which approximate mineralogical composition of other samples is based) are given below. The chemical analysis data were obtained by use of the procedures described by Bowden (1949) and Hillebrand (1953). The analytical methods employed were those generally used by clay mineralogists for the identification of clay minerals. X-ray analysis results were obtained using Philips X-ray diffraction equipment. Thermal analysis data, using procedures described by Grim (1951), were also obtained.

(a) *Kaolinitic clays* (Bath, South Carolina): density, 2.55-2.58; base exchange capacity 3.3-3.6; X-ray analysis, 7.1 Å basal spacing and strong second order 3.58 Å line, 4.17-4.12 Å doublet; thermal analysis, dip at 585° C-600° C, peak at 950° C-1000° C; representative chemical analysis (percent), SiO<sub>2</sub>-45.38, Al<sub>2</sub>O<sub>3</sub>-38.34, Fe<sub>2</sub>O<sub>3</sub>-0.19, MgO-0.16, CaO-0.28, MnO-0.0, FeO-0.0, K<sub>2</sub>O-0.42, Na<sub>2</sub>O-0.24, TiO<sub>2</sub>-0.86, ignition loss-14.11, weight loss (105° C-110° C)-0.83.

(b) *Montmorillonitic clays* (Upton, Wyoming): density, 2.01-2.08; base exchange capacity, 148-151; X-ray analysis, 17.7 Å basal spacing with glycol, 14-15 Å without glycol; thermal analysis, dips at 145° C-150° C, 740° C-750° C and 850° C-860° C, peak at 945° C-953° C; representative chemical analysis (percent), SiO<sub>2</sub>-60.92, Al<sub>2</sub>O<sub>3</sub>-18.25, Fe<sub>2</sub>O<sub>3</sub>-2.83, CaO-0.41, MgO-2.30, K<sub>2</sub>O-0.15, Na<sub>2</sub>O-0.60, MnO-0.0, FeO-0.0, TiO<sub>2</sub>-0.08; ignition loss-14.38, weight loss (105° C-110° C)-7.53.

(c) *Illitic clays* (Fithian, Illinois): density, 2.68-2.74; base exchange capacity 26-36; X-ray analysis, diffuse 10 Å spacing, 18 Å spacing (glycol) absent; thermal analysis, dip at 590° C-600° C, couple at 900° C, slight flexures near 700° C, no thermal peak near 1000° C; representative chemical analysis (percent), SiO<sub>2</sub>-56.85, Al<sub>2</sub>O<sub>3</sub>-18.45, Fe<sub>2</sub>O<sub>3</sub>-5.12, FeO-0.26, CaO-0.32, MgO-2.25, K<sub>2</sub>O-5.71, Na<sub>2</sub>O-0.35, MnO-0.0, TiO<sub>2</sub>-0.82, ignition loss-9.67, weight loss (105° C-110° C)-2.96.

(d) *Other Clay Materials*: The approximate clay mineral composition of other clay materials is mentioned upon introduction under Results of Peptization.

(e) *Chemical reagents*: All chemical reagents employed conformed to A.C.S. specifications except the Calgon (so-called "sodium hexametaphosphate") and the "sodium lignosulfonate" (Marasperse N).

(f) "Sodium hexametaphosphate": This material known commercially as "Calgon" is not a hexametaphosphate but a polymer of 15-30 PO<sub>3</sub> groups. The Calgon solutions employed in these investigations were analyzed by the method of Teichert *et al.* (1948-49). The polymerization indicated by this method was about 28. The water solution of this product also contained pyrophosphate and orthophosphate.

(g) "Sodium lignosulfonate": This product known commercially as Marasperse N was not studied from a chemical analysis point of view.

*Methods*

Pipette analyses and Oden balance techniques at constant temperature were employed in measuring the degrees of apparent dispersion of clay materials reported herein (Krumbein and Pettijohn, 1938; Oden, 1915). Visual flocculation value techniques (see Kruyt and van Klooster, 1927) were found applicable to limited extent but generally did not yield the precision sought in these investigations. The latter techniques are less tedious than the pipette or Oden balance techniques. However, the visual observation of the initiation of peptization and flocculation did not prove reliable for the detection of many real differences in the peptization response of clay materials.

