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PARTICLE INTERACTION AND STABILITY OF SUSPENDED SOLIDS

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FOREWORD

The following selection of papers on Studies on Suspended Solids has recently been published -

1. Yong, R.N. (1984) Particle interaction and stability of suspended solids. Proc., ASCE Symposium on SEDIMENTATION CONSOLIDATION MODELS, San Francisco. pp.30-59.

2. Yong, R.N. and Elmonayeri, D.S. (1984) Convection-diffusion analysis of sedimentation in initially dilute solids-suspensions. Proc., ASCE Symposium on SEDIMENTATION CONSOLIDATION MODELS, San Francisco, pp. 260-274.

3. Yong, R.N. and Wagh, A.S. (1985) Dispersion stability of suspended solids in an aqueous medium. Proc., Engrg. Found. Conference on FLOCCULATION, SEDIMENTATION AND CONSOLIDATION. Georgia Island. *In press*.

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PARTICLE INTERACTION AND STABILITY OF SUSPENDED SOLIDS

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ABSTRACT

The physics of particle interaction, which is responsible for the problem of the apparent tardy settling of suspended solids in tailings discharge slurries containing initially low concentrations of solids, is examined in this study. The degree to which the solids remain in a quasi-suspended state is identified as the dispersion stability of the suspension. This study first identifies the basic elements of the general situation, and discusses the characteristics of interactions of surface-active solids which are common to many types of slurries and fundamental to the development of suspension properties. The basic principles established from the physics of interaction of the suspended solids identify dispersion stability as a function of the composition of the solids and the chemistry of the suspending fluid. The equilibrium concentration of solids remaining in suspension at any one time can be calculated in terms of the balance of energy (internal and external) of the system. The concept of equilibrium suspension volumes is tested with comparisons between theoretically computed and measured values of solids concentrations.

INTRODUCTION

The phenomenon of settling of suspended solids (fines) is one which is common to (a) natural processes in soil sedimentation such as the initial stages for formation of sedimentary soils, and (b) management of tailings discharge from mineral resource industries. In both general types of situations, one of the major items of interest is the problem of prediction of the rate of settling of the suspended solids and the consolidation of the sediment layer.

The intent of this paper is to present a view of the phenomenon of interaction of surface-active solids in a fluid medium which produces the situation commonly identified as a solids-suspension. Because of the surface activities of the solids and their resultant interactions, the phenomenon of suspended solids occurs in many containment ponds associated with mineral resource industry discharges.

We begin by identifying the general situation of pond containment

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and the establishment of a solids concentration profile in the pond. This is followed by a discussion of the characteristics of interactions of surface-active solids which are fundamental to the development of the suspension properties - with a view to establishing the thesis that the solids are dispersed in the suspending fluid at a particular equilibrium concentration, consistent with (a) the composition of solids, and (b) the balance of energy (internal and external) of the system. To demonstrate the thesis, several types of discharge slurries are examined in this study. The laboratory methods of compositional analysis and the pertinent compositional features of the slurries studied are also listed. Finally, using the concept of the equilibrium suspension volume described by each type of solid which comprises the types of solids present in the system, the theoretically computed solids concentrations for some of the slurries studied are compared with the actual measured solids concentrations.

THE PHYSICAL PROBLEM

The solids (fines) concentration by weight, in a solids-suspension tailings discharge from many mineral extraction process industries is generally very dilute - in the range of 1 to 3%. If the solids are non surface-active, and if they are silt-sized or larger, it is likely that they will settle in accord with the general predictions advanced by the simple Stokesian model. However, if the particles are clay-sized or less, and if they are surface-active in nature, simple Stokesian predictions will not accurately portray the settling behaviour of the solids.

As the solids settle, their concentration will increase to the point where proximal hindrances become significant. Thus, even if initial settling of the suspended solids can be predicted by the simple Stokesian model, subsequent settling of the solids will render the model invalid in application. The problem of the inability of the solids to settle in accord with gravitational mechanisms has been documented previously - e.g. [1,5,25] and will not be repeated here. Figure 1 which shows the essence of the problem, portrays the solids concentration profile in a settling pond. This profile is common to the settling performance of initially dilute suspensions from tailings discharge or natural processes after a period of several years.

Zone A which is sometimes defined as the top, water layer, is the supernatant water layer. This represents the water released in the immediate settling of the discharge tailings slurry plus the accumulation of the water derived from the sedimentation/consolidation processes occurring in the lower portions of the containment pond. Below Zone A, the solids concentration appears to increase to the point where a somewhat constant solids concentration is obtained. The transition solids concentration zone is identified as Zone B whilst the apparent "constant" solids concentration zone is labelled as Zone C. This zone is sometimes called the stagnant zone - in recognition of the fact that the rate of solids concentration increase is remarkably low in contrast to that observed in Zone B.

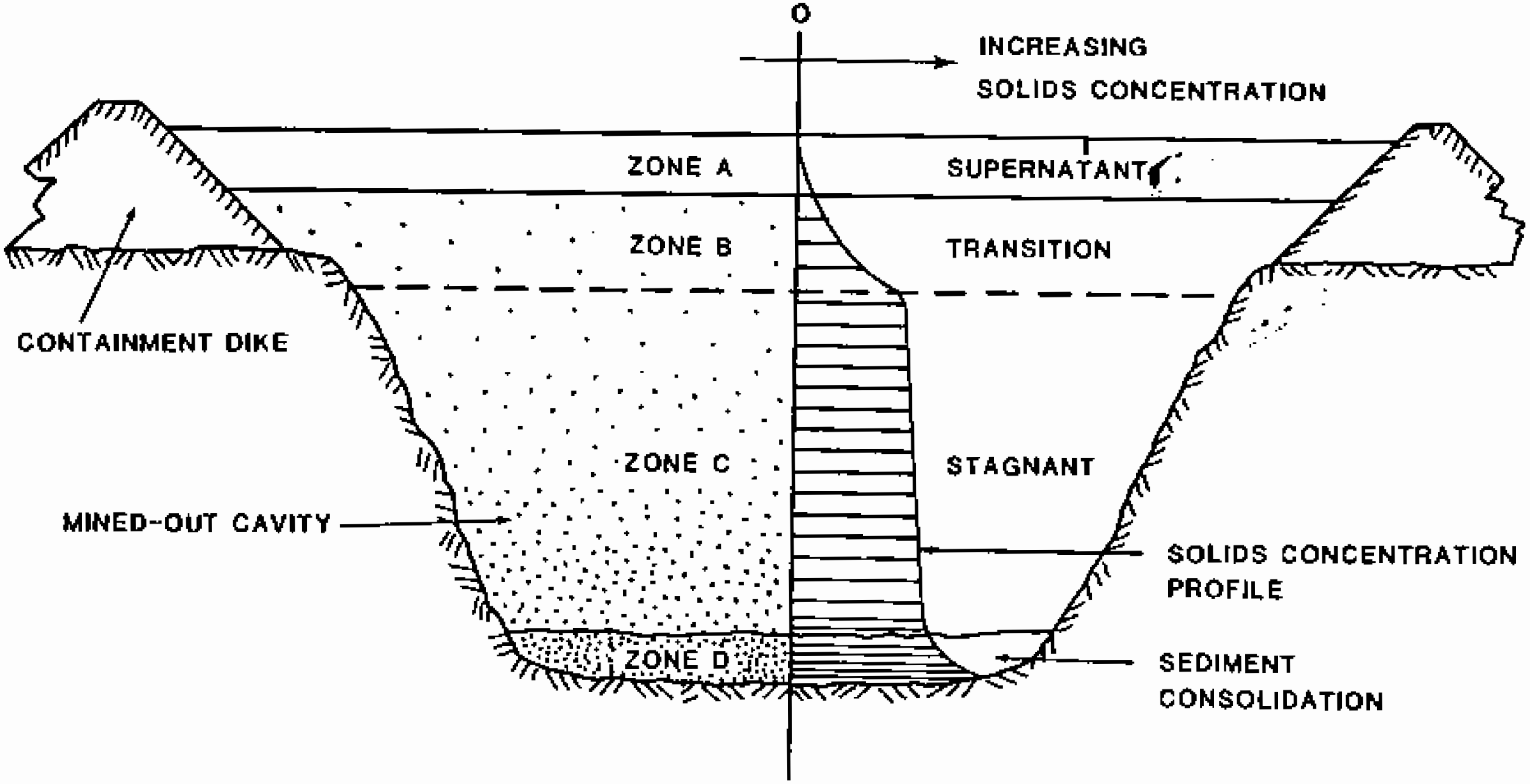


Fig. 1 Ideal representation of settling of suspended solids in a containment pond.

The transition between Zones C and D is not well-established. Zone D represents the proper sediment layer where consolidation is known to occur. However, there is considerable evidence available from field measurements to show that even though the solids concentration in the lower portion of Zone C might be low, (void ratios of about 5 or less), some success in the application of large-strain consolidation methods of analyses can be obtained in the prediction of settling rate. This is discussed further in the next Section of this paper.

We should note however that the situation shown in Fig. 1 represents the ideal containment pond in a stagnant situation, and that the pond filling process is assumed to produce an initial uniform distribution of solids. The real field situation however is not as easily described. Figure 2 for example shows the development of a typical pond where the tailings slurry is discharged from the "upper" end of the pond. This idealized sketch represents the ongoing discharge occurring in several operations presently under study. Relying on the characteristics of the settling material in combination with natural solar drying processes (where applicable), a kind of inclined layering effect is generally achieved. The coarser particles or solids settle out in the near end of the pond whilst the finer fractions will get "transported" to the further extremes of the pond. In effect therefore, a segregative effect is developed.

The three sections identified in Fig. 2 show an attempt in broadly classifying the apparent segregative effect. Section I shows the delta layering effect. Present experience in the ongoing two studies being conducted in S.E. Asia and Jamaica shows that with proper sequencing of tailings discharge, densification of the layers through partial drying of the tailings discharge layers can be achieved. By moving the discharge pipe from one location to another to allow for this drying process to occur, a quasi-stable beach can be formed. Drilling and sampling through some of these beaches have shown that the solids distribution profile and especially the water content profile are not uniform. This is because operational procedures generally do not permit the time required for each tailings discharge layer to fully dry before accepting the next load.

Section II in Fig. 2 shows a greater presence of coarser particles in the suspension in contrast to Section III. The coarser particles which sediment more readily in Section II and the other solids remaining in suspension in Section II are obviously influenced by the input conditions at the pipe entry. The settling performance of the suspended solids in Section III may be assumed to approach the ideal pond containment situation shown in Fig. 1.

Many terms have been used to describe the combination of suspended solids and water, e.g. "slime", "slurry", "mud", etc. By and large, these terms have generally been associated with certain industries, processes, or types of discharge. The fundamental phenomenon of suspended fines or solids however remains the same. For the sake of simplicity in communication in this presentation, the term "slurry waste" will be used in discussions concerned with the general solids-suspension phenomenon associated with tailings discharge. However, where specific terms have been used in particular industries, e.g. red mud for bauxite slurry

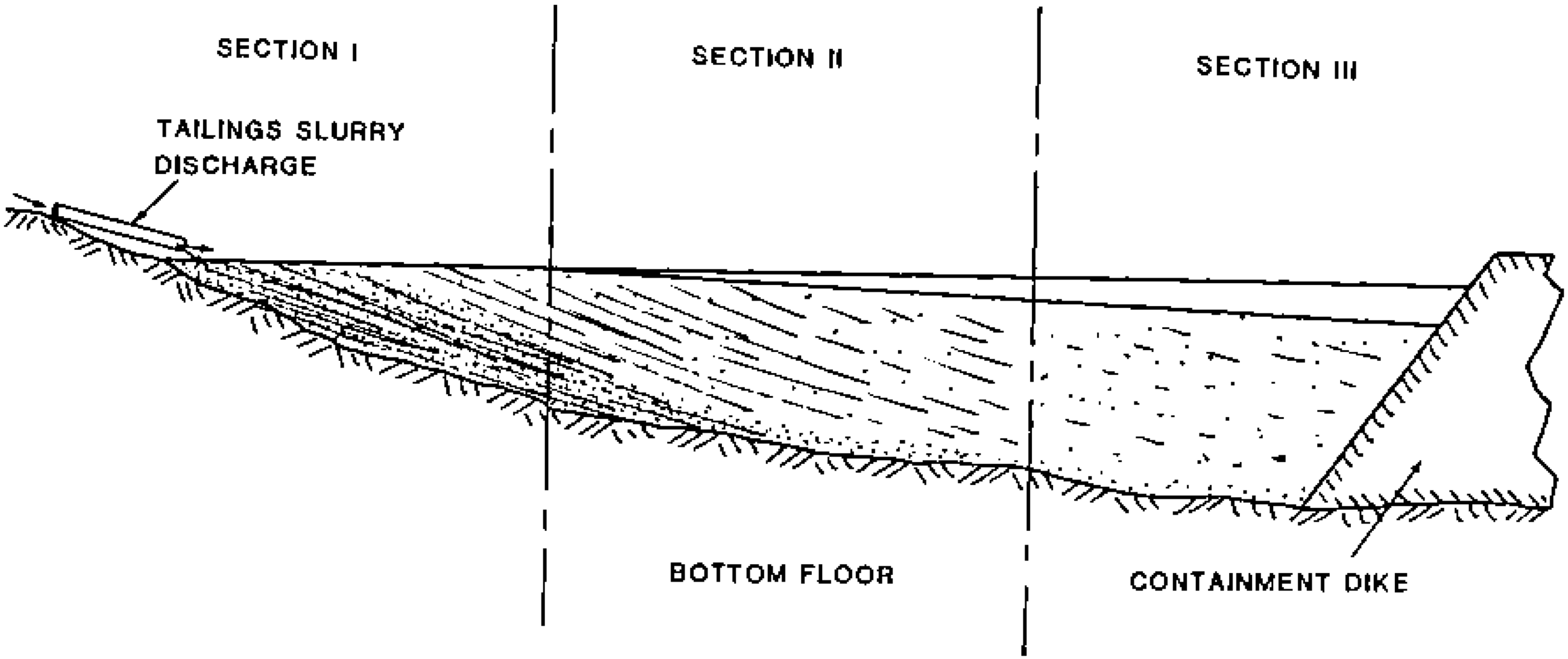


Fig. 2 Actual schematic representation of a typical containment pond showing slurry discharge from the input pipe at left. Note that the pipe can be moved periodically to other locations to build up a "competent" beach.

waste discharge, these will be used at the appropriate times.

INTERACTION CHARACTERISTICS IN DEVELOPMENT OF DISPERSION STABILITY OF SLURRY WASTES

Since the composition and properties of a specific slurry waste is a direct function of (a) the nature and composition of the host material, (b) the extraction/process variables and techniques used, and (c) the end product requirement, it is apparent that considerable variations in exact compositional characteristics and properties of product slurries will be obtained. The preceding notwithstanding, the fundamental issues concerning the nature of the problem remain somewhat constant, i.e. nature and characteristics of the suspended solids (generally surface-active solids such as clay mineral particles), and chemistry of the suspending fluid. Some examples of typical slurry wastes, such as those considered in this study, include: (a) phosphatic clay slimes, (b) bauxite red mud, (c) tar sand sludge, (d) humic slimes, (e) tin mine slimes, and (f) clay slimes.

The phenomenon of slow self settling of suspended solids which is most likely due to the increased dispersion stability of the solids in suspension can be traced to at least three mechanisms:

(i) Mechanism 1. Mutual net repulsion caused by the surface-active nature of the solids and the low salt concentrations, or predominance of (a) monovalent cations, or (b) potential determining anions.

(ii) Mechanism 2. Adsorption or coating of amorphous material (small lyophilic colloid) on a large electronegative colloid. The affinity of amorphous material for water exceeds the net attraction of the van der Waals forces.

(iii) Mechanism 3. Steric hindrance due to adsorption of organic molecules such as demonstrated in the tar-sand sludge.

In a suspension containing various kinds of constituents, all three mechanisms are expected to be present - with differing degrees of influence - in promoting the dispersion stability of the suspension. It is indeed likely that other mechanisms may exist which are complex variants of the above three mechanisms. These have yet to be fully identified and documented. All these mechanisms contribute not only to the slow self settling rate of the suspended (or dispersed) solids, but also to the suspension volume i.e. stagnant condition in Zone C.

The three mechanisms and complex variants of the three mechanisms are basic contributors to the dispersion stability of suspensions. The surface forces are mainly due to the electrical field developed from the charge balancing cations - generally identified as counter ions. The effect of surface electrical fields on the properties of adsorbed molecules needs to be understood. Approximate calculations for the surface electrical fields suggest that they are strong since a unit positive point charge away from a surface is about 1500 million volts per cm or 15 volts per Angstrom Unit.

In suspensions consisting of lyophobic colloids, such as slurry wastes, their stability (i.e. dispersion stability) depends on the characteristics of particle (solid) interaction - i.e. solid-to-solid interaction in the presence of a fluid medium containing various ionic species. Colloidal theory appears to be most useful in providing the basis for evaluation of interparticle action. The quantitative theory of stability of lyphobic colloids, identified as the DLVO theory (after Derjagin, Landau, Verwey and Overbeek), constructs its analytical model on the basis of (a) electrostatic repulsive forces due to interpenetration of the diffuse ionic layers, and (b) van der Waals attraction forces. Net repulsion occurs between particles (colloids) when double layer repulsion overwhelms van der Waals attraction. The presence of potential determining anions such as bicarbonates, carbonates, hydroxides, phosphates, etc. in the fluid phase, all contribute to the enhancement of net repulsion.

When attractive forces dominate, the system becomes unstable and coagulation occurs. At least two factors are important in the coagulation process: (a) Brownian motion of the constituent particles, and (b) particle interaction. In a system where the repulsive forces are vanishingly small and can be neglected, Brownian collision between particles will lead to agglomeration or aggregation of the particles - thus leading to the production of floc units. Not every collision however will result in aggregation. For two different systems, given the same collision frequency, the effectiveness of aggregation upon collision depends on the properties of the particle surfaces. Under such circumstances, this kind of phenomenon is identified as "slow coagulation".

When the rate of aggregation upon collision no longer depends on the properties of surfaces, and is conditioned only by the collision frequency, the process of "fast coagulation" has been attained. This state occurs when the properties of the surfaces of the constituents in the suspension are ineffective insofar as collision aggregation is concerned.

In solids-suspensions characterized by clay minerals, the zeta potential at any given clay:water ratio depends on the concentration of electrolyte in the suspension. The mono-molecular layer of the electrolyte on the clay surface is formed at a particular concentration. There does exist a strong relationship between the dispersion stability (of the suspension) and the zeta potential of the system, as shown previously by Yong and Sethi (1977) - see Table 1.