The methods employed are in general use for "particle size distribution" determinations and utilize gravitational settling of solid material suspended in a liquid as the fundamental basis for estimation of "size." "Size" is usually computed on the basis of Stokes' Law or Wadell's Law (Stokes, 1851; Wadell, 1936). Settling rates measured by these techniques are usually interpreted in terms of "equivalent diameters," *i.e.*, the "size" the falling particles would have if they were solid spherical units. Size ranges determined in this way are often selected on the basis of the Wentworth-Udden grade scale (Wentworth, 1922; Udden, 1914), a logarithmic transformation of the Wentworth scale (the phi scale) (Krumbein, 1934), the Atterberg (1905) grade scale, or a logarithmic transformation of the Atterberg scale (the zeta scale) (Krumbein, 1937).

The phi scale, wherein  $\phi = -\log_2 d$ , was employed as the basis for degrees of dispersion given herein.  $d$  is the "equivalent diameter" in millimeters. Median phi, the degree of dispersion representing fifty percent by weight of the sample on a cumulative curve, was employed as a measure of the "apparent dispersion" of the sample.

A change in median phi of 0.1-0.15 was used as the experimental limit of measure of dispersion.

The results obtained were subjected to interpretation on the basis of the *peptization resistance factors* previously described. The following expression for the *peptization resistance factor of the clay* was found to have single values for the exposure of some clay materials to the peptizing agents employed:

$$(d) \quad P_{RS}^f = \frac{S_e \cdot R_e \cdot C_m}{S_m \cdot R_m \cdot C_e} \cdot \frac{(\phi_m - \phi_e)}{(\phi_e - \phi_a)}$$

wherein  $R_e = \frac{(\Delta\phi)}{(\Delta d_a)_e}$ ,  $R_m = \frac{(\Delta\phi)}{(\Delta d_a)_m}$ .  $S_e$  is the concentration change on the actual experimental curve just above  $C_e$  for a dispersion change equivalent to  $(\phi_e - \phi_a)$ .  $S_m$  is sensitivity factor of similar type just below  $C_m$  on the experimental curve.

The  $P_{RS}^f$  values given were obtained by numerical graphical integration. The results are expressed as multiples of the threshold area per unit (one percent) change of  $D_e$  over the range  $D_e$  to  $D_m$ .

Since the peptization resistance factors are dimensionless any measure of concentration can be employed for a specific experimental run. The constant temperature employed was 26° C but investigations at room temperature are possible employing a control portion of the sample in distilled water. It is the change in dispersion relative to distilled water that is important. Fluctuating temperature may introduce changes in the electroviscous tension, particularly in the case of montmorillonite, that are not compensated by such control, but reproducibility of the results in twenty experimental runs may be considered significant.

Figure 2 shows the idealized concept of the *peptization resistance of the clay*.  $P_{RC}$  is considered to be the slope of the linear path the suspension resistance would follow if no alteration in the original chemical clay identity occurred as the concentration of electrolyte was increased until  $C_m$  was reached. Since  $P_{RC}$  predetermines  $C_m$ , any nonlinear form of the experimental  $D, C$  curve is dependent to some extent upon  $P_{RC}$ . Upon the nature of such dependence rests the facility of determining the parameter  $k_e$  of equation (c).

On the basis of equation (c) (see General Discussion, Peptization Resistance Factors),  $P_{RC}^f$  has the following characteristics. If  $C_m$  and  $C_e$  are the same at constant  $k_e$  the sample does not resist peptization no matter how great  $C_e$  may be, *i.e.*  $P_{RC}^f = 0$ . If  $\phi$  is increased without experimentally detectable limit as the concentration of peptizing agent increases,  $P_{RC}^f$  becomes infinite. If  $\phi_e = \phi_m$ , despite increasing concentration of peptizing agent,  $P_{RC}^f$  is indeterminate. The precise determination of  $C_e$  experimentally will control the value of  $P_{RC}^f$ . However,  $C_e$  and  $S_e$  of equation (d) above are reciprocally related and approach the same value at dilute concentrations. Under such conditions the value of  $P_{RC}^f$  is controlled by  $C_m$  and  $S_m$  when other variables are constant.  $C_m, C_e, S_e, S_m$  were determined by aliquot addition of stock peptizing solution and aliquot dilution with distilled water when necessary.