In considering the dispersion stability of suspensions consisting of solids and fluids, it is useful to note that the dispersions which are stable due to the presence of strong mutual repulsive forces can be agglomerated or flocculated in one of at least six different ways:

TABLE 1 - Relation between Dispersion Stability of Clays and Zeta Potential

	Stability characteristics	Average zeta potential mv
1.	Maximum agglomeration and precipitation	+3 to 0
2.	Excellent agglomeration and precipitation	-1 to -4
3.	Fair agglomeration and precipitation	-5 to -10
4.	Threshold of agglomeration (tactoids or domains)	-11 to -20
5.	Plateau of slight stability (few domains)	-21 to -30
6.	Moderate stability (no domains)	-31 to -40
7.	Good stability, i.e. stable suspension	-41 to -50
8.	Very good stability	-51 to -60
9.	Excellent stability	-61 to -80
10.	Maximum stability	-81 to -100

1. Through lowering of the zeta potential of the system to zero with the use of a strong cationic electrolyte.

2. Through the use of a strong cationic electrolyte in conjunction with an appropriate alkali. (Optimum pH is required).

3. By adding a reagent which results in the formation of an insoluble matrix which engulfs and binds the water in the system.

4. Agglomeration through the addition of sufficient cationic polyelectrolytes.

5. Agglomeration with long chain or branched-chain anionic polyelectrolytes.

6. Agglomeration with non-ionic long chain or branched-chain polymers.

The protective coating of amorphous material on the surfaces of primary minerals and larger-sized solids [24] may result in strong repulsion between particles, thus rendering stable dispersion conditions. In suspension systems derived with soil particulates, the amorphous material is seen to be composed of silica with or without sesquioxides. It has a strong affinity with water and its properties change on drying.

SETTLING/SEDIMENTATION PROCESS

The simplest procedure for description of the total settling/sedimentation and consolidation process is to trace the "life" or status of a typical representative solid, beginning with its initial state. Following introduction of the tailings slurry, the solids in the slurry will settle in a fashion more or less controlled by either gravitational forces or by interactive forces dictated by surface-active relationships. The concentration of solids at this time is not sufficient to account for proximal hindrances, and is identified in Fig. 1 as Zone A. It is indeed important to stress that the "line" separating any of the Zones shown in Fig. 1, e.g. Zone A from Zone B, is not a line but will be a transition Zone of variable thickness.

When initial settling of the representative solid has proceeded to the stage where neighbouring solids begin to interfere because of their highly active surfaces, a hindered settling performance characteristic becomes evident - shown as Zone B in Fig. 1. Beyond this stage, the settling of the representative solid becomes tediously slow and is apparently hindered not only by the physical interferences of neighbouring solids, but also by interactions controlled by surface active relationships. It is not clear where Zone B ends and where Zone C begins. The kinds of mechanisms operative in these two Zones are not totally different. The specific items which separate them are perhaps better thought of in terms of the more or less dominant solid-to-solid (i.e. interparticle) interactions established via physico-chemical forces.

Zone C can be said to represent the region where even though no physical contact between solids is established - void ratios of 4 to 6 - the physical evidence shows that some small value of excess hydrostatic pressure (pore pressure) can be measured [25]. A form of compression settling of the solids can be said to be occurring at this stage. When the representative solid undergoes further settling to the point where physical contact between adjacent solids is achieved, the consolidation process becomes the dominant mechanism (Zone D).

RECONCILIATION WITH ANALYTICAL MODELS

Table 2 shows the elements of the settling process in relation to representative analytical models. The comments made are not meant to be comprehensive; only the highlights are listed. In viewing the Table, it is obvious that at the present time, total analysis of the problem can only be achieved by breaking up the problem into the four Zones for separate analytical treatment using available classical models - or their variants thereof. This procedure might be expedient, but is by no means satisfactory. The first significant problem that comes to mind is the definition of initial conditions for each particular mode of analysis. Whilst this might not be especially critical in analysis, it is decidedly so if predictions are to be made! Where does one transit from Zone B to Zone C? What are the material output values forthcoming from Zone B - for use as input values for modelling of performance in Zone C?

Obviously, until a unified (continuous) theory can be successfully developed, which trespasses the various boundaries, one will be constrained to work within the limits of the present available theories. The problem obviously begins with the need to fully understand the nature of the interactions producing dispersion stability. As discussed in the previous Section, the surface active nature of the solids and the various interactions producing the three possible mechanisms for the suspended state can indeed provide a very complex system which is not easily portrayed by standard models (or variants thereof) which rely on gravitational principles. Table 3 for example, lists some relationships available for prediction of settling velocity of the solids as a function of their concentration [21] - thought to be applicable to the prediction of solids settling performance in Zones A and B. Surface active relationships however do not appear to have been considered directly - except via "appropriate" constants.

TABLE 2 - Settling and Theory Applications

	Stokesian	Hindered Theories	Consolidation Theories
Zone A			
No measurable pressures. (no excess hydrostatic pressures)	Limited to non surface-active particle suspensions.	Empirical models require extensive laboratory testing for derivation of correction coefficients.	Not applicable because of absence of relationships defining effective stress and material properties.
Zone B			
No measurable pore pressures	Not directly applicable.	Same restrictions as for Zone A	Same restrictions as for Zone A.
Zone C			
Detectable pore pressures	Not applicable	Not applicable	Large strain consolidation phenomenon. Requires accountability for non-linear relationships and self-weight.
Zone D			
Pore pressures and effective stresses.	Not applicable	Not applicable	Classical theories applicable if self-weight is accounted for.

The very common quandry facing analysts and modellers in the study of settling ponds or very soft sediments is the establishment of the point at which effective stress can be considered to be operative, i.e. when pore pressures are measurable in a solids suspension. Experience in matching predictions and actual field values suggest that the models relying on pore pressure development can be satisfactorily used at void ratios of between 4 and 5, and less. This can indeed be puzzling since computations will show that solid-to-solid contact (thought necessary for transfer of intergranular stress) is not established at these high void ratios. To overcome this apparent inconsistency, it is perhaps better to visualize the suspended solids system in terms of the dispersion stability of the suspension.

The dispersion stability of the solids suspension which follows from the fact that surface active solids interact in the fluid medium in the sense of lyophobic colloids, is indicative of the degree to which the solids remain in suspension. This is a direct outcome of the water holding capability of the solids. At a zero osmotic pressure (i.e. zero

TABLE 3 - Relationship between Solids Concentration and Settling Velocity - From [21]

Equation	Source
$v = v_o(1 - KC)^{4.65}$	Richardson and Zakie(1954)
$v = v_o(1 - KC)^2 \cdot 10^{-1.82KC}$	Steinour (1944)
$v = v_o 10^{-aKC}$	Thomas (1964)
$v = ac^{-b}$	Cole (1968)
$v = v_o[1 - 2.78(KC)^{2/3}]$	Bond (1960)
$v = v_o c^{-ac}$	Vesilind (1969)
$v = v_o[1 + \frac{3}{4} KC \ (1 - \frac{8}{KC - 3})]$	Brinkman (1948)
$v = v_o(1 - KC)^a$	Maude and Whitmore (1958)
$v = v_o(1 - aKC)\ [1 - b(KC)^{1/3}]$	Oliver (1961)
$v = \dfrac{v_o(3 - \frac{9}{2}(KC)^{1/3} + \frac{9}{2}(KC)^{5/3} - 3(KC)^2)}{3 + 2\ (KC)^{5/3}}$	Happel (1958)

where v = interface velocity of solids concentration, C;
v_o = Stokes settling velocity for a single discrete particle;
K = conversion factor, so that KC = volume fraction of solids in the slurry; and
a,b = constants (unique to each equation)

midplane potential), the volume of water associated with each solid or floc is at its maximum value. Figure 3 shows a mineral particle (solid) surrounded by its equilibrium shell of water. The thickness of this shell, or the volume of water, can be computed from theoretical considerations using the DLVO model [26]. The energy-separation distance calculations will give the most likely equilibrium interparticle spacing and void ratio of the system. Figure 4, which has been idealized into a parallel particle arrangement to portray the use of cationic and anionic relationships, shows the development of the attraction and repulsion forces for an ideal three parallel-particle system. Obviously, real slurry systems will not have ideal parallel particle arrangements. As can be seen from the relationships given in the Appendix, the DLVO model permits one to consider various modes and configurations of particles (flat plates and spheres) in its computations for equilibrium separation distances. The relationships shown take into account (a) non-parallel particle arrangements, (b) mixed minerals in the suspension, and (c) salt concentrations in the suspending fluid. Calculations for long range repulsive and attractive energies corresponding to face-to-face, edge-to-edge and edge-to-face mode of particle or solid interaction in the presence of various salt concentrations can be made.

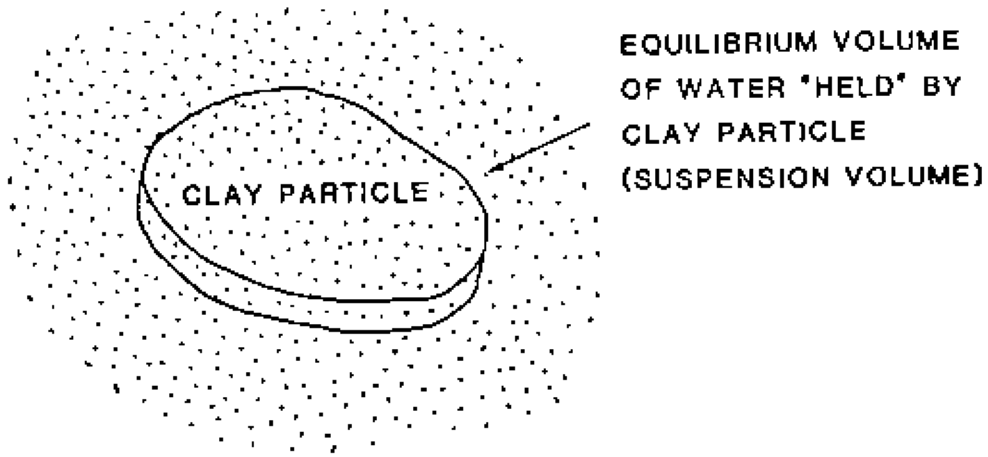
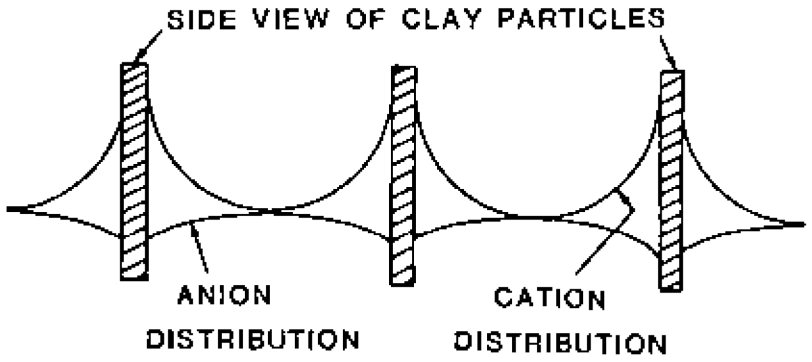


Fig. 3 Schematic representation of a water shell surrounding a clay particle.



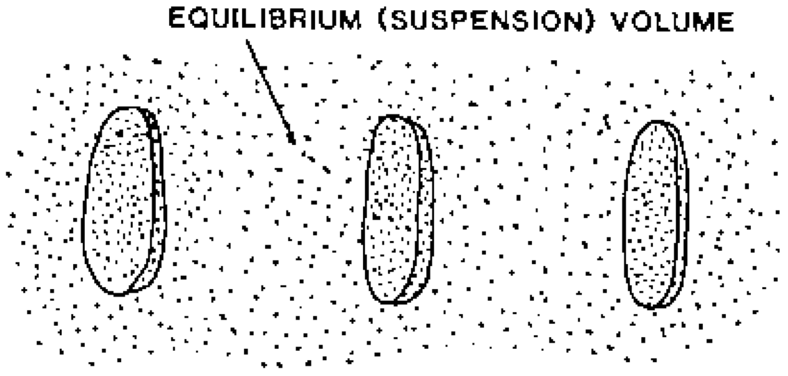


Fig. 4 Schematic diagram showing dispersion of particles and contained water. Note that particles are shown in parallel only to illustrate the distribution of ions above. Actual conditions will show non-parallel particles and flocs.

If each solid, or if each floc "holds" onto a specific volume of water as its "equilibrium" shell of water (defined as the suspension volume) - consistent with the balance of internal and external energies - the total stable dispersed state of the suspended solids at a particular depth in the containment pond, will show that the total volume of water retained in a representative unit volume would be equal to the sum of the suspension volumes of the individual component solids. In the experiments conducted by Yong and Sethi (1978) to determine the equilibrium (suspension) volume of water associated with specific minerals, the values obtained (Table 4) show good correspondence with those computed on the basis of the theoretical interaction model, - provided that proper accounting is given to the presence of the potential determining anions.

TABLE 4 - Suspension Volume for Various Minerals
and Method of their Determination

"equilibrium" suspension states were achieved prior to measurement of the solids content in the supernatant. The suspension volume, expressed in terms of cubic centimeters of fluid per gram of mineral solid, has been calculated from the amount of solids remaining in the supernatant. The suspension volumes measured do not require any preferred orientation of solids, and are thus used in comparing theoretically predicted equilibrium solids concentrations with actual measured values for the slurry samples studied.

LABORATORY ANALYSES OF SLURRY WASTES

To further elaborate on the thesis that surface-active solids participate through interparticle action in producing dispersion stability, and hence slow settling of the suspended solids, laboratory analyses of various slurry wastes were performed. Attention was paid to the physical, chemical and mineralogical composition of the slimes. The total types and numbers of tests conducted, by and large depended on the quantity of samples received. The following methods were used for analyses:

1. <u>Mineralogy</u>:

The oriented slide used for the X-ray diffraction test was prepared by depositing 4 ml of slime, diluted to about 1% solids concentration (by weight) onto a glass slide and subsequently air-dried. Horizontal particle orientation is generally achieved with this technique - thus allowing for enhancement of basal reflections and more ready mineral identification. Because the slurry sample contained the suspending fluid, no pre-treatment was given to the sample.

In other mineralogical studies on dried powdered samples, untreated and treated samples are used. Preparation of the samples for analysis required 100 mg of the powdered sample to be dispersed in 10 ml of distilled water, from which 4 ml of the dispersion was deposited on the glass slide. Subsequent to the first X-ray analysis, the slide was treated with glycerol/ethanol mixture and the test conducted again for detection of swelling minerals.

The Siemen's X-ray diffractometer with CuKα radiation was used for all the tests conducted. The percentage of minerals was generally estimated by comparing the peak heights of pure standard reference clay minerals with the peak heights of the minerals found in the test samples. This semi-quantitative technique is by no means accurate, but is used primarily to provide an indication of the approximate proportions of minerals present in the sample.

2. <u>Pore (Suspension) Fluid Analysis</u>:

The suspension fluid was obtained from the slime samples by vacuum filtration or through centrifugation and decantation of the clear supernatant. The fluid was subsequently analyzed for soluble ions and pH. The methods of analysis used includes:

Atomic Absorption Spectrophotometry (Emission):	Na^+, K^+, Ca^{2+}
Atomic Absorption Spectrophotometry (Absorption):	Mg^{2+}
Titration with H_2SO_4 to colorimetric end point:	HCO_3^-, CO_3^{2-}, Cl^-

Turbidimetry: for SO_4^{2-}

Beckman pH meter: for pH

3. Organic Content:

Since only the total amount of organic matter (and not species) need to be determined in the initial phases of all the studies, and since precise methods are indeed too time consuming and complex, the simple approximate method of H_2O_2 washing was adopted. Two to three grams of dried and pulverized slime samples were weighed into a beaker, to which a small amount of distilled water was added to wet the sample. Following placement of the beaker on a hot plate at low heat, 30% H_2O_2 was periodically added until no further bubbling reaction was observed. The sample was then centrifuged and oven-dried and the resultant weight compared with the initial dry weight.

4. Cation Exchange Capacity:

To determine the cation exchange capacity of the suspended solids, 0.25 grams of the dried pulverized slurry sample was weighed into a centrifuge tube and 40 ml of silver nitrate-thiourea solution was added and shaken overnight. The sample was then centrifuged and the supernatant was tested for Ag^+. A Jarrel-Ash Atomsorb Atomic Absorption Flame Emission Spectrophotometer was then used for analysis. The CEC of a sample determined in this manner corresponds to the amount of Ag_3 absorbed on the clay surfaces.

5. Determination of Sand, Silt and Clay Fractions:

Prior to determination of the various size fractions in the slime, 15 meq/l sodium bicarbonate was added to the test sample and the combined solution shaken and placed in an ultrasonic bath. This was left overnight to equilibrate - to ensure dispersion of the suspended solids. Following the "curing" period, the dispersion was then wet-sieved and centrifuged for determination of sand (>53μ), silt (2 - 53μ), and clay (<2μ).

LABORATORY ANALYSES OF SOME SLURRY WASTES

1. Soil-Organic Slime:

The source of the soil-organic slime samples examined in this study was the humates occurring as organic residues cementing sand grains in localized areas in the heavy minerals ore body in Northwest Florida. With the presence of the organic residues, the slimes obtained as the slurry waste product of wet milling processes associated with heavy mineral extraction in that region can be reasonably expected to contain soil-organic acids. In the samples obtained for examination the primary compositional constituents were humic acids, fulvic acids and soil minerals (quartz, feldspar, and chlorite). Since humates are generally composed of the two general classes of soil-organic acids - (a) humic, and (b) fulvic acids - it is therefore to be expected that the slimes obtained from the milling process would consist of these acids.

In preparing the samples used in the study for analysis of humic substances, the techniques used for separation of humic and fulvic acids required prewashing with 0.1 N HCl and water to remove the salts. Since (a) humic acids are soluble in dilute base but not soluble in alcohol and acid, and since (b) fulvic acids on the other hand are water soluble and are known to remain in solution after neutralization and after all humic acid has precipitated out, the separation techniques used followed procedures which first precipitated the humic acids.

The two types of samples received for analysis represented depth sensitivity of the slimes - (a) near-surface samples where the solids concentration was low because of the initial settling of the solids following deposition of the slime, and (b) samples at depth where equilibrium solids concentration existed. The assignment of infra-red absorption bands in the humic and fulvic acids extracted from the test samples is shown in Table 5.

TABLE 5 - Assignment of I.R. Absorption Bands in Humic and Fulvic Acids

Frequency 1/cm	Assignment	Present in
3400	Hydrogen bonded OH	HA, FA*
1725	C = O of CO_2H, C = O stretch of ketonic carbonyl	HA
1630	Aromatic C = C or hydrogen bonded C = O or double bond conjugated with COO^-	FA
1610	Same as sample 1630 cm^{-1}	HA
1460	Aliphatic C-H	FA
1400	COO^-, aliphatic C-H	HA
1200	C-O stretch or OH deformation of CO_2H	HA
1020	SiO of silicate impurities	HA

*HA and FA = humic and fulvic acids respectively.

For the samples taken at depth where equilibrium solids concentration was thought to exist, analyses conducted showed a solids concentration of about 19% by weight (and 81% water). The composition of the solids showed, on the average, 6.7% minerals, 72% humic acid and 30.3% fulvic acid. The minerals present included quartz, chlorite and feldspar. In the samples obtained near the surface, the solids concentration averaged about 2.0%. In the solids traction, the minerals concentration was about 3.7%. The humic and fulvic acids were, on the average, about 68% and 28.3% respectively.

2. Phosphate Slimes:

The problems and general properties of the Florida phosphate slimes have received considerable attention, and have been well reported, e.g. [5]. The results of studies on the composition of the slime indicate a high degree of variability in the proportions of the constituent, obviously dependent on source material (host rock), processing, end product requirements, spatial and temporal variational effects in the recovery of slime sample used for analysis. By and large, the following minerals have been recorded as present in most slimes:

Carbonate-flourapatite
Attapulgite
Heavy minerals
Crandallite
Quartz
Wavellite
Dolomite
Illite
Montmorillonite
Feldspar
Kaolinite

In addition to the minerals listed above, the samples analyzed in this study showed the presence of amorphous materials. The dominant ions in the suspending fluid included:

Calcium
Potassium
Magnesium
Bicarbonate
Sodium
Sulphate

with pH variation from 7.0 to 8.0.

3. Aggregate Slimes:

The production of aggregate slimes arising from wash-extraction of coarse aggregates from weathered granite constitutes a major containment problem. In many regions, because of the scarcity of sources of coarse aggregates, surface layer soils derived from weathering of granite and other types of rock provide a ready supply of granular material - provided that these materials can be separated from the finer fractions (usually clay particles). Wash procedures are commonly used to extract the coarse fractions in gravitational separation processes.

The aggregate slimes which were examined in this study came from S.E. Asia. Analysis of the physical composition of the slimes showed on the average:

Water - 84.9% by weight
Organics - 0.4%
Sand - 0.1%
Silt - 1.2%
Clay - 13.5%

Analysis of the minerals detected in the X-ray diffractograms using the approximate peak height matching technique described earlier, showed about 54% kaolinite, 35% montmorillonite, and 11% illite. These values are to be considered as approximate values.

Analysis of the chemistry of the suspension fluid, obtained by centrifuging the slime, showed the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, and SO_4^{2-}. These were in very small quantities, with Na^+, at 0.5 meq/l being the highest. The suspending fluid pH = 7.5 and specific electrical conductivity was measured as 0.101 millimhos.

Analysis of the exchangeable cations and cation exchange capacity of the mineral fractions of the suspended particles showed the presence of Na^+, K^+, Ca^{2+}, Mg^{2+}, the latter two being more dominant at 5.4 and 4.3 meq/100gm respectively. Na^+ and K^+ were registered as 2.5 and 1.5 meq/100gm respectively, bringing the total exchangeable cations to be 13.7 meq/100gm. The cation exchange capacity was determined as 31.1 meq/100gm.

As noted from the above, the exchangeable cations were found to be composed of mainly divalent cations. The total exchangeable cations of 13.7 meq/100gm and CEC of 31.1 meq/100gm indicate that only about one half of the exchangeable cations found in the suspended particles are made up of Na^+, K^+, Ca^{2+}, and Mg^{2+}. The remaining could be attributed to H^+ and Al^{3+} - since the pH of the slime was found to be acidic (pH = 4.7).

4. Tin Mining Slimes:

The tin mining slimes examined in this study are located in areas of limestone formation in S.E. Asia. The tin ore bearing material derived from erosion of the parent rock was deposited in areas of highly weathered limestone formations. The resultant topography at the interface is rather complex, consisting of troughs, channels and pinnacles - typical of deeply weathered limestone. The slime material examined came from gravel-pump mining discharge of the wash material. Because of depositional techniques, sand segregation occurs at the immediate point of pump discharge and resultant finer material slimes are found at the distant points from pipe discharge. This situation is not unlike that represented in Fig. 2.

The solids concentration (weight basis) for the samples studied averaged around 52% - with solids specific gravity of 2.76. Analysis of the typical X-ray diffractograms obtained for the samples studied showed estimated mineral compositional contents as (about) 48% kaolinite, 2% gibbsite, 10% mica, 30% quartz, and 3% other types of solids.

Analysis of the pore water chemistry revealed the presence of Na^+, Ca^{2+}, K^+, and Mg^{2+}, with Ca^{2+}, being the dominant cation at 4.74 meq/l. The settled slime at the solids concentration of 52% does not provide any realistic strength for support of any type of load.

5. Bauxite Red Mud:

The samples for examination of red mud obtained from the Bayer processing of bauxite for extraction of aluminium came from Jamaica. The suspended solids showed at least 80% of the solids (by weight) smaller than two microns. From an analysis of X-ray diffractograms of the samples, the main minerals appear to consist of hematite, goethite, and anatase, with some Bayer sodalite. Detailed studies conducted [27] using both scanning and transmission electron microscopy coupled with electron diffraction and energy dispersion analyses, show the system to be quite complex - especially in the resolution of whether the minerals are totally crystalline or whether they are indeed surrounded by a degraded amorphous shell. Because standard pure sample slides are not available for the minerals identified, no possible estimate of specific proportions of the minerals has been attempted.

The amorphous content determined using the method previously described by Yong et al. (1979) showed: Fe_2O_3 = about 50 to 60 mg/g of solid fraction, Al_2O_3 = 40 to 60 mg/g, with about less than 1 mg/g of SiO_2.

The pH of the samples varied from about 12.0 to 12.8, depending on the source of sample - primarily depth. By and large the solids concentration by weight also varied with respect to depth location, - from about 30 to 40%.

Analysis of the chemistry of the suspending fluid showed:

Cations	Meq/l	Anions	Meq/l
Na^+	222	HCO_3^-	41.5
K^+	0.58	Cl^-	0.25
Ca^{2+}	0.07	CO_3^{2-}	351
		SO_4^{2-}	11

6. Clay Coating Slurry:

The clay coating slurries studied came from a clay production industry in the Southeastern part of the U.S. These clays constitute the base material used in the paper coating industry, and more specifically in paper machine wet end processes. Because of the requirements of the paper Industry, the slurries studied were fairly consistent insofar as basic properties and compositional constituents were concerned.

One of the primary problems encountered in the production of the material for use in the paper Industry is the "economic water content" of the slurry. By this is meant the maximum amount of water that can be extracted from the slurries before shipment to the paper industry so that minimum bulk and weight can be attained. Excessive energy requirements to remove water that is "held" to the clay material must be considered in balance with production costs. Thus the samples received for study represented the solids-suspension equilibrium volume state of interest.

Analysis of the chemistry of the suspending fluid showed the presence of CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}. Na^+, and SO_4^{2-}, were the largest amount of ions present at 22.30 and 18.0 meq/l respectively. The concentration of HCO_3^- and 5.0 meq/l and the remaining ions showed concentrations less than 1 meq/l. The specific electrical conductivity was 2.12 mmhos/cm and the pH was 8.69.

The minerals identified in the samples were illite, montmorillonite, mixed layer material, chlorite, and quartz. The proportions of the minerals which were estimated again on the basis of peak ratios indicated: (a) montmorillonite, 6.7%, (b) illite, 5.2%, (c) chlorite, 2.2%, (d) mixed layer material, 2.1%, and (e) quartz, 83.8%. The solids concentration by weight was 35.5% (water = 64.5%), and the total mineral content in the solids was 95.8%. The remaining 4.2% of the solids was organics.

7. Beneficiation Slurry:

The coal beneficiation slurry studied which came from Western Canada was the product of procedures implemented to clean the clay coatings from the ore deposits. The solids concentration of the slurry was 8.7% by weight. The slurry remained in suspension for an interminable period without apparent settling out of the solids. The estimated proportions of the minerals present, determined from the X-ray analysis, showed:

(a) montmorillonite, 42%, (b) illite, 21%, (c) feldspar, 14%, (d) kaolinite, 13%, and (e) chlorite, 10%.

Analysis of the suspending fluid showed the presence of CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, Na^+, Ca^{2+}, K^+, Mg^{2+}. The dominant ions were SO_4^{2-} and Na^+, at 32.5 and 21.1 meq/l respectively. The specific electrical conductivity was 2.27 mmhos/cm whilst the pH was measured as 10.87.

8. Tar Sands Sludge:

The analyses for the sludge obtained from the hot water processing of tar sands in the Western part of Canada for recovery of bitumen have been reported previously by Yong and Sethi (1978). The typical composition of the sludge material is shown in Table 6 whilst the basic characteristics and mineralogical analysis of some typical samples are shown in Table 7.

The material is seen to be composed of many types of minerals, with the major minerals identified as kaolinte, illite and some lesser fraction of montmorillonite. The presence of amorphous materials should also be noted.

SUSPENSION VOLUMES AND SOLIDS CONCENTRATIONS

Using the values shown in Table 4, the theoretical suspension volumes (of water) associated with the individual components can be summed to estimate the "as-is" solids equilibrium volumetric water content. These values have been used to compute the theoretical solids concentration and compared with the actual values of solids concentration de determined for the samples obtained from the ponds studied. To illustrate the computational procedure, the procedure used in computing the values for the tin mine sample from S.E. Asia is cited as follows:

Mineral	Suspension Volume cc/gram (from Table 4)	Specific Volume in Sample cc/100 gram
Kaolinite - 45%	1.3	58.5
Mica - 10%	3.0	30.0
Gibbsite - 2%	1.0	2.0
Quartz - 40%	0.14	5.6
Other - 3%	0.15	0.45
Total = 100% (or 100 gram of solids)		96.55 cc/100 gram of solids

Hence, weight of water = 96.55 gram
Total weight = (100 gram of solids) + (96.55 gram of water)
= 196.55 gram.

Computed solids concentration = 100/196.55 = 50.8%
Measured solids concentration = 52%

The comparison between measured and computed solids concentration accords well.

TABLE 6 - Typical Composition of Tar Sands Sludge (from [23])

	Sludge 20' deep	Sludge 40' deep	Sludge 60' deep
Composition, wt. %			
Bitumen	3.3	3.9	4.5
Water	74.7	70.1	65.5
Mineral	22.0	26.0	30.0
Particle Size, wt. % Mineral			
Sand (> 44μ)	∿.0	∿.0	∿.0
Silt (2 - 44μ)	59	62	58.5
Clay (< 2μ)	41	38	41.5
Clay/Water	0.12	0.14	0.19

TABLE 7 - Basic Characteristics and Mineralogical Analysis of some Typical Samples of Tar Sands Sludge (from [23])

Depth	Particle Size Distribution			Sludge Composition			Percent Minerals in Bitumen-Free Sludge Solids												
(ft)	% Sand (> 44μ)	% Silt (2 - 44μ)	% Clay (< 2μ)	% Mineral	% Water	% Bitumen	Kaolinite	Illite	Mont-morillonite	Chlorite	Illite-Mont-morillonite Intergrade (70:30)	Quartz	Feldspar	Calcite	Siderite	Ankerite	Pyrite	Amorphous Fe_2O_3
20	1.9	50.1	48.0	24.6	73.[illegible]	2.2	54.4	8.4	1.4	0.7	1.8	24.8	1.1	0.9	2.6	0.0	0.0	3.9
45	13.5	51.6	34.9	33.0	62.5	4.5	42.8	8.4	1.1	0.6	1.5	38.5	1.1	0.8	2.5	0.0	0.0	3.5
60	44.6	31.3	24.1	40.8	56.4	2.8	27.2	5.8	0.9	0.7	1.0	59.1	0.9	0.7	1.4	0.0	0.1	2.2
70	47.5	34.5	18.0	47.5	51.1	1.4	25.1	4.2	0.5	1.1	0.6	63.8	0.8	0.6	1.2	0.0	0.0	2.1

Using this same procedure, the computed solids concentrations for the various types of samples examined, and the measured values are reported in Table 8. It must be stressed that both the theoretically computed and measured values must be considered as "average representative" values since: (a) the method used for determination of the proportion of various minerals from X-ray diffractograms, (b) sampling procedures, (c) quality of samples and how well they represent the actual conditions of the material in the ponds, are indeed pertinent and significant considerations. The preceding notwithstanding, it is noted that the theoretically computed values for solids concentrations do accord well with the measured values, - except for the aggregate slime - as seen in the extreme right hand column in Table 8.

TABLE 8 - Comparison of Theoretically Computed and Measured Solids Concentration (S.C.) for Samples Studied

Source	Theoretical S.C. %	Measured S.C. %	$\frac{\text{Theo. S.C.}}{\text{Meas. S.C.}}$ %
Phosphatic Slime	13.4	14	0.96
Aggregate Slime	10.5	14.3	0.71
Tin Mining Slime	50.8	52	0.98
Clay Coating Slurry	51.8	52.7	0.93
Beneficiation Slurry	9.1	8.7	1.05
Tar Sands Sludge	42.2	41.9	1.01
Bauxite Red Mud	Not computed	20-40	
Soil-Organic Slime	Not computed	2-19	

Note that since the equilibrium suspension volumes have not been determined for the humic and fulvic acids in the soil-organic slimes, and also for the various components in the red mud, no predicted values of solids concentrations have been obtained for these two types of waste slurries at this time. Much work remains to be done to assess (a) the apparent high dispersion stability of the soil-organic slimes, and (b) the theoretical and experimental values of suspension volumes for the humic and fulvic acids, and the red mud components.

In regard to the humic and fulvic acids which are generally referred to as humic substances, it is known that they are polycarboxylic acids with phenolic, alcoholic, and carbonyl groups, and aromatic rings. The structures for the humic and fulvic acids show properties for metal chelation and base exchange. They have a high affinity for protein and a capability for adsorption of many materials.

CONCLUDING REMARKS

From the preceding discussions, it is apparent that the nature of the suspension, at least for Zones A and B appears to be accountable in part by the water-holding capability of the solids - as a physical measure of the interaction of the solids. The initial settling process is clearly dominated by surface-active relationship, and sedimentation therefore is not readily described by simple gravitational relationships.

Theories which rely on Stokes' principles and solids concentration, which have been generally used to model the settling process in these two Zones [A and B] have not necessarily been successful because of the degree of surface activity (dispersion stability) of the solids. Corrections using a hindrance concept to augment these theories have also generally been unsuccessful if the dispersion stability of the suspension is high. The inability of the sedimentation models to account for the surface and physico-chemical interparticle actions has by and large been responsible for the less than accurate predictive capability of these models.

Insofar as the settling stages where effective stresses are operative, models relying on the general principles of consolidation appear to be capable in predicting settling performance. The apparent lack of physical particle (solid) contact at void ratios of about 5, (for initial consideration of consolidation) where successful predictions have been made (e.g. [25]) does not necessarily mean the absence of "effective" stresses. The measurements made from field experiments show that for the settling ponds tested by Yong et al. (1984), measurable values of pore pressures were obtained. If "effective" stress is defined as the difference between total stress and measured pore pressure, (disregarding the lack of computed physical contact from a void ratio value of 5 or more), application of the consolidation model appears as an acceptable procedure.

The mechanisms describing surface active relationships and interactions permit modelling for evaluation of the so-called equilibrium status of the suspended solids - i.e. the reasons for the amount of solids remaining in suspension. Modelling of the settling rate of the solids can take several forms - collision theory, relative fluxes for description of convection-diffusion phenomena, and consolidation theory. Since a continuous theory (i.e. unified model) does not as yet exist which would cover the entire spectrum of the settling phenomenon, it is necessary to consider appropriate submodels which would overlap in their predictions of the settling problem over its entire range. Two such theories are available at the present time: (a) the convection-diffusion model which encompasses solids settling performance in Zones B and C [28, 29], and (b) large-strain consolidation which encompasses the lower part of Zone C and all of Zone D, [7, 14, 25].

In making predictions of settling performance and comparisons between predicted solids concentration profile and measured values, we should note that experimental procedures require that the suspensions studied in the laboratory for characterization of the void ratio and permeability or void ratio and effective stress relationships must realistically model the field conditions. By and large, long column settling tests need to be performed if the proper modelling of settling behaviour is to be obtained. Consolidation testing, using long columns, will not necessarily produce the kinds of information needed since the external stress situation can affect the self-settling characteristics of the suspended solids. This is particularly true if dilute solids-suspensions are to be examined.

Finally, it should again be noted that analytical modelling of settling of suspended solids in sedimentation processes for prediction of time-rate of settling of suspended solids, is complicated by several physical issues related to:

(a) non-gravitational interactions - i.e. surface-active phenomena,

(b) complications in laboratory measurements of properties of suspensions, and

(c) defining initial conditions and effective stress-void ratio relationships.

It is important to recognize the limits of applicability of the total settling submodels in order that proper predictions of the total settling phenomenon can be made. Application of the concept of suspension volumes in the development of dispersion stability of the solids-suspension, explains why the suspended solids appear reluctant to settle in the time frame predicted by gravitational settling theories. It should be noted that whilst the DLVO model, together with the relationships presented in the Appendix, can be used to calculate the theoretical suspension volumes associated with the kinds of surface-active solids present in the system, the experimentally measured values of suspension volume given in Table 4 are indeed more appropriate. This is because the experimentally measured values implicitly account for the various particle (solids) configurations in the suspension, and also the likely presence of floc formations and interactions - without the need for tedious calculations of interactions involving geometries and floc formation.

Much more work remains to be done in the study of dispersion stability - especially in regard to the magnitude and potential for floc formation in suspension. The results shown in Table 8 for the aggregate slimes suggest very strongly that floc formation is indeed much more prevalent than anticipated - as witness the higher measured solids concentration in contrast to the lower computed values. Other work that needs to be done concerns the presence of micro-organisms in contained slurries. Development of gaseous products as a result of activities associated with micro-organisms will undoubtedly affect both dispersion stability and settling performance of the suspended solids.

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APPENDIX I.