### Results of Peptization

Suspensions of ten grams of clay per liter were subjected to the peptizing action of sodium hydroxide, sodium carbonate, ammonia solution, Calgon, sodium pyrophosphate, and "sodium lignosulfonate." Concentrations of electrolytes were expressed in grams per liter except in the case of ammonia solution where normality as prepared was used. The use of chemical equivalents as a concentration measure may not be applied to Calgon in terms of "hexametaphosphate" units. The chemical equivalent character of sodium lignosulfonate was not investigated. However, since the *peptization resistance factor* is dimensionless the use of other concentration measures gives similar results.

Figure 3 shows the apparent dispersion-electrolyte curves for the reference specimens of kaolinitic, montmorillonitic, and illitic clay materials and five of the six dispersing agents mentioned. The clay type is designated by

the letters K, M, and I respectively. The numbers (e.g., 0.81) under each curve are values of the *peptization resistance factor of the clay*. The use of the logarithmic ordinate,  $\phi$ , instead of  $1/d_a$ , tends to give more non-linear appearance to the  $D, C$  relationship than arithmetic plotting indicates. The vertical columns represent the results obtained by treatment of different clay types with the same alkaline dispersing agent (e.g., column  $A$  represents treatment with Calgon). The fact that these  $P_{RC}^f$  values relatively parallel the more laboriously calculated  $P_{RS}^f$  values is shown in Table I.

Observe that the degree of dispersion attained is a function of the concentration of the dispersing agent and flocculation generally ensues quite sharply upon slight increase in electrolyte concentration after maximum dispersion is attained. It should be mentioned, however, that montmorillonite samples of median size greater than  $\phi=11$  (i.e., smaller average size) in distilled water often exhibit higher flocculation values in terms of concentration than is shown in Figure 3 even though the value of the *peptization resistance factor* remains approximately the same. The results cited in Figure 3 and in Table I are based upon one hundred and twenty experimental runs per clay type and the average deviation of the *peptization resistance factor values* was  $\pm 0.03$ .

The *peptization resistance factor values* do not indicate the dispersing agent that served best to give maximum dispersion for each clay type. Reference to column  $\phi_m$  of Table I will serve in this connection. Reference to columns  $C_m$  and  $C_e$  will supply useful maximum and minimum electrolyte concentration data.

The electrolyte concentration requirements for different concentrations of clay have not yet been quantitatively evaluated. However, such relationships must not be assumed as linear or specific for the dispersion of clay materials. Such an absence of stoichiometric relationships is characteristic of colloidal systems. The flocculation values,  $C_m$ , do not necessarily increase or decrease as the concentration of clay is varied over wide ranges. For example, the values of  $C_m$  given in Table I may often induce similar stability in clay suspensions over a clay concentration range of two to twenty grams per liter. Generally speaking, the lower the flocculation value the more likely its directional dependence upon the clay concentration of the sol. In some dilute suspensions of clay suspensions such dependence may be an inverse dependence due to decrease in probability of mutual particle approach to effect association.

The sol concentration effect is then quite variable and is dependent upon the extent and type of anionic adsorption, the solvation and ionic exchange tendencies of the particular system, and the ionic antagonisms within the system. In many cases, the pH of the system is a useful, but not always reliable, guide. Quite often after the pH of the system first reaches a value of 11.5, further increase in dispersing agent concentration will initiate flocculation.