NET ENERGIES OF INTERACTION

Face-to-Face Interaction

Long range repulsive energies due to diffuse ion cloud interaction for constant surface charge density [18]:

$$V_R = \frac{64\ n\ kT}{K} \Upsilon^2 \exp(-2\ Kd) \tag{1a}$$

where

$$\Upsilon = \frac{e^{z/2} \bullet 1}{e^{z/2} - 1} \tag{1b}$$

$$\sinh z = \sigma\left(\frac{\pi}{2n\ \varepsilon\ kT}\right)^{1/2} \tag{1c}$$

$$z = \frac{\nu\ e\ \Psi_o}{kT} \tag{1d}$$

d = interparticle half distance

K = Debye-Huckel reciprocal length

$$K = \left(\frac{8\pi\ ne^2\nu^2}{\varepsilon kT}\right)^{1/2} \tag{2}$$

n = molarity x Avagadro's number
e = unit electronic charge
ν = effective cation valence
k = Boltzman constant
T = temperature (°K)
ε = dielectricity constant

Long range repulsive energies - for constant surface potential [19]:

$$V_R = \frac{4n\ kT\ z^2\ \exp(-Kd)}{K[1+\exp(-2Kd)]} \tag{3}$$

Attractive long range interaction energies:

$$V_A = \frac{-A}{12\pi}\left[\frac{1}{(2d)^2} + \frac{1}{(2d+2\delta)^2} - \frac{1}{(2d+\delta)^2}\right] \tag{4}$$

A = Hamaker constant
δ = thickness of interacting particles

Edge-to-Face Interaction

The relationships developed for edge-to-face and edge-to-edge interactions make use of approximations in terms of spherical particle interactions.

Long range repulsive energies:

$$V_R = \varepsilon R_1 R_2 [\frac{(\Psi_1^2 + \Psi_2^2)}{4(R_1+R_2)} (\frac{2\Psi_1\Psi_2}{\Psi_1^2+\Psi_2^2} \cdot \ln\frac{1+\exp(-2Kd)}{1-\exp(-2Kd)} + \ln(1-\exp(-4Kd))] \tag{5}$$

ε = dielectric constant of the medium
R_1, R_2 = radii of interacting spheres
Ψ_1, Ψ_2 = surface charge potential of interacting spheres

Long range attractive energies [8]:

$$V_A = \frac{-A}{6} [\frac{2R_1R_2}{x} + \frac{2R_1R_2}{x+4R_1R_2} + \ln(\frac{x}{x+4R_1R_2})] \tag{6}$$

where $x = 4d^2 + 4d(R_1 + R_2)$

Edge-to-Edge Interaction

Long range repulsive energies - for constant surface potential [10]:

$$V_R = \frac{\varepsilon R \Psi_o^2}{2} \ln[1 + \exp(-2Kd)] \tag{7}$$

Long range attractive energies [8]:

$$V_A = \frac{-A}{6} [\frac{2R^2}{x} + \frac{2R^2}{x+4R^2} + \ln(\frac{x}{x+4R^2})] \tag{8}$$

where $R_1 = R_2 = R$
$x = 4d^2 + 8Rd$

PARTICLE INTERACTION FORCES

Long range attractive forces (van der Waals forces)

Face-to-Face Interaction

$$F_a = \frac{\pi^2}{240} \cdot \frac{hc}{(2d)^4} \cdot \frac{1}{(D_{30})^{1/2}} \cdot \frac{D_{10}-D_{30}}{D_{10}+D_{30}} \cdot \phi(\frac{D_{10}}{D_{30}}) \tag{9a}$$

where

D_{10} = static dielectric constant of clay particle
D_{30} = static dielectric constant of pore fluid
h = Planck's constant
c = velocity of light

Edge-to-Edge Interaction

$$F_a^{ee} = \frac{A}{12}\{16R^2\ (d+R)\ [\frac{1}{(4d^2+8Rd)^2} + \frac{1}{4d^2+8Rd+4R^2} + \frac{2}{(4d^2+8Rd)^2+4R^2(4d^2+8Rd)}]\} \qquad (9b)$$

R = the effective radius of each interacting particle edge.

Edge-to-Face Interaction

$$F_a^{ef} = \frac{A}{12}(2R_1R_2(8d + 4(R_1+R_2))\ [\frac{1}{z(d)^2} \cdot \frac{1}{(z(d)+4R_1R_2} \cdot \frac{2}{z(d)^2+4R_1R_2z(d)}] \qquad (9c)$$

$z(d) = 4d^2 + 4d\ (R_1 + R_2)$

R_1, R_2 = the effective radii of the interacting particle faces and edges.

Long range repulsive forces

Face-to-Face Interaction

The repulsive osmotic pressure P_{osm} [11]:

$$P_{osm} = 2n_o\ kT(\cosh\ y_c - 1) \qquad (10a)$$

where for constant surface charge, y_c is given by

$$y_c = 2\ n\ \frac{\pi}{0.32\ \sigma\ \bar{\zeta}_c\ d} \qquad (10b)$$

and midplane electrical potential can be calculated by

$$K\ (d+x_o) = 2\ \exp(\frac{-y_c}{2}) \int_{\phi=0}^{\phi=x/2} \frac{\phi d}{[1-\exp(-2y_c \sin^2\phi)]^{1/2}}$$

x_o = stern layer thickness

K = Debye-Huckel reciprocal length

For mixed mono-divalent ion system [3]:

$$P_{osm} = B\ [R(e^{y_c}-1) + e^{2y_c} - 1 + (R + 2)\ e^{-y_c} - 1)] \qquad (11)$$

$B = k\ L_A\ T\ C_o/1000\ (R+1)$

$R = C^+/C^{++}$

Edge-to-Edge Interaction

$$F_R^{ee} = \frac{K \varepsilon R \Psi_o^2}{2} \cdot \frac{\exp(-2Kd)}{1+\exp(-2Kd)} \tag{12}$$

Edge-to-Face Interaction

$$F_R^{ef} = \frac{K \varepsilon R_1 R_2 (\Psi_1^2 + \Psi_2^2)}{2(R_1 + R_2)} \left[\frac{1}{1-\exp(-4Kd)} \left(\frac{2\Psi_1 \Psi_2}{\Psi_1^2+\Psi_2^2} \exp(-2Kd) - \exp(-4Kd)\right)\right] \tag{13}$$

Interparticle Spacing

$$\underset{(\mathring{A}\text{ngstroms})}{d} = \frac{10{,}000\ e}{G_s\ SA} \tag{14}$$

SA = specific surface area ($m^2\ gm^{-1}$)

One-dimensional Theoretical Free Swell

$$\varepsilon_a = \frac{G_s \cdot \Delta_d\ (SA)}{100\ (1+e_o)} \tag{15}$$

G_s = specific gravity of soil

e_o = initial void ratio of soil

Δd = change in particle separation half distance.

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CONVECTION-DIFFUSION ANALYSIS OF SEDIMENTATION IN INITIALLY DILUTE SOLIDS-SUSPENSIONS

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ABSTRACT

The settling of suspended solids in solids-suspensions is treated from the viewpoint of the relative fluxes established as a result of the upward diffusion of water and the downward convection of the solids. The convection-diffusion analysis approaches the problem by first calculating the fluid diffusion coefficients from actual laboratory solids-settling experiments. The calculated diffusion coefficients are then used with the convection-diffusion relationship to predict the settling rate of the solids and also the solids concentration profile. Predictions for various experiments and a field settling pond are compared with actual measured values.

INTRODUCTION

The term "solids-suspension" refers to the physical phenomenon where a suspending fluid medium contains material (generally identified as solid particles, i.e. solids) which remain in suspension for very long periods of time. If the suspended solids do settle at all, they will settle at sedimentation rates not readily modelled by classical Stokesian or modified Stokesian models. Typical situations where solids-suspension behaviour arise include slime/sludge ponds, coastal sediments, and waste-discharge containment lagoons.

In studying the development of sediments such as those obtained in slime/sludge containment ponds and in many coastal areas (i.e. as coastal sediments), their composition and physical/mechanical properties constitute major items of interest. Recognizing that the physical and mechanical properties of the sediments are both source and time dependent, it has been found convenient to analyze the development of sediment layers in respect to rates of settling of the solids "suspended" in the fluid medium. By doing so, the analyses which require actual material properties input will thus implicitly factor in the resultant effects of source material in the settling process which leads to the development of the sediment layers [4,5,7,11].

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When the concentration of solids in suspension is small, as is the case for many solids-suspensions derived from tailings discharge (solids concentration from 2 to 5 percent by weight), and when these solids contain surface-active material, Yong and Sethi (1978) have shown that the dispersion stability and settling behaviour of the solids are controlled more by surface-active relationships (i.e. by interactions between surface-active solids) than by gravitational mechanisms. The problem of model development which would permit one to evaluate and predict the continuous solids-settling process in initially dilute solids-suspensions, from solids sedimentation (suspension "thickening") to compact sediment, remains one of the more challenging problems facing analysts in this field. Present analytical methods using Stokesian, Kynchian and large-strain consolidation models [1,3,4,5,6,9] as separate and individual models for analysis of the various "stages" of solids sedimentation, testifies to the present state of prediction capabilities and reinforces the need to provide a better means for overall prediction of the continuous process of sediment formation.

In this study, the recently developed convection-diffusion method of analysis of solids-settling in initially dilute solids suspension [10], is used to predict solids-settling performance of mixed clay mineral suspensions. Comparisons are made between predicted settling performances and actual laboratory measured values. The method of analysis permits one to address the entire solids concentration range heretofore covered by: (a) the Stokesian model - for the more dilute solids concentration, and (b) hindered fall methods of analysis - for higher solids concentration. When the actual sediment layer is formed, large strain consolidation analyses can be applied successfully to predict consolidation performance.

CONVECTION-DIFFUSION ANALYSIS

Denoting the various known and unknown internal driving forces in the solids suspension in terms of a resultant potential difference $\Delta\psi$ acting between two arbitrary points separated by a distance $\Delta\zeta$, the relative fluid flux q_{fs}, - i.e. upward flux of fluid past the suspended solids which are themselves moving downward in the opposite direction to the fluid flux - can be expressed as:

$$\text{Relative fluid flux } q_{fs} \propto -\frac{\partial\psi}{\partial\zeta} \qquad (1)$$

$$= -k\frac{\partial\psi}{\partial\zeta}$$

and

$$\frac{\partial q_{fs}}{\partial\zeta} = \frac{\partial}{\partial\zeta}\left(-k\frac{\partial\psi}{\partial\zeta}\right) \qquad (2)$$

where k = proportionality constant.

The net result of the relative fluxes established because of the downward movement of the settling solids and upward movement of the fluid will be physically demonstrated in terms of the time-rate settling of the solids-liquid (fluid) interface as shown in Fig. 1. For simplicity in viewing, one might consider the total initial solids-suspension as a stacking of an infinite number of thin "compressible" solids-suspension layers with solids concentration varying in the fashion shown on the LHS drawing in Fig. 1. The supernatant layer that is formed above the solids-liquid interface at any one time is the result of the relative fluxes, and is the accumulation of the fluid-release from the infinite number of "compressing layers", as seen in the RHS drawing in Fig. 1.

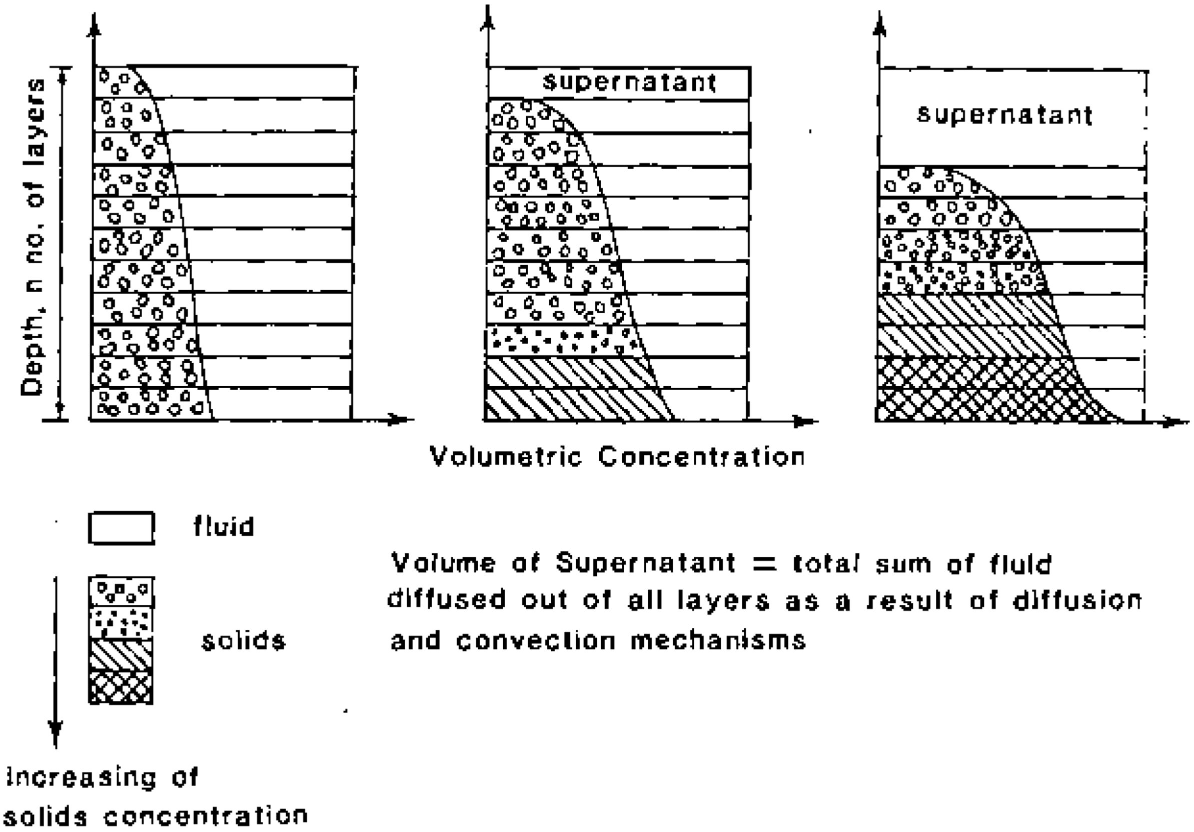


Fig. 1 Schematic representation of the solids settlement and supernatant development processes

To elaborate further on the so-called "compressible" nature of the solids-suspension layer, Fig. 2 shows a more detailed illustration of the fluxes developed in the solids settling process in a control unit volume in a typical solids-suspension layer. The quantity of fluid volume α_d released in a unit time is the result of the upward fluid flux q_{fs} relative to the downward flux of solids q_s. The volume of fluid associated directly with the solids consists essentially of two parts: (a) the part that remains above the datum line separating layer C_{n-1} from C_n, and (b) the part that moves in concert with the solids flux q_s in the settling process, bringing them below the datum line into layer C_n - as shown in Fig. 2. The fluid associated with the solids represents that volume of fluid held by the solids because of surface-active forces [11], and is determined by the balance between the internal and external energy of the local element.

Representing β as the volumetric content of the fluid associated with the convecting solids, i.e. volume of fluid directly tied in with the convecting solids in a unit solids suspension volume (Fig. 2) divided by that same suspension volume, the total flux of fluid associated with the settling solids passing below the datum separation into layer C_n will be given by $\beta q_s = \alpha_{cv}$. The total change in volumetric fluid content in the control volume after time Δt is due to (a) loss of fluid represented by the relative fluid flux q_{fs} and (b) the loss of fluid associated with the convecting solids as represented by the flux βq_s as shown in Fig. 2.

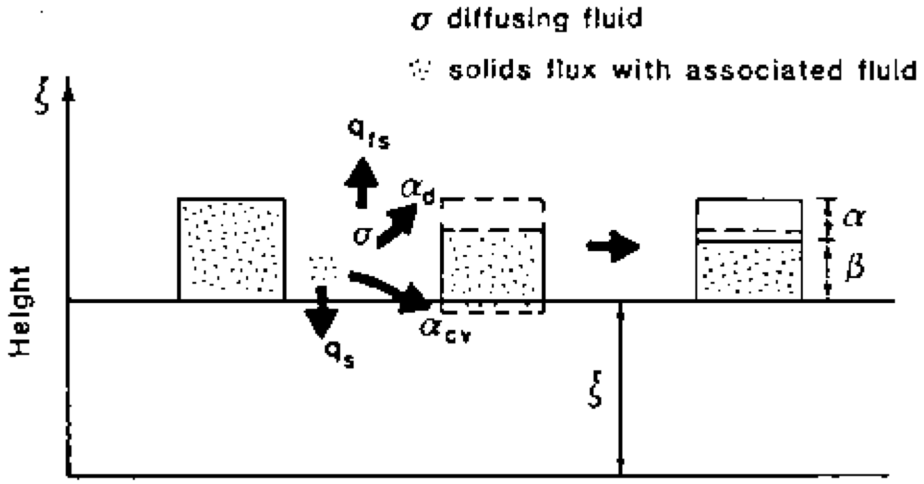


Fig. 2 Schematic representation of developed fluxes in a control volume, showing fluid flux relative to solids q_{fs} flowing in the upward side direction, and q_s solids flux leaving the control volume with associated fluid $\beta q_s = \alpha_{cv}$. Note that fluid flow due to $q_{fs} = \alpha_d$.

The total fluid volume which diffuses to the top of the settling column or pond to form the clear (solids-free) supernatant is the accumulation of all the α_d quantities from the individual layers. Because α_{cv} moves below the datum plane, the solids-liquid interface movement that will be visually evident is the result of the sum of all the α_d and α_{cv} quantities. The resultant fluid flux q_f has been previously given [10] as follows:

$$q_f = q_{fs} + \beta q_s \tag{3}$$

where

q_f = fluid flux,

q_{fs} = flux of fluid relative to the convecting solids,

q_s = flux of solids, and

β = volumetric content of fluid directly associated with the convecting solids.

Considering the movement of fluid in the ζ direction, (Fig. 2), the continuity condition can be written as:

$$-\frac{\partial\alpha}{\partial t} = \frac{\partial q_f}{\partial\zeta} = \frac{\partial(q_{fs} + \beta q_s)}{\partial\zeta}$$

$$= \frac{\partial q_{fs}}{\partial\zeta} + \frac{\partial(\beta q_s)}{\partial\zeta} \tag{4}$$

where

ζ = the upward positive spatial coordinate with origin of axis at the base,
$\alpha = \alpha_d + \alpha_{cv}$,
α_d = volumetric content of fluid lost (released) due to diffusive flow, and
α_{cv} = volumetric content of fluid lost due to convective flow.