TABLE I<sup>1</sup>  
(10 grams clay per liter, 26° C)

Clay	Peptizer	$\phi_m$	$\phi_o$	$\phi_a$	$C_m$	$C_o$	$R_e$	$R_m$	$S_o$	$S_m$	$P_{RC}^f$	$P_{RS}^f$
K	A	10.8	7.9	7.8	1.1221	0.502	0.25	2	0.0102	0.1002	0.81	1.02
M	A	11.9	10.5	10.4	2.9112	0.520	2	4	0.0051	0.0050	0.97	1.22
I	A	9.5	8.5	8.4	3.5121	0.820	0.5	1	0.4300	0.4303	0.75	0.94
K	B	11.4	7.8	7.7	0.6120	0.1701	0.25	4	0.0204	0.2102	0.83	1.04
M	B	11.3	10.4	10.3	0.4010	0.0630	2	4	0.0030	0.0921	0.93	1.19
I	B	10.3	8.6	8.5	0.4100	0.0521	0.5	2	0.0051	0.2052	0.77	0.92
K	C	11.2	7.9	7.8	1.215	0.3103	0.25	4	0.0321	0.3184	0.84	1.02
M	C	11.6	10.3	10.2	1.122	0.0821	2	4	0.0230	0.2191	0.94	1.20
I	C	11.2	8.5	8.4	1.714	0.4311	0.5	4	0.0420	0.7501	0.74	0.90
K	D	11.6	8.0	7.9	0.0110N	0.0030N	0.25	4	0.0003N	0.0030N	0.83	1.05
M	D	11.9	10.5	10.4	0.0212N	0.0101N	2	4	0.0005N	0.0080N	0.93	1.20
I	D	10.4	8.7	8.6	0.0150N	0.0050N	0.5	2	0.0005N	0.0083N	0.77	0.91
K	E	10.9	7.9	7.8	1.1401	0.5103	0.25	2	0.0210	0.2082	0.84	1.02
M	E	11.6	10.3	10.2	2.6202	0.4041	2	4	0.0052	0.2401	0.98	1.23
I	E	11.3	8.4	8.3	1.7201	0.6153	0.5	4	0.0291	0.3703	0.72	0.93

<sup>1</sup> K = Kaolinite, M = Montmorillonite, I = Illite, A = Calgon, B = Sodium Hydroxide, C = Sodium Carbonate, D = Ammonia Solution, E = Sodium Pyrophosphate.



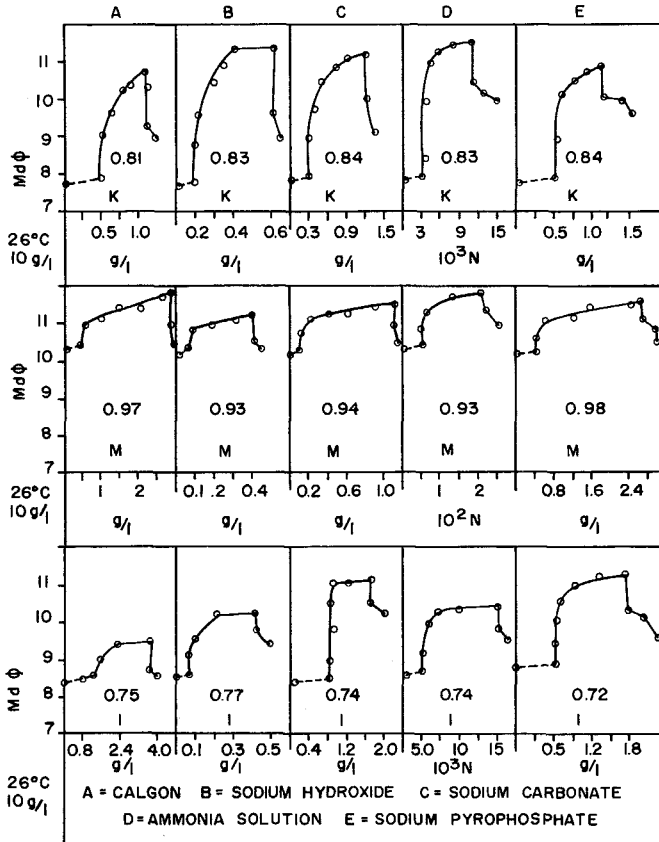


FIGURE 3. — Apparent dispersion—electrolyte curves.