Recalling Eq.(2):

$$\frac{\partial q_{fs}}{\partial\zeta} = -\frac{\partial}{\partial\zeta}\left(k\frac{\partial\psi}{\partial\zeta}\right)$$

$$= -\frac{\partial}{\partial\zeta}\left(k\frac{\partial\psi}{\partial\alpha_d}\,\frac{\partial\alpha_d}{\partial\zeta}\right)$$

$$= -\frac{\partial}{\partial\zeta}\left(D\frac{\partial\alpha_d}{\partial\zeta}\right) \tag{5}$$

where D = coefficient of diffusion of the diffusing fluid $= k\left(\frac{\partial\psi}{\partial\alpha_d}\right)$

Combining Eqs.(4) and (5), we obtain the governing relationships previously given by Yong and Elmonayeri (1984):

$$\frac{\partial\alpha}{\partial t} = \frac{\partial}{\partial\zeta}\left(D\frac{\partial\alpha_d}{\partial\zeta}\right) - \beta\frac{\partial q_s}{\partial\zeta} - q_s\frac{\partial\beta}{\partial\zeta} \tag{6}$$

we should note that the applicability of this relationship to fully account for sediment consolidation after sediment formation and initial compression, will need to be critically examined - especially when actual interparticle contact becomes a significant issue. In its present form, experiments show that the convective-diffusive relationship can model sedimentation of the pure clays-suspensions tested - to void ratios of about 3.

DETERMINATION OF DIFFUSION COEFFICIENT

Since the convective terms on the RHS of Eq.(6) deal with the solids flux and associated effects, determination of the fluids diffusion coefficient D can be readily accomplished by considering only the diffusive term on the RHS, - so long as the Peclet number, which refers to the ratio of the convective velocity to the diffusion constant over the domain of interest, is small. The property of maximum principle which is well-demonstrated when the Peclet number remains small, is indeed important if non-oscillating numerical solutions are to be sought. It is useful to note that the standard diffusion model is also the generic model used in the derivation of the classical consolidation relationship.

Solving Eq.(6) in the usual form of a diffusion equation, by dropping off the last two convective terms on the RHS, Yong and Elmonayeri (1984) have used a similarity solution technique to obtain the relationship between the diffusion coefficient of the fluid D with the total fluids concentration at any one time. Note that the fluid concentration θ is given in terms of a volume ratio - i.e. volume of fluid per unit volume of total solids-suspension - and is also easily identifiable as the porosity n. The diffusion coefficient D is obviously a variable since it is directly related to the proportion of solids present (i.e. solids concentration). The relationships for D for various suspensions are given later in Fig. 5 - in terms of the volumetric water content.

The procedure used to obtain the necessary information for calculation of the diffusion coefficient for any one particular solids or fluid concentration in the solids-suspension, requires experimental input which describes the rate of fall of the suspended solids. Consequently, laboratory settling column experiments similar to those previously conducted [10] were used. These consist of essentially producing solids-suspensions of various initial solids concentrations, using pure clay minerals dispersed in 15 meq/l $NaHCO_3$. The settling columns which consisted of lucite tubes measuring 208 mm diameter and 600 mm high had sampling ports located at various heights of the column - to permit periodic sampling of the solids-suspension for determination of solids or fluids concentration profile. Since the volume of suspension removed via a macro-hypodermic syringe was considered to be miniscule in relation to the total volume of suspension material tested, no corrections were considered necessary in measurements of the height of the solids-liquid interface. A listing of the experiments conducted is given in Table 1. Since it was easier to weigh the basic constituents, the fluid concentrations were reported in terms of water contents instead of the volume concentrations used in the calculation procedures. With known specific gravities, it was an easy procedure to convert the water contents to volumetric fluid concentrations.

The typical kind of solids-settling information obtained in experimentation is shown in the top and LHS drawings shown in Fig. 3. The profiles drawn can be in terms of density variation or solids concentration variation with height of settling column. For convenience in calculation of the diffusion coefficients, the information presented in Fig. 3 is given in terms of volumetric concentrations, e.g. volume of solids divided by the total suspension volume (Fig. 3a) for the volume element under scrutiny. Since the sampling ports provide information with respect to fluid or solids concentration, Fig. 3b can be determined directly. This corresponds with Fig. 3a since the sum of these two concentrations should provide one with the total solids-suspension volume. By measuring the fluid concentrations at various times and locations, it is possible to produce information concerning the diffused fluid concentration at any particular time period (Fig. 3c). This represents the quantity referred to in the procedure for calculation given in Fig. 4.

TABLE 1 - Tests Conducted for Solids Settling

1 Experiment	2 Source	3 Mass of Solids (particles) gm	4 Initial Water Content w/w	5 Initial Height mm	6 Duration of Test hr
1	GRC Experiment Set #1	1012.1	1900%	600	15.5
2		1222.1	1566.7%		
3		1435.1	1328.6%		
4		1667	1150%		
5		2568	733.33%		
6	GRC Experiment Set #2	511.5	613.9%	350	24.0
7		652	455.5%		
8		935	316.6%		
9		1078.5	257%		
10		1170.5	233.3%		
		FD* + DSB**			
13	GRC Experiment Set #3	0 + 647.5	796.2%	600	24.0
14		53.5 + 593.5	"		
15		107.5 + 539.5	"		
16		160.5 + 485.6	"		
17		215.8 + 431.6	"		
18		269.8 + 377.7	"		
19		323.7 + 327.7	"		
20		377.7 + 269.8	"		
21		431.61+ 215.8	"		
22		485.6 + 160.5	"		
23		539.5 + 107.5	"		
24		593.5 + 53.5	"		
25		647 + 0	"		

* FD = Hydrite Flat D Kaolinite ("pure" kaolinite)

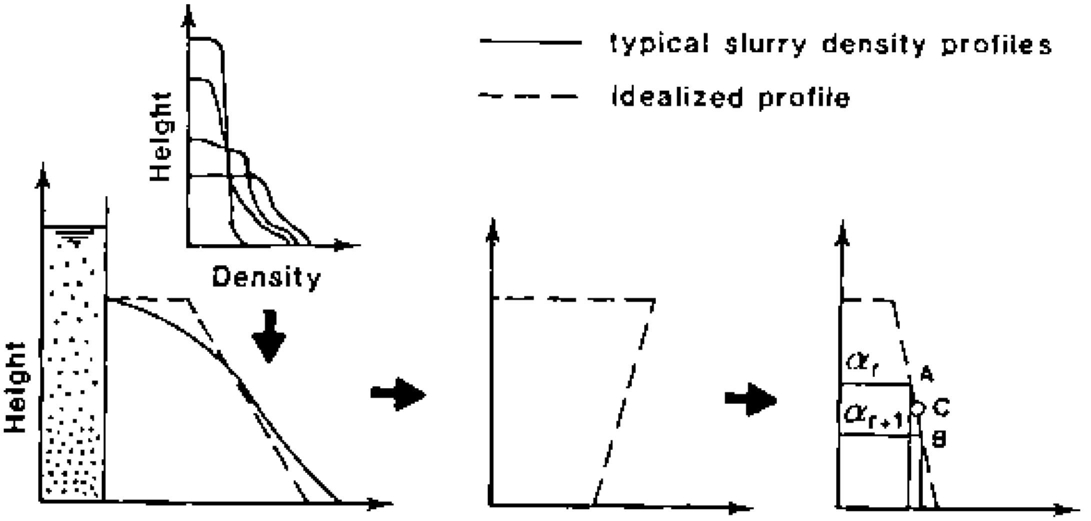
** DSB = Domtar Sealbond

To calculate or predict the settling rate of the interface established by the supernatant lying atop the solids-suspension (due to continuous accumulation of diffusing fluid), the fluids diffusion coefficient D, which is obtained as a function of α_d the diffused fluid volumetric content, is used to enter into the solution of the convection-diffusion equation - given previously as Eq.(6). At this time, the total equation (together with the convective terms) is used in the calculations. This is identified in Fig. 4. The output information from solution of the equation permits one to view settling rate, fluid or solids concentration profiles at any specified time, and obviously sediment formation. Note that the calculation procedure used in Fig. 4 stops when the solids concentration reaches 40%. This point is arbitrary in that we expect that particle contact forces will begin to become relevant issues and perhaps will need separate consideration. This is not to say that the governing equation will not operate beyond this region. However, much work remains to be done to further elaborate on the convective-diffusive phenomenon when particle contact stresses and excess pore water pressures become significant.

CONCLUDING DISCUSSION

The diffusion coefficients previously calculated for tests 4, 5 and 10 in Table 1, and included in calculations with other test material types used for comparison with field test results [10] have been shown to apply for all the kaolinite suspension test results obtained in this study. This is not surprising, since the tests were all concerned with the same type of clay material. The diffusion coefficients are shown in Fig. 5 - together with comparisons with other suspensions reported previously. Note that by and large, the slopes of the various D relationships are essentially similar. The relationship calculated for D using the test results reported by Been and Sills (1981) is basically identical in slope to the kaolinite test series obtained in this study. The same can be said for the D values calculated for actual field experiments conducted [10].

Using the kaolinite D values reported in Fig. 5, predictions for settling rate can be made and compared with test measurements - as for example for tests 4 and 5 in Table 1. The close agreement between measurement and prediction shown in Fig. 6 is evident for all the samples studied. A better summary is given in Fig. 7 where the slopes of the initial settling curves (i.e. settling velocity) represented in Fig. 6



(a) Solids Concentration (volumetric)
(b) Fluid Concentration (volumetric)
(c) Diffused Fluid Concentration (volumetric)

Fig. 3 Idealized representation of solids settling at any one time, together with distribution of solids, fluid and diffused fluid.

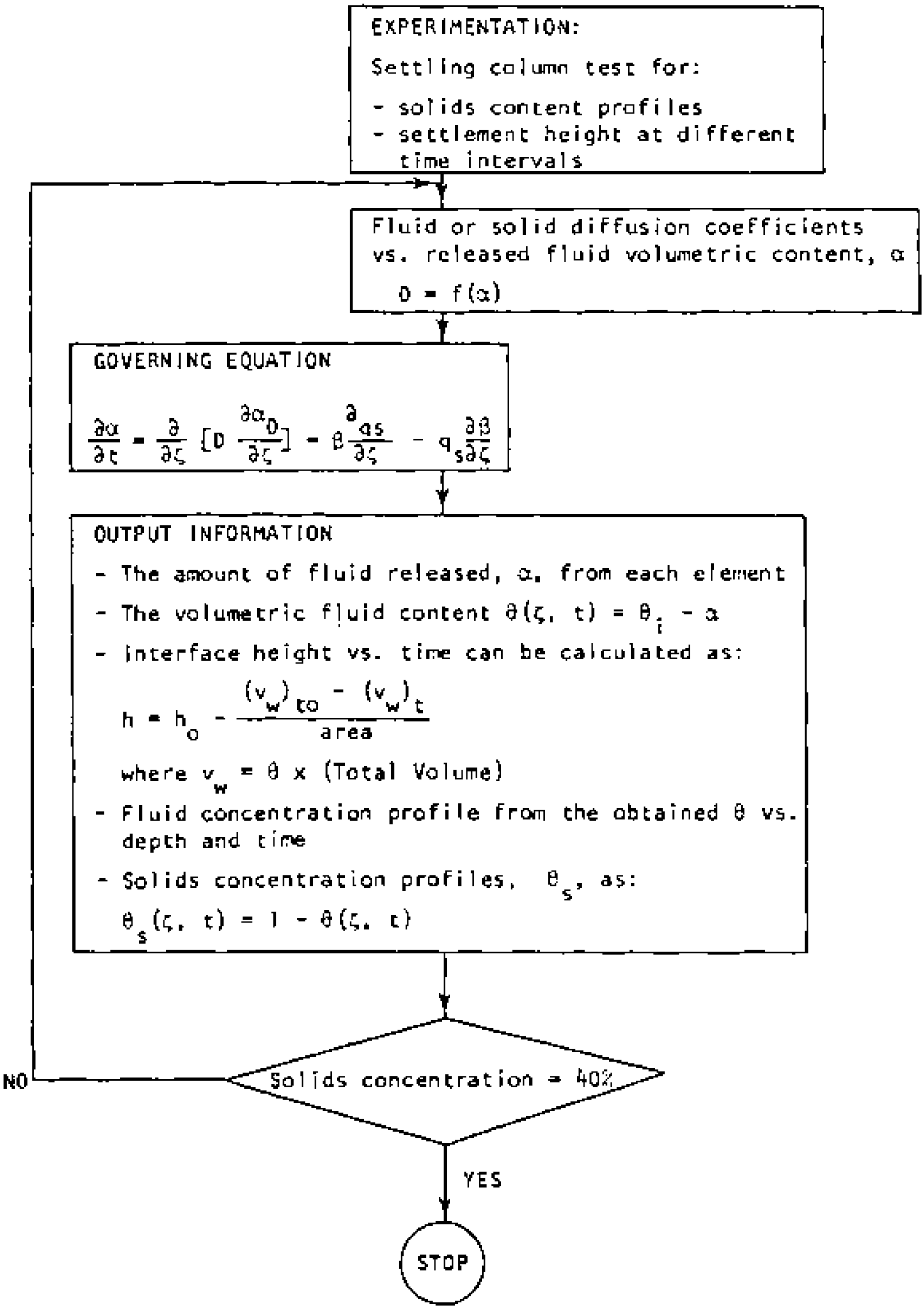


Fig. 4 Schematic diagram illustrating procedure for calculation

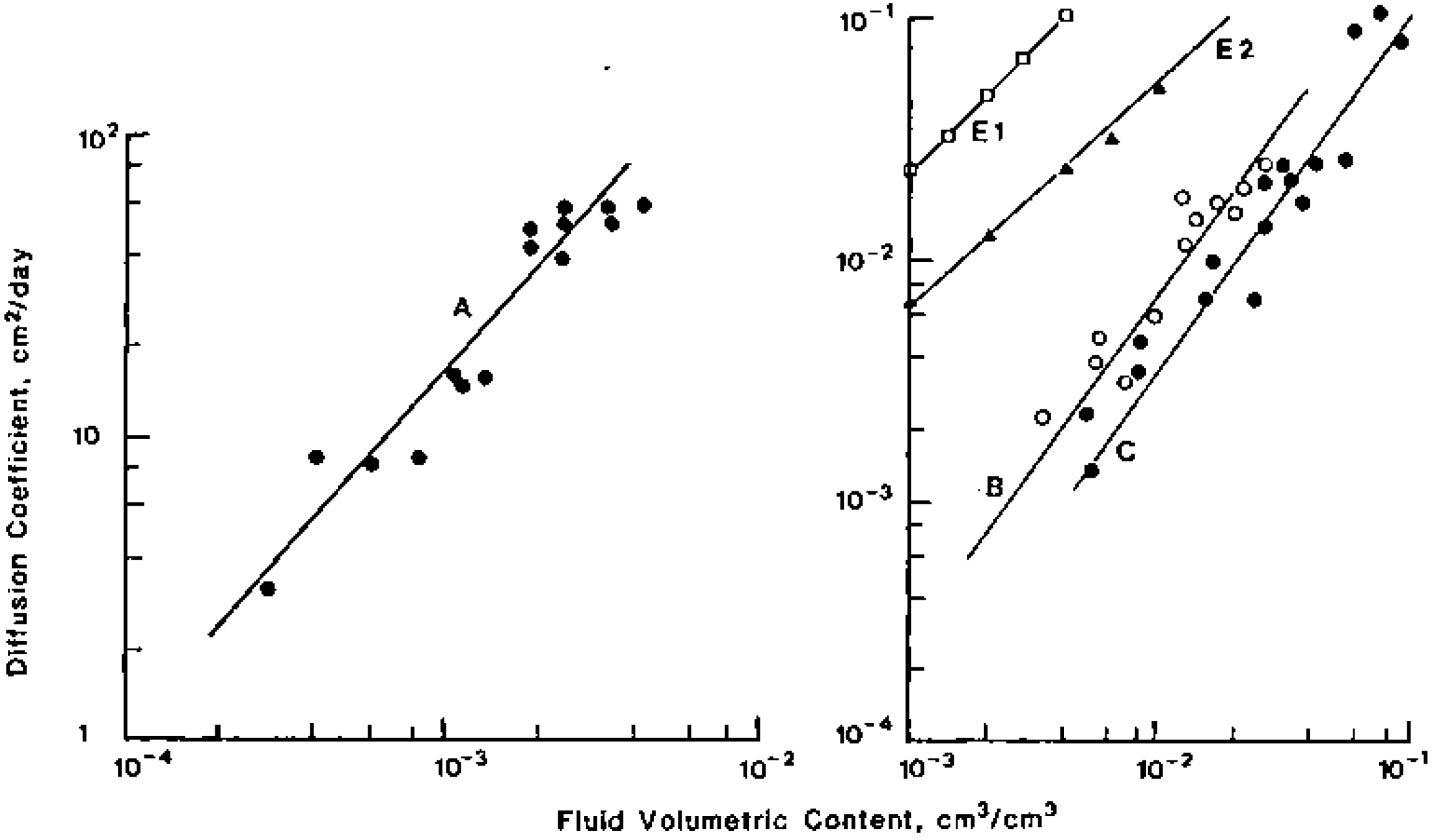


Fig. 5 Diffusion coefficients for "A" tar sand sludge, "B" kaolinite, "C" Been and Sills Tests, and E1 and E2 (in cm^2/sec) for Domtar Sealbond/Kaolinite mixtures (Exp. #15 and 19 respectively)

for example, are plotted against the initial solids concentration of the solids-suspension. This shows the effect of initial solids concentration on the velocity of settling of the solids-liquids interface. Although not directly shown, the close accord represented in Fig. 6 between predicted and measured values is obviously repeated for Fig. 7.

To further test the applicability of the method of analysis, two other mixtures (reported in Table 1) were used. These consisted of a mixture of kaolinite and illite minerals. The hydrite flat D kaolinite was mixed with illite, identified as Domtar seal bond, in two proportions as shown in Fig. 8. The diffusion coefficients used were the ones calculated from experiments with the mixtures, and the resultant predictions are shown together with the measured rate of fall in Fig. 8. Whilst the agreement between prediction and measurement is not as good - in comparison with the pure kaolinite samples - it is nevertheless acceptable. The bottom boundary effect in constraining sedimentation can be seen in the lower portions of the experimental curves.