The calcium montmorillonite (from Polkville, Mississippi) reacted to peptization in a manner similar to that of the reference Wyoming montmorillonite except that greater concentrations of dispersing agent were required to initiate peptization.

“Sodium lignosulfonate,” the sixth peptizing agent mentioned earlier, seems to have one special characteristic. Its peptization resistance values for the reference clay types have the same approximate magnitudes as listed for the other five reagents but its  $C_m$  value was found to be the same (0.12 grams per liter) for all three reference samples. That is to say, the same concentration of this reagent brought about its maximum dispersal of all three clay types. This could imply that it is less selective of clay type in dispersal action than the other five reagents. The same  $C_m$  value is also exhibited by this reagent in the peptization of mixtures of the clay types. However, as far as maximum apparent dispersal is concerned, it is less



effective than Calgon on kaolinite but more effective than Calgon on illite and montmorillonite.

All the kaolinitic and illitic samples mentioned under materials exhibited peptization character similar to the reference samples. The montmorillonitic-illitic materials from Gallup, New Mexico responded in the same way as a mixture of 81 percent reference montmorillonite and 19 percent reference illite.

Figures 4 and 5, and Table II show the comparison of  $P_{RC}^f$  variations for selected clay samples, mixtures of clay samples of the clay fraction of river sediments, and samples of the clay fraction of marine sediments. In the Figures, the titles below a horizontal sequence of five curves indicate the material treated, *e.g.* the top five curves in Figure 4 represent a 20% K, 40% M, 40% I mixture by weight.

The sediments from Brazos River, Texas, Atchafalaya Bay, Louisiana and the Gulf of Mexico (Fig. 5) were washed with distilled water and

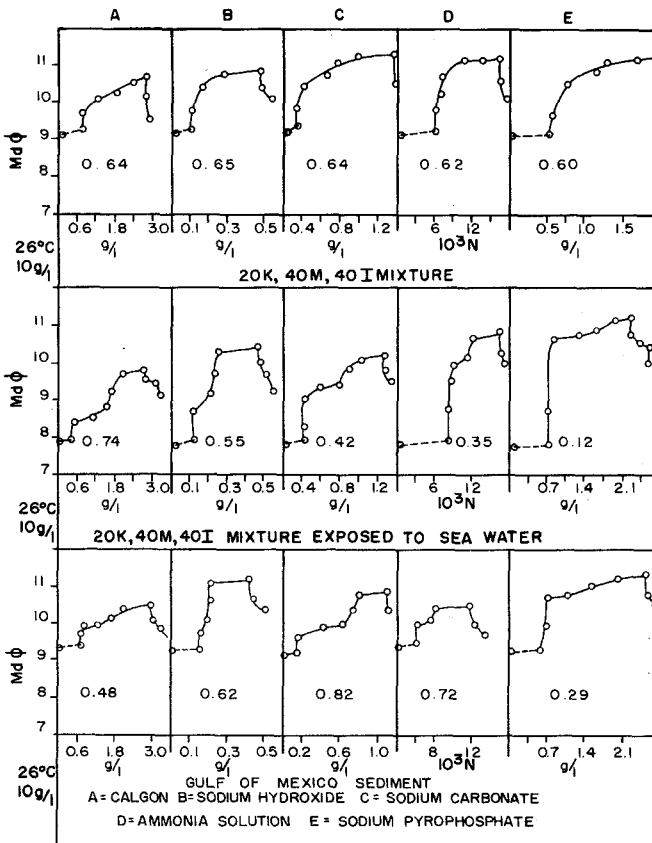


FIGURE 4. — Apparent dispersion — electrolyte curves.

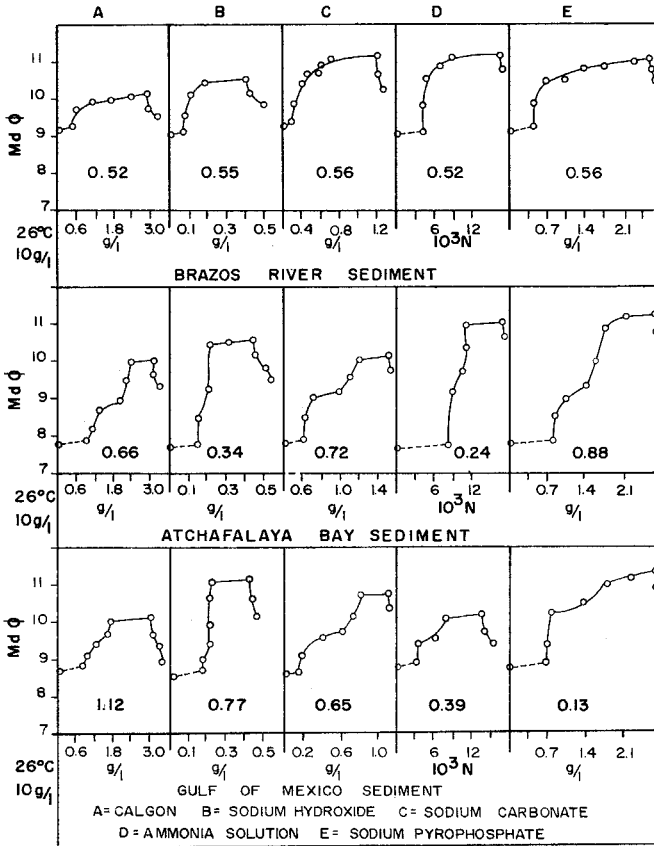


FIGURE 5. — Apparent dispersion—electrolyte curves.

dilute sodium carbonate solution, treated with six percent hydrogen peroxide to remove the oxidizable organic matter, washed with distilled water, sieved wet through 250 mesh, dried at  $50^\circ C$ , and quartered several times. From each sample six 10 gram portions that exhibited nearly the same  $Md\phi$  in distilled water were chosen for exposure to the peptizing agents. The sixth portion served as the distilled water control.

The Brazos River, Texas clay materials were more than ninety percent montmorillonitic in terms of the X-ray diffraction and chemical analysis data available. The Atchafalaya Bay material, Sample 14 (Table II) contained approximately seventy-five percent montmorillonite, ten percent illite, and fifteen percent kaolinite. Sample 15, from the same area but at greater distance from shore, contained more than ninety-five percent montmorillonite and some chloritic-montmorillonite mixed layer aggregates. Both samples from the Gulf of Mexico analyzed more than ninety-five percent montmorillonite with minor amounts of illite.

TABLE II\*  
(10 grams solid per liter, 26° C)

Sample	P <sub>RC</sub> <sup>f</sup> values				
	A	B	C	D	E
(1) Kaolinite	0.81	0.83	0.84	0.83	0.84
(2) Montmorillonite	0.97	0.93	0.94	0.93	0.98
(3) Illite	0.75	0.77	0.74	0.74	0.72
(4) 50% K 50% M	0.83	0.85	0.87	0.88	0.85
(5) 50% K 50% I	0.75	0.76	0.80	0.78	0.76
(6) 50% M 50% I	0.86	0.82	0.85	0.82	0.83
(7) 20 K, 40 M, 40 I	0.64	0.65	0.64	0.62	0.60
(8) 40 K, 20 M, 40 I	0.72	0.74	0.72	0.78	0.76
(9) 20 K, 40 M, 40 I†	0.74	0.55	0.42	0.35	0.12
(10) 40 K, 20 M, 40 I†	1.05	1.20	0.32	0.74	0.62
(11) Brazos River Sediment	0.52	0.55	0.56	0.52	0.56
(12) Brazos River Sediment	0.59	0.62	0.65	0.62	0.60
(13) Brazos River Sediment	0.72	0.72	0.76	0.75	0.74
(14) Atchafalaya Bay Sediment	0.66	0.34	0.72	0.25	0.88
(15) Atchafalaya Bay Sediment	1.22	0.22	0.75	0.95	0.52
(16) Gulf of Mexico Sediment (600 fathoms)	1.12	0.77	0.65	0.39	0.13
(17) Gulf of Mexico Sediment (600 fathoms)	0.48	0.62	0.82	0.72	0.29

\* A = Calgon, B = Sodium Hydroxide, C = Sodium Carbonate, D = Ammonia Solution, E = Sodium Pyrophosphate.