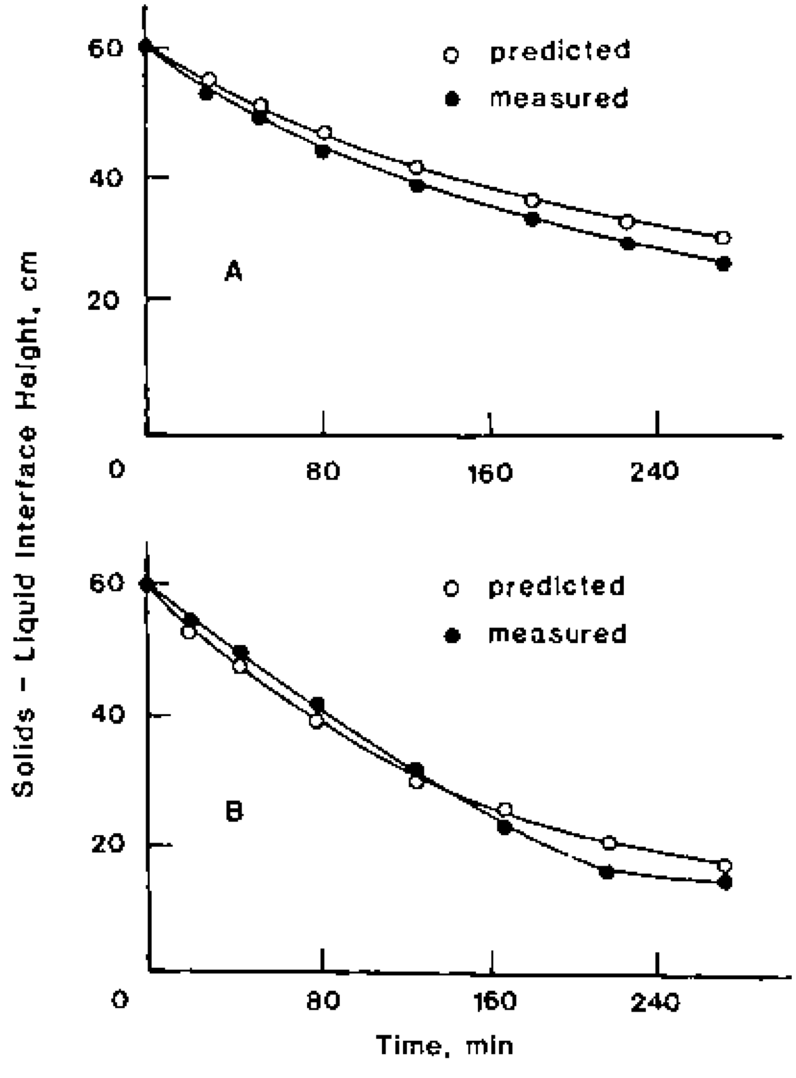


Fig. 6 Comparison between predicted and measured settling rates for Tests 4 and 5, reported in Table 1.

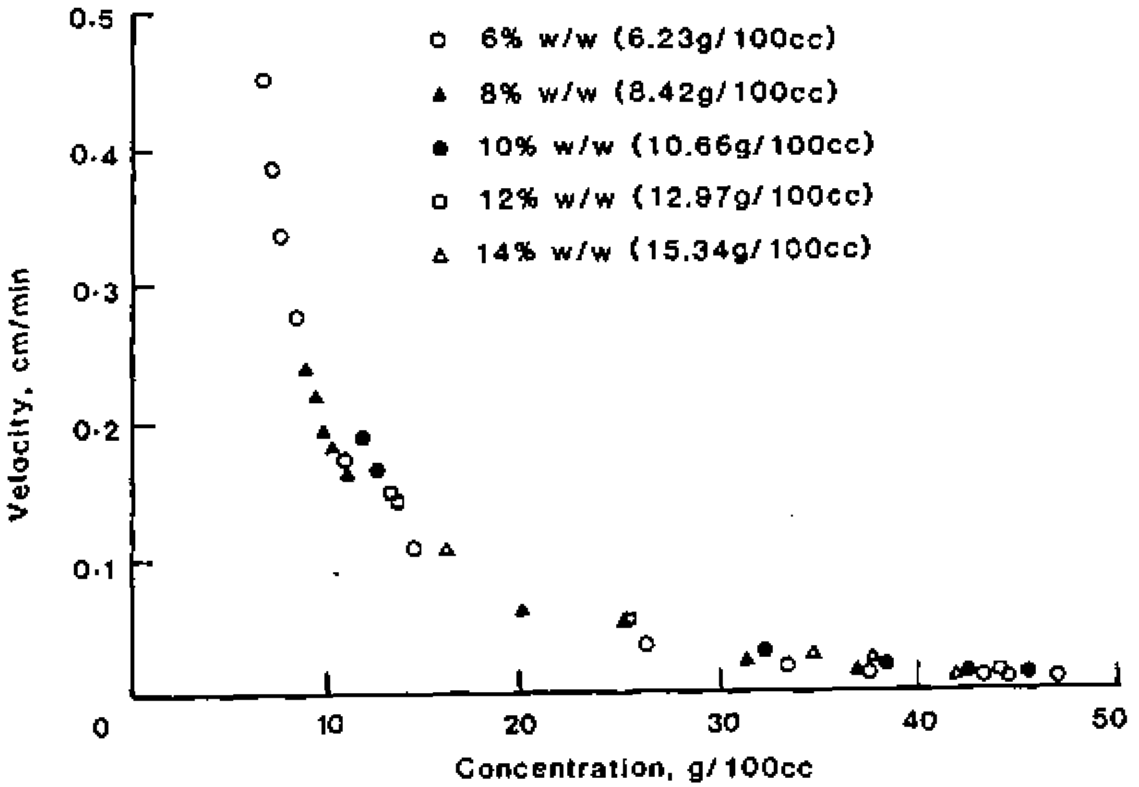


Fig. 7 Relationship between the interface settling rate and its concentration for different initial uniform solids concentration

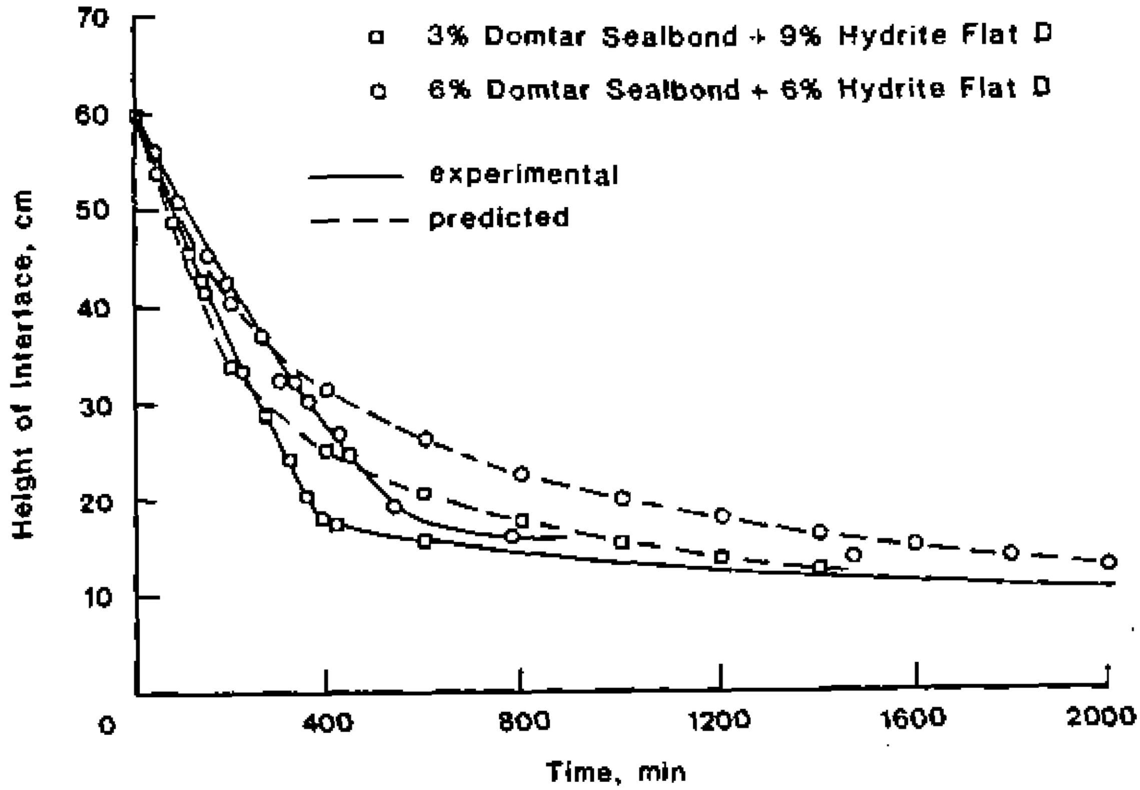


Fig. 8 Experimental and predicted height of interface for kaolinite and illite mixtures

Much work remains to be done to further develop the method of analysis - as witness the test/prediction results in Fig. 8. Because of the addition of a more surface-active material component (illite), complete demarcation between pure supernatant and solids-suspension is not always achieved, i.e. the solids-liquid interface is not clearly evident A slightly turbid supernatant is developed and some of the more active component material remains in the supernatant. Thus visual observations of the first part of the initial settling process tends to lag behind predictions if visual comparisons are made with predictions - since observations can only be made by viewing the interface which is visible because of the more dominant settling component (kaolinite). The process is akin to the more drastic "settling-out" phenomenon seen in sand-clay-fluid suspensions, where the granular component segregates out of the total suspension and settles through the suspension to form the sand sediment layer. Bottom sediments showing the general gradation of coarse fractions at the very bottom, grading to the very fine fractions (silts and clays) at the top testify to this phenomenon.

As time progresses, a "catching-up" process occurs because the initial higher settling rate due to the more dominant settling component (kaolinite and coarser fractions of illite) obviously reaches the stage where the lagging component (illite) finally settles out of the slightly turbid supernatant. The interface which now can be better distinguished will be more representative of the total mixture of kaolinite and illite. If the general modelling approach is indeed viable, the differences between prediction and measurement should become diminishingly small as time progresses. This appears to apply for the study conducted on the mixed system. It would indeed be interesting to see if one could predict the settling rate of the various components in a mixed solids-suspension. This would permit one to anticipate the layering and gradation phenomenon in sediment formation. Further study will need to be performed to address this and other problems concerned with large convective effects.

Figure 9 shows the prediction of solids distribution in tar-sand sludge pond (about 2 km long and 1 km wide) using the information given by Yong and Elmonayeri (1984). The procedure used is outlined in Fig. 4, and the values for D were determined from laboratory settling column tests on samples obtained at various depths in the actual pond. The mixed solids components (sand, silt and various kinds of clay minerals) in the pond have all been lumped together as a general "solids" content. It is useful to note that the void ratio of 4.3, which corresponds to a solids concentration of 19% is well within the 40% cut-off point shown in Fig. 4. Agreement between predicted and measured void ratios (as determined from actual sampling in the field pond) shown in Fig. 9 is indeed good.

ACKNOWLEDGEMENTS

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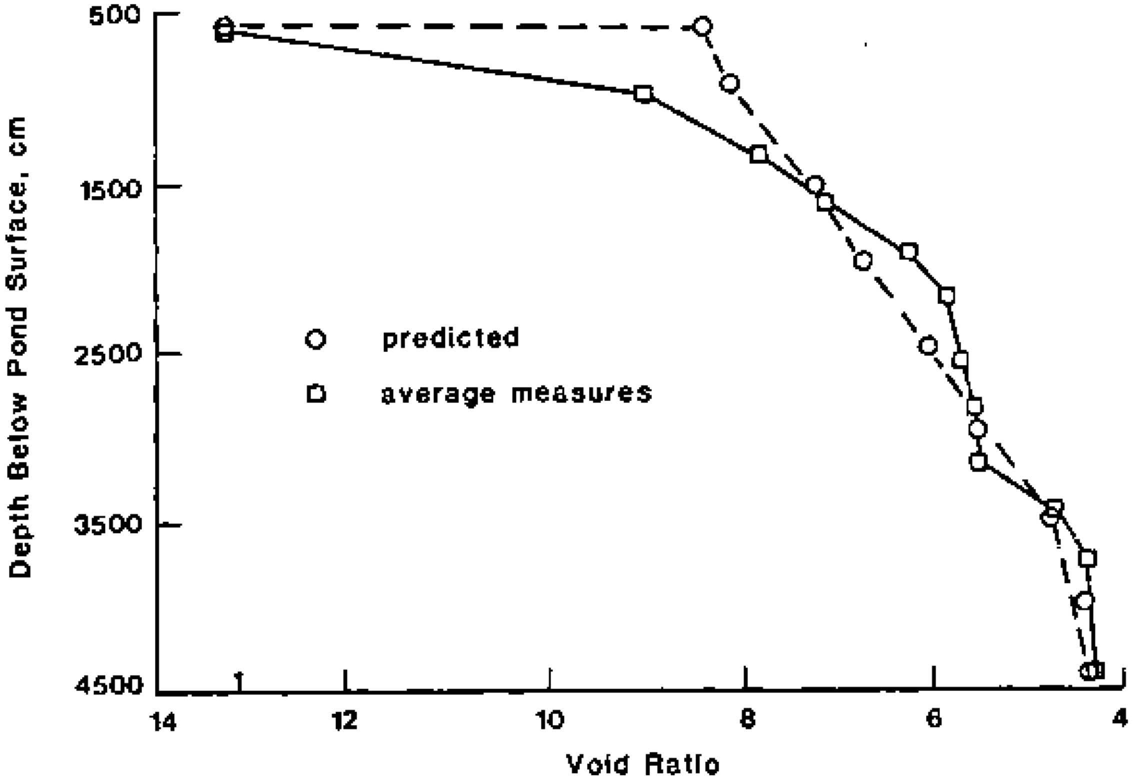

Fig. 9 Comparison between predicted and measured void ratio profile in tar sands tailing sludge pond

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DISPERSION STABILITY OF SUSPENDED SOLIDS
IN AN AQUEOUS MEDIUM

by

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ABSTRACT

The stability of solids suspensions is determined by the dispersion stability of the solids suspended in the suspending medium. In cases where the solids are extremely small (fine), the inactive solids situation permits calculations to be made along the lines of interparticle collision. When surface-active forces become dominant, the calculations for energies of interaction of the long-range repulsive and attractive forces permit description of the interaction stability of the suspended particles. Dispersion stability, which is not a time-infinite state, can be evaluated and determined as a variable decreasing stable state (with time) using methods of calculations based on interparticle collision and/or energies of interaction.

INTRODUCTION

The term "solids suspensions", used in this presentation, refers to various kinds of suspended solids (in the micron and submicron size range) in a dispersed state in an aqueous medium. The reluctance of the suspended solids in many kinds of suspensions to settle in a timely fashion, in accord with predictions based on models relying on gravity-driven mechanisms, has been well documented, (Yong (1), Bureau of Mines (2)). Considerable interest has been focussed on predictions of thickening, sedimentation, settling, and consolidation, - especially in the field of slurry and slime waste disposal - because of several economic and environmental pressures.

In seeking to develop predictive models, and especially in instances where specific treatments are contemplated for enhancement of the dewatering capability of the suspension, there exists a need to obtain a better understanding of the various issues that define the stability of the suspensions in the "natural" state. In this presentation, the dispersion stability of the suspended solids (particles) is studied - in terms of interaction of inactive and surface-active solids. (By "surface-active" solids, we mean solids which possess active surfaces.)

SUSPENSION STABILITY

The stability (i.e. dispersion stability) of a suspension can be defined or assessed in several ways. The simplest method is to focus on some significant (measurable) properties or characteristics, - e.g. settling rate, flocculation or coagulation, and/or viscosity-time relationship. It is acknowledged that even in a supposedly stable colloidal solution (sol), settling of the suspended solids will indeed occur - albeit at an extremely slow rate. Perfect dispersion stability (i.e. infinite-time stability) will not really exist, primarily because of ageing effects - e.g. insufficient repulsion between very small solids (particles), alteration and transformation of some of the solids, transport of matter from smaller particles to the larger ones, and development of flocculates. In a slurry waste system consisting of various kinds of constituent solids, and in the presence of a chemical environment, the preceding kinds of ageing phenomena coupled with other processes associated with biological activities and biochemical reactions, will eventually destabilize the initially stable suspension, and demonstrate itself in terms of observed sedimentation of the solids.

The demonstrated slow self-settling characteristics of the suspended solids which are indicative of the dispersion stability of the suspension, (and also of the degradation of dispersion stability), can be attributed to at least four mechanisms: (1) Interaction of the solids with the molecules of the medium resulting in Brownian motion; (2) Mutual net repulsion caused by the surface-active nature of the solids and the low salt concentrations, or predominance of monovalent cations, and/or potential determining anions; (3) Adsorption of coating of amorphous material (small lyophilic colloid) on a large electronegative colloid - since the affinity of amorphous material for water exceeds the net attraction of the van der Waals forces; (4) Steric hindrance due to adsorption of an organic molecule.

The four mechanisms and their complex variants cannot be easily quantified insofar as calculations for determination of the degree of dispersion stability are concerned. We can however separate the problem into two parts for ease in viewing the results of interaction of the suspended solids. To do so, we recognize that the suspended solids are under the influence of at least three different kinds of forces: (a) gravitational forces, (b) interaction forces developed when the forces of collision of the molecules of the medium begin to overpower gravitational forces, and (c) mutual interaction of the solids because of the surface active nature of the solids - via electrostatic repulsions and attractions.

In examining dispersion stability, we will initially consider the system in terms of interactive forces - developed either by collision or by electrostatic means. This provides the opportunity to develop the analysis in terms of resultant energies. The simplest sequence in analysis considers the suspension to be made up of very fine inactive solids or particles susceptible to Brownian activity. One studies thereby, the collision frequency and the evolution of the distribution function in time due to external forces and interparticle collision.

Proceeding therefrom to consideration of surface-active solids, the quantitative theory of stability of lyphobic colloids, identified as the DLVO theory (after Derjagin, Landau, Verwey and Overbeek), which constructs its analytical model on the basis of (a) electrostatic repulsive forces due to interpenetration of the diffuse ionic layers, and (b) van der Waal's attraction forces, appears to provide a reasonable set of calculations which could provide a qualitative measure of the problem at hand. It is noted that in considering net repulsion occurring between particles when double layer repulsion overwhelms van der Waal's attraction, the presence of potential determining anions such as bicarbonates, carbonates, hydroxides, phosphates, etc. in the fluid phase, all contribute to the enhancement of net repulsion.

Several problems should be noted in application of the above type of modelling procedure. The presence of amphoteric surfaces, which is indeed likely in many waste slurries, is not generally factored in considerations for analyses - partly because compositional analyses generally do not pay much attention to the problem, and partly because of the extreme difficulty in assessing the charge characterization of the surfaces. As another set of problems, it should be noted that the system becomes unstable and coagulation occurs when attractive forces become very dominant. Thus, when repulsive forces are vanishingly small and can be neglected, Brownian collision between particles may or may not lead to agglomeration or aggregation of the particles. Not every collision results in aggregation. For two different systems, given the same collision frequency, the effectiveness of aggregation upon collision depends on the properties of the particle surfaces.