† Exposed to artificial sea water for eight months.

The marine sediments and the clays exposed to artificial sea water both show considerably more variation in P<sub>RC</sub><sup>f</sup> than is observed for the river sediments and the selected clay types. This variation seems to indicate that the peptization resistance of marine materials to the alkaline peptizing agents employed may differ significantly not only in degree but in kind. The curves in Figures 4 and 5 for marine materials exhibit secondary maxima to greater extent than do similar curves for the non-marine materials. The locations of such secondary maxima are random. Such effect distorts the dependence of P<sub>RC</sub><sup>f</sup> upon any initial threshold adjustment and decreases the significance of the S<sub>e</sub> and S<sub>m</sub> values.

This variation may result from different ionic exchange and ionic antagonism relationships that are induced by and result at specific concentration levels of the dispersing agent. In other words, "adjustment mechanisms" along the peptization path may vary in kind as well as in degree. Whatever the reason, more intensive investigation of the relative surface activities of terrestrial and marine clay materials seems in order.

## SUMMARY AND CONCLUSIONS

Kaolinitic, illitic, and montmorillonitic clay materials generally exhibit a maximum in apparent dispersion at specific concentrations of the alkaline dispersing agents discussed herein. A "plateau" of slowly increasing dispersion as the concentration of dispersing agent increases may occur near this maximum apparent dispersion, but such maximum is usually followed by a sudden decrease in dispersion, *i.e.*, flocculation.

Differences in the degree of apparent dispersion effected by the different alkaline dispersing agents upon the same clay type may be resolved by relating the observed differences to experimentally defined "threshold concentrations."

Flocculation values vary both with type of clay material and type of dispersing agent.

On the basis of distilled water apparent dispersion as a reference state, montmorillonitic clays exhibited the greatest peptization resistance to further dispersion by alkaline peptizing agents. However, the reference state of apparent dispersion was greater for these materials than for kaolinitic and illitic materials.

On the other hand, the reference state of dispersion for illitic materials was higher than for kaolinitic materials, yet the peptization resistance of the illites was less than such resistance of the kaolins.

The decreasing order of peptization resistance was found to be montmorillonite, kaolinite, illite.

The apparent dispersion (peptization) — dispersing agent concentration curves presented herein have been only generally discussed and more detailed interpretation that may be offered later should yield additional information.

The selection of best dispersing agent for a particular application is a function of the degree of dispersion desired and the required quantity and cost of the reagents involved. On the basis of the evidence thus far obtained the use of "sodium lignosulfonate" seems preferable for applications involving clay materials if selective peptizing action toward clay type is not desired.

No specific stoichiometric relationships between the concentrations of clay in the sol and the flocculation values ( $C_m$ ) of the dispersing agents have yet been recognized. Such apparent independence is characteristic of colloidal systems but this investigation is being continued.

The observed greater variation in  $P_{RC}^f$  values for the examined marine materials than for the examined non-marine materials may be due to differences in solvation characteristics, to the presence of adsorbed organic molecules of marine origin, to ionic exchanges and ionic antagonism considerations, or to the associated mixed layer clay mineral content of the marine sediments. Nevertheless, the differentiation of marine and terrestrial clays on the basis of relative surface activities of the clays may be within the realm of present scientific possibility. The length of time the material is

exposed to the marine environment is probably critical to this differentiation, however. It also must be considered that some terrestrial clay deposits may exhibit more  $P_{RO}^f$  variation than the river sediments available for this study.

Advances in the scientific understanding of the stability and peptization of clay suspensions will require that more attention be given to the possible associations of all chemical entities throughout the suspension system with adequate regard for the surface activities and interlamellar forces of the clay micelles.

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