Yong and Sethi (3) have shown that there is a strong relationship between the dispersion stability (of the suspension) and the zeta potential of the system (Table I).

TABLE I - Relation Between Dispersion of Clays and Zeta Potential

Stability Characteristics	Average Zeta Potential, mv.
1. Maximum agglomeration and precipitation	+ 3 to 0
2. Excellent agglomeration and precipitation	- 1 to - 4
3. Fair agglomeration and precipitation	- 5 to -10
4. Threshold of agglomeration (tactoids or domains)	-11 to -20
5. Plateau of slight stability (few domains)	-21 to -30
6. Moderate stability (no domains)	-31 to -40
7. Good stability, i.e. stable suspension	-41 to -50
8. Very good stability	-51 to -60
9. Excellent stability	-61 to -80
10. Maximum stability	-81 to -100

It is pertinent to note that dispersion stability which is characterized by strong mutual repulsive forces can be reduced or eliminated by agglomeration or flocculation via:

1. Reduction of the zeta potential of the system with strong cationic electrolytes - to achieve the effect shown in Table I.

2. Addition of a strong cationic electrolyte in conjunction with an appropriate alkali (Optimum pH is required).

3. By adding a reagent which results in the formation of an insoluble matrix which engulfs and binds the water in the system.

4. Agglomeration with long chain or branched-chain anionic polyelectrolytes.

5. Agglomeration with non-ionic long chain or branched-chain polymers.

INTERPARTICLE COLLISION

To consider dispersion stability in terms of interparticle collision, we begin by specifying a distribution function $f(\underline{r},\underline{u},t)$ which describes the number of particles at a position $\underline{r}$, having a velocity $\underline{u}$ at time t. The evolution of this function over the course of time at different positions $\underline{r}$ needs to be studied. The number density of the particles at $\underline{r}$ and t will be given by:

$$n(\underline{r},t) = \int f(\underline{r},\underline{u},t)\, d\underline{u} \qquad (1)$$

where the integration is over all possible values of $\underline{u}$. The function $n(\underline{r},t)$ can be normalized by:

$$N = \int n(\underline{r},t)\, d\underline{r} \qquad (2)$$

where N is the total number of particles in the entire suspension under consideration. The average velocity $\underline{v}(\underline{r},t)$ can now be given as:

$$\underline{v}(\underline{r},t) = \frac{1}{n} \int \underline{u} f(\underline{r},\underline{u},t)\, d\underline{u} \qquad (3)$$

and the particle energy $\underline{e}(\underline{r},t)$ as:

$$e(\underline{r},t) = \frac{1}{n} \int 1/2\; m\underline{u}^2 f(\underline{r},\underline{u},t)\, d\underline{u} \qquad (4)$$

Because of the frequent collisions of liquid molecules, the particle velocity $\underline{u}$ will be fluctuating about a mean value $\underline{u}_o$, with a mean fluctuation time τ^*. Since $\tau >> \tau^*$ we can write:

$$\underline{u} = \underline{u}_o + \underline{u}' \qquad (5)$$

where $\underline{u}'$ is the fluctuating value. We now obtain:

$$f(\underline{r},\underline{u},t) = f_o(\underline{r},\underline{u}_o,t) + \underline{u}'\cdot\frac{\partial f}{\partial \underline{u}_o} + \frac{u'^2}{2}\,\frac{\partial^2 f}{\partial \underline{u}_o^2} + \ldots \qquad (6)$$

where $f_o(\underline{r},\underline{u}_o,t)$ is the stable part of the distribution function unaffected by the fluctuations. This is not generally considered to change in a time scale of the order of τ^*. When f_i is averaged over a time scale of τ, we have:

$$\text{average of } f = \bar{f} = f_o + \frac{1}{\tau}\frac{\partial f_o}{\partial \underline{u}_o} \cdot \int_o^{\tau} u'dt' + \frac{1}{\tau}\frac{\partial^2 f_o}{\partial \underline{u}_o^{\,2}} \int_o^{\tau} \underline{u}'^2 \, dt' \qquad (7)$$

Using the ergodic theorem and the law of equipartition of energy to express the integral in terms of the Boltzmann constant k and temperature T, we obtain

$$\int_o^{\tau} \underline{u}'dt' = 0; \ \frac{1}{\tau} \int_o^{\tau} \underline{u}'^2 dt' = \langle \underline{u}'^2 \rangle \ = \text{ensemble average}$$

$$= \frac{3kT}{m} << 1 \text{ for micron-sized particles} \qquad (8)$$

Thus, $f = f_o(\underline{r},\underline{u}_o,t)$ indicates that it is now possible to define a distribution function averaged over the Brownian fluctuations as a function of average velocity $\underline{u}_o$. Using the same procedure, the net force $\underline{F}$ acting on a particle, consisting of the gravitational force $mg\hat{z}$ acting along the vertical direction $\hat{z}$, and liquid particle interaction expressed as $\underline{F}_{int}$ can be obtained. Expressing $\underline{F}_{int}$ as: $\underline{F}_{int} = \underline{F}_o + \underline{F}'$, we note that since the average force of interactions due to liquid molecules $\underline{F}_o$ can be expressed as: $\underline{F}_o = -6\pi\eta a\underline{u}_o$, and $\underline{F}'$ is a fast oscillating function whose average over a time scale always vanishes, the net external force $\underline{F}$ will be given by:

$$\underline{F} = (m'g - 6\pi\eta a\underline{u}_o)\ \hat{z} \qquad (9)$$

where m' is the submerged mass of the particle in the liquid.

When this force is zero, we note that the particle attains the velocity $\underline{V}$ given by:

$$\underline{V} = \frac{m'g}{6\pi\eta a}\ \hat{z} \qquad (10)$$

For a typical two-particle collision system, the Boltzmann equation, which is a microscopic evolution equation which describes the evolution of the distribution function in time due to external forces and interparticle collisions, can now be invoked (Chapman and Cowling (4)):

$$\frac{\partial f}{\partial t} + \underline{u} \cdot \frac{\partial f}{\partial \underline{r}} + \frac{\underline{F}}{m} \cdot \frac{\partial f}{\partial \underline{u}} = C(f) \qquad (11)$$

$$\text{where } C(f) = \int |v(\underline{r}-\underline{r}')|^2 \{f(\underline{r},\underline{u},t)f(\underline{r},\underline{u}_i,t) - f'(\underline{r},\underline{u}_i',t)f'(\underline{r},\underline{u}',t)\}$$

$$\times\ \delta(m\underline{u} + m\underline{u}_i - m\underline{u}' - m\underline{u}_i')$$

$$\times\ \delta(1/2m\underline{u}^2 + 1/2m\underline{u}_i^2 - 1/2m\underline{u}'^2 - 1/2m\underline{u}_i'^2) \qquad (12)$$

$$\times\ d\underline{r}'\ d\underline{u}_i\ d\underline{u}_i'\ d\underline{u}'$$

The first term on the lhs of Equation (11) describes the time evolution, the second term is due to the position variation, the third term is the change due to the external force, and the rhs C(f) is the interparticle collision term given by Equation (12). The unprimed and primed notations refer to before and after collision. The delta functions assure conservation of momentum and energy during the collision and ν is the collision potential. Note that the collision term describes two-particle collisions and ignores triple and higher order collisions. Such a situation is valid only in dilute systems. For higher concentrations where higher order collisions can occur, it becomes necessary to consider simultaneous multiple collision terms.

The equation obtained for the physical quantities averaged over the Brownian motion collision, and averaged over a large time period compared to τ^* will be given as:

$$\frac{\partial f_o}{\partial t}(\underline{r},\underline{u}_o,t) + \underline{u}_o \cdot \frac{\partial f_o}{\partial \underline{r}}(\underline{r},\underline{u}_o,t) + g(1 - \frac{u_z}{V}) \frac{\partial f_o}{\partial u_z}(\underline{r},\underline{u}_o,t)$$

$$= C(f_o) \qquad (13)$$

The collision term $C(f_o)$ is obtained from its definition given in Equation (12) by replacing all f by f_o, and $\underline{u}$ by $\underline{u}_o$. Note that although the Boltzmann equation describes the concentration increase of the particles and the transports associated with the phenomenon, the extraction of information is quite difficult - primarily due to the existence of the collision term. Several methods of solutions exist which can tackle the problem - e.g. the Chapman-Eskog method (Chapman and Cowling (4)). However, these methods are in themselves fairly involved. Instead of seeking a perfect but complicated solution in which important aspects of the problem might be lost, we now seek a simple but significant and relevant solution to the problem by applying approximate methods. We begin by writing the simpler form of the equation, using the so-called relaxation time approximation technique. In this approximation, we assume that the system is only slightly away from the local equilibrium, and that the collision term can be replaced by:

$$-\frac{f(\underline{r},\underline{u},t) - f^{eq}(\underline{r},\underline{u},t)}{\tau} \qquad (14)$$

which gives the approximate rate of change of the distribution function. For notational convenience, the subscript o has been dropped from Equation (14) and hereafter. The local equilibrium function f^{eq} is the equilibrium Maxwell-Boltzmann distribution function given by:

$$f^{eq}(\underline{r},\underline{u},t) = n(\frac{m}{2\pi kT})^{3/2} \exp [- \frac{mu^2}{2kT}] \qquad (15)$$

The temperature T of the medium can be a function of $\underline{r}$ and t. With the relaxation time approximation, Equation (13) can now be given as:

$$\frac{\partial f}{\partial t} + \underline{u}\,\frac{\partial f}{\partial \underline{r}} + g\left(1 - \frac{u_z}{V}\right)\frac{\partial f}{\partial u_z} = - \frac{f - f^{eq}}{\tau} \qquad (16)$$

Though τ has a significance relative to the average time between collisions, it attains the status of a parameter of the particle properties. Instead of using an explicit potential in which constants need to be adjusted to suit the obtained results, we use a single parameter τ. Obviously, the success of the approximation technique depends on how well it can describe physical observations.

INTERPARTICLE COLLISION AND SETTLING VELOCITY

The dependence of the settling velocity of fine particles or solids on the concentration is based on two aspects: (1) As the concentration increases, the apparent viscosity of the medium will increase and the particle velocities will change, and (2) concurrently, particle motion will be hindered by the collisions due to the presence of other particles. These two contributions can be calculated from Equation (13).

Since the system is close to local equilibrium, we can assume:

$$f = f^{eq} + f' \quad \text{where } f' << f^{o} \qquad (17)$$

so that the normalization relation remains undisturbed, i.e.

$$n = \frac{1}{\Omega}\int f\, d\underline{r}\, d\underline{u} = \frac{1}{\Omega}\int f^{eq}\, d\underline{u}\, d\underline{r} \qquad (18)$$

In the steady state, the distribution function will no longer be an explicit function of t and if we consider a homogeneous medium, then it will also not be a function of $\underline{r}$. This leave Equation (16) as:

$$g\left(1 - \frac{u_z}{V}\right)\frac{\partial f(\underline{u})}{\partial z} = - \frac{f'(\underline{u})}{\tau} \qquad (19)$$

Using Equation (17), we can write (approximately):

$$g\left(1 - \frac{u_z}{V}\right)\frac{\partial f^{eq}}{\partial u_z} = - \frac{f'(\underline{u})}{\tau} \qquad (20)$$

Making use of Equation (15), we obtain:

$$f'(\underline{u}) = \frac{m u_z}{kT} \cdot g\left(1 - \frac{u_z}{V}\right)\tau f^{eq} \qquad (21)$$

and hence:

$$f(\underline{u}) = f^{eq}(\underline{u}) + g\left(1 - \frac{u_z}{V}\right)\frac{m\tau}{kT}\, u_z\, f^{eq} \qquad (22)$$

The average velocity will be given by:

$$\underline{v} = \langle u_z \rangle = \frac{1}{n}\int u_z\, f(\underline{u})\, d\underline{u} \qquad (23)$$

Taking note of the fact that the viscosity of the suspension changes as solids concentration changes, we invoke the Boltzmann relationship in relaxation time approximation to obtain:

$$\eta = \eta_o + nkT\tau = \eta_o + \eta_1 \tag{24}$$

It can be shown that with Equations (10), (22), (23) and (24), that:

$$u_z = \frac{1}{8}\left(\frac{m}{2\pi kT}\right)^{1/2} V^2 \left[1 - \left(\frac{2nkT}{\eta_o} + \frac{gmV}{kT}\right)\tau + \frac{3mng}{\eta_o} V \tau^2\right] \tag{25}$$

This relationship has been used to evaluate the actual laboratory settling experiments conducted on a bauxite red mud waste (Yong and Wagh (5,6)) and a standard kaolinite slurry suspension - as shown in Figure 1. The analysis requires that one seeks a relationship between the relaxation time τ and the concentration n. Simple kinetic arguments indicate that the relaxation time should vary as the reciprocal of the concentration. In the bauxite red mud, because of the greater presence of very fine particulates, the last term in the square bracket in Eqn. (25) becomes dominant while in the kaolinite suspension, this term is small.

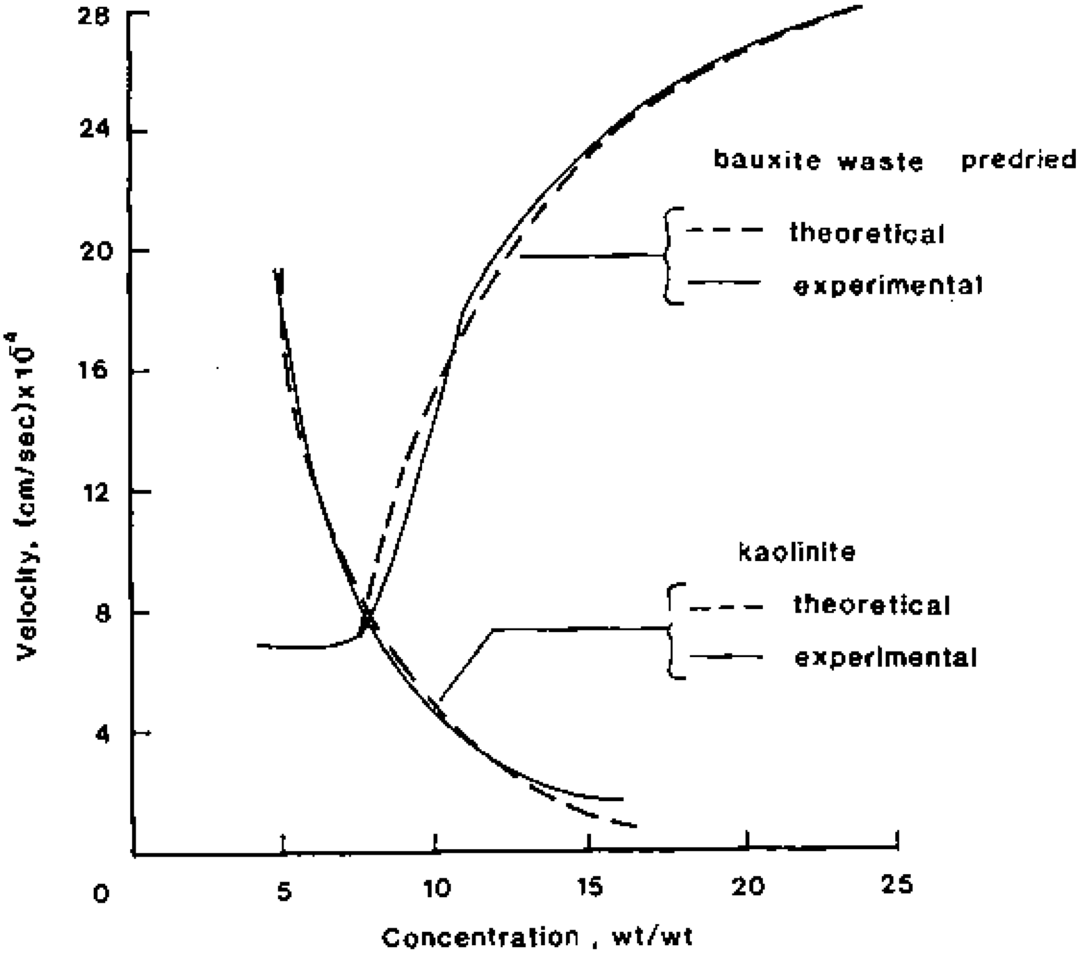

Fig. 1 Comparison of theoretically computed and experimentally measured values for settling velocities of bauxite waste and kaolinite

INTERACTION ENERGIES

When the energies of interaction of the suspended solids depend on the charged surfaces and interparticle forces, the chemical composition of the fluid medium, solids composition, as well as the mode of particle interaction become important considerations. Changes in the suspending fluid chemistry, charged surfaces and particle arrangement will alter the internal force system needed to establish dispersion stability of the suspension. Assuming the suspended solids to be plate-like in shape, the three principal modes of two-particle interaction include: face-to-face, edge-to-edge, and edge-to-face. For each mode of interparticle configuration, a relationship between net intersection energy and particle separation distance can be obtained. If repulsive energies dominate, input energy must equal or exceed the maximum repulsive energy in order that dispersion stability can be overcome - i.e. in order to destabilize the system. Conversely, if attractive energies dominate, input energy must equal or exceed the maximum attractive energy if the system is to be destabilized.

It is pertinent to note that whilst it is possible to predict the distribution of ions between particles using the Gouy-Chapman theory, applied to constant surface potential (Kruyt (7)), or constant surface charge (van Olphen (8)) models in a suspension system containing a homoionic symmetric electrolyte, no exact method is available to account for heterovalent systems. For purposes of calculation, a weighting procedure for estimation of the effective valence of cations in the system can be used. In the mixed mineral particle interaction scheme used in this study, the modes of particle interaction have been chosen as shown in Table 2, for montmorillonite (M), illite (I), and kaolinite (K), in the combinations as noted in the Table.

TABLE 2 Interparticle Configuration

Mode of Particle Interaction	Mineralogical Combination
Face-to-Face (F-F)	M-M, K-K, I-I, M-I, M-K, I-K
Edge-to-Face (E-F)	M-M, K-K, I-I, M-I, M-K, I-K, I-M, K-M, K-I
Edge-to-Edge (E-E)	M-M, K-K, I-I, M-I, M-K, K-I

In addition to the above particle configuration scheme, two effective cation valences computed as 1.05 and 1.76 are used in the computations performed to illustrate development of interaction energies. These two effective valences have been identified as "low salt" and "high salt" respectively in the graphical results shown as Figures 2 through 7.

To calculate the long range repulsive energies between suspended particles, we need to determine the Debye-Huckel reciprocal length K as follows:

$$K = \left(\frac{8\pi n e^2 v^2}{2kT}\right)^{1/2} \qquad (26)$$

Assuming $\varepsilon = 78$ and $kT = 0.4 \times 10^{-13}$ ergs at room temperature, the

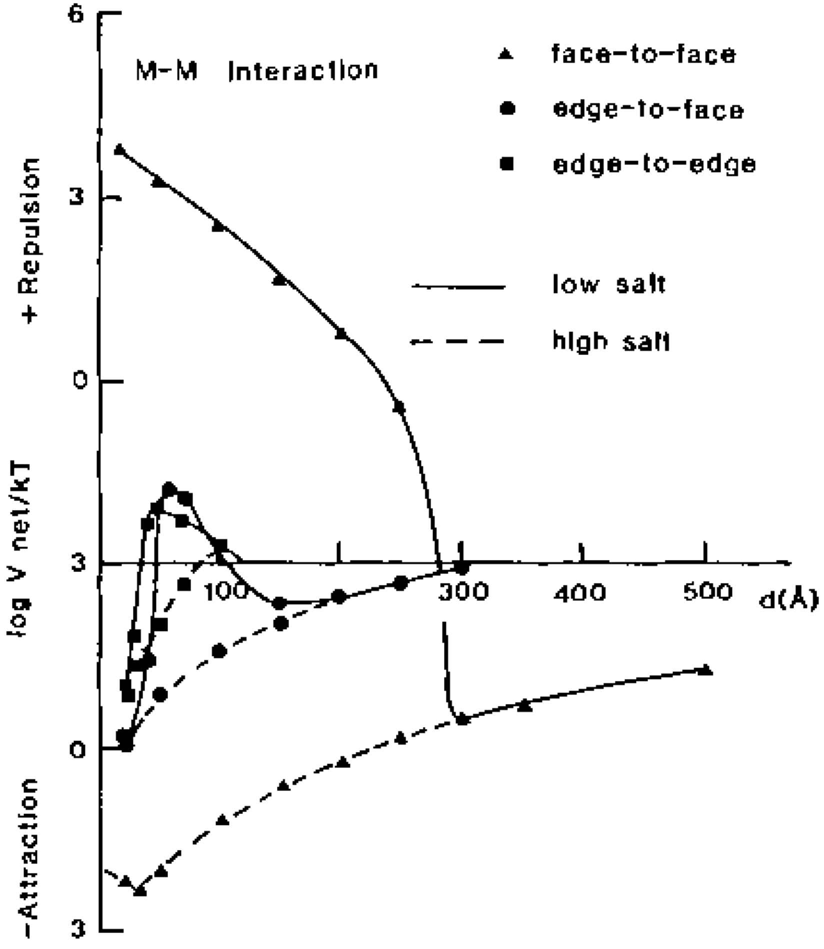

Fig. 2 Energy Interaction Diagram for M-M Interaction

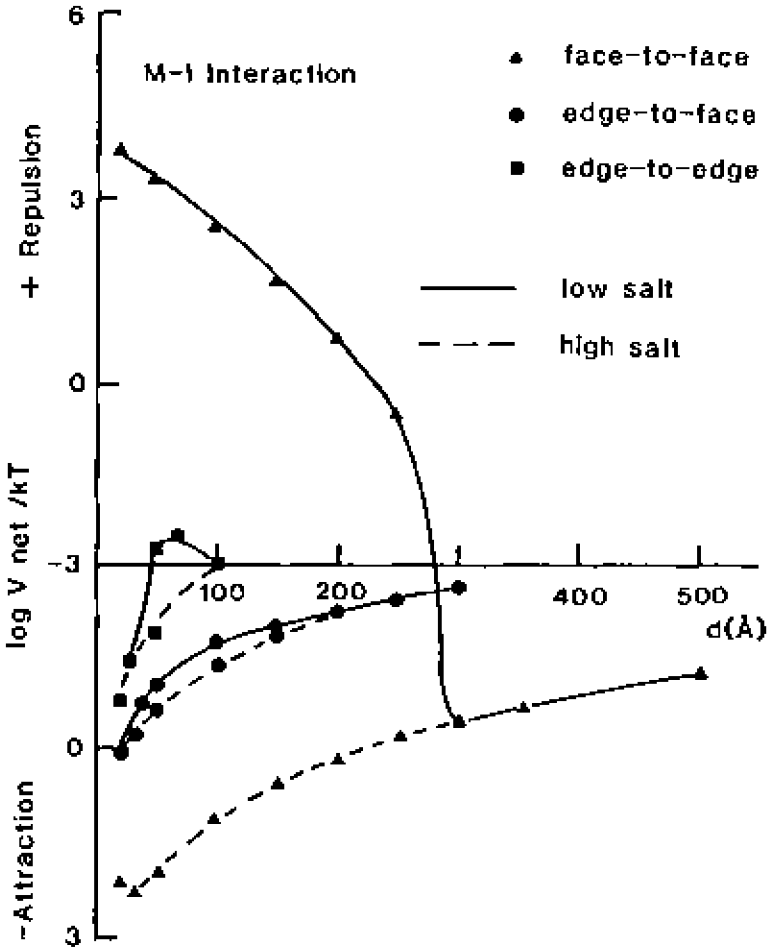

Fig. 3 Energy Interaction Diagram for M-I Interaction

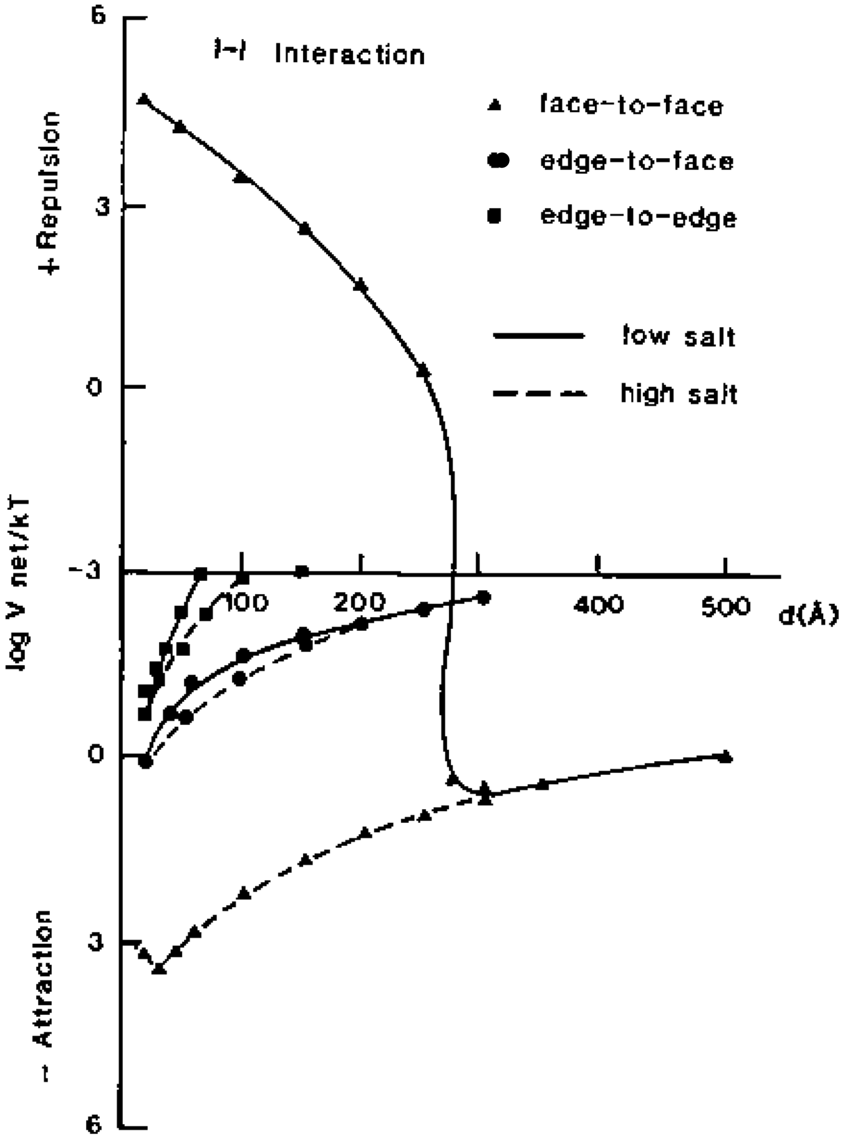

Fig. 4 Energy Interaction Diagram for I-I Interaction

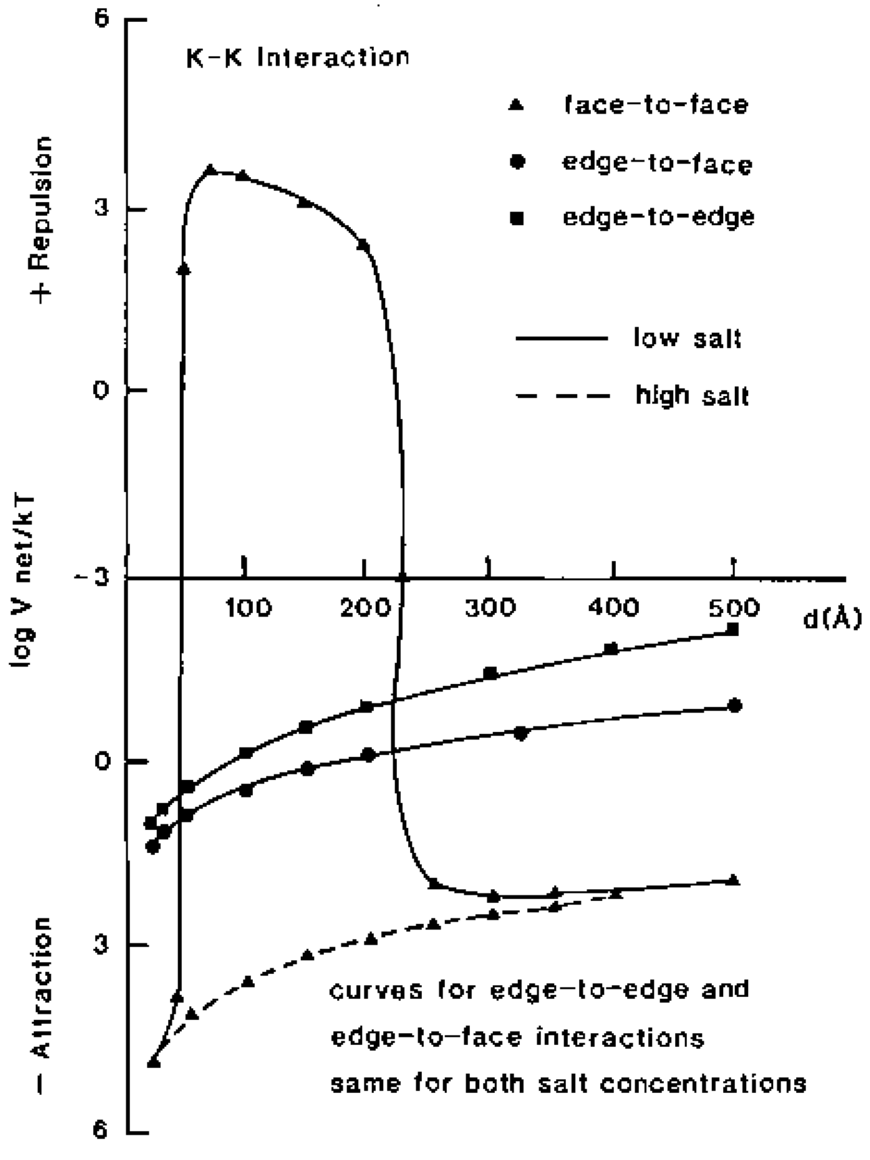

Fig. 5 Energy Interaction Diagram for K-K Interaction

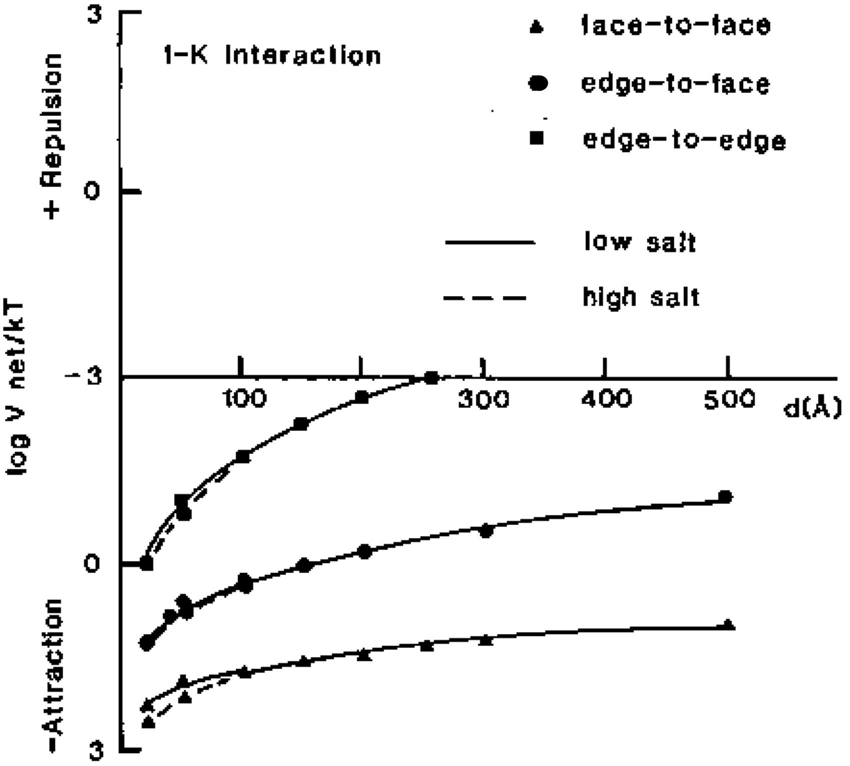

Fig. 6 Energy Interaction Diagram for I-K Interaction

value of K is computed to be 1.922×10^6 cm^{-1} and 8.52×10^6 cm^{-1} corresponding to the low and high salt concentrations. For a constant surface potential model, the long range repulsive energy for the F-F configuration is given as (Kruyt (7)):

$$V_R = \frac{4nkTz^2 \exp(-Kd)}{K[1+\exp(-2Kd)]} \qquad (27)$$

For F-F attractive long range interaction energies (Ludwig (9)):

$$V_A = \frac{-A}{12\pi}\left[\frac{1}{(2d)} + \frac{1}{(2d+2\delta)^2} - \frac{1}{(2d+\delta)^2}\right] \qquad (28)$$

In the case of E-F interaction, the long range repulsive energies become:

$$V_R = \varepsilon R_1 R_2 \frac{(\psi_1^2+\psi_2^2)}{4(R_1+R_2)} \left\{ \frac{2\psi_1\psi_2}{\psi_1^2+\psi_2^2} \ln \frac{1+\exp(-2Kd)}{1-\exp(-2Kd)} + \ln[1-\exp(-4Kd)]\right\} \qquad (29)$$

The corresponding long range attractive energies for E-F configuration can be calculated from:

$$V_A = -\frac{A}{6}\left[\frac{2R_1R_2}{x} + \frac{2R_1R_2}{x-4R_1R_2} + \ln\left(\frac{x}{x+4R_1R_2}\right)\right] \qquad (30)$$

where $x = 4d + 4d(R_1 + R_2)$

In the E-E configuration, the long range repulsive energies are calculated from:

$$V_R = \frac{\varepsilon R\psi_o^2}{2} \ln[1 + \exp(-2Kd)] \qquad (31)$$

and the corresponding long range attractive energy calculations will use

$$V_A = -\frac{A}{6}\left[\frac{2R^2}{x} + \frac{2R^2}{x+4R^2} + \ln\left(\frac{x}{x+4R^2}\right)\right] \qquad (32)$$

where $x = 4d^2 + 8Rd$.

Using the mineralogical parameters shown in Table 3 energy interaction diagrams such as those shown in Figures 2 through 6 can be drawn. The zeta potentials shown in Table 3 are based on measurements of surface and edge potentials (Ludwig (9); Sethi, Yong and Jorgensen (10)) for the three different clay minerals (M,K,I). The zeta potential specified on the edges has been assumed to be one-fifth that on the face, in accordance with the observation by Ferris and Jepson (11). Gross errors with respect to the assumption of the magnitude of the edge potential are seen in terms of alterations in the magnitudes of net energies of interaction rather than in interparticle configurations.

The calculations which are represented in graphical form in Figures 2 through 6 indicate that under low salt conditions, represented by the effective cation valence of 1.05, dispersion is best achieved

TABLE 3 Mineralogical Parameters Used in Computations

Clay Mineral	Surface Potential	Edge Potential	Surface Charge Density	Particle Diameter	Particle Thickness
	mV	mV	esu/cm	angstroms	angstroms
Montmorillonite	25	5	3 x 10	2000	90
Illite	20	4	3 x 10	2000	110
Kaolinite	15	3	3 x 10	20000	800

when particles are aligned in an F-F configuration - especially for interactions of particles with the highest surface areas such as montmorillonite and illite. The results indicate that the influence of effective valence of cations (represented as low and high salts) is most evident for the F-F interaction mode and for particles with large specific surface areas. Interaction energies developed by particles with small specific surface areas will show some dependence on suspension salt composition in the F-F mode (i.e. dispersed), but not as much in the other modes of interaction. For the high salt condition shown in the diagrams, the DLVO theory indicates that the particles will tend to stabilize into tactoids with F-F interaction.

CONCLUDING REMARKS - THE REAL WORLD

The stability of suspensions (i.e. slurries, slimes, etc.) which is determined by the dispersion stability of the suspended solids, cannot be characterized in terms of a unique value, i.e. dispersion stability is not a static phenomenon. The level (or degree) of dispersion stability is dependent on the energies of interaction developed within the system at any one time. Because of the three different kinds of forces acting on the suspended solids (particles), and because of ageing processes, destabilization of the suspension (which occurs gradually) through self-flocculation and agglomeration mechanisms will demonstrate itself in observed settling of the solids. Calculations for prediction of sedimentation, thickening and consolidation, deal with the observed settling and compression/consolidation behaviour of the 'solids'. However, it is useful to bear in mind that what is observed in this stage of calculations is essentially the results of a destabilization process. By providing the framework for consideration of the temporal dispersion stability of the suspension (system) in terms of (a) interparticle collision for inactive solids, and (b) energies of interaction for surface-active solids, a better appreciation of the capabilities of the various sedimentation/consolidation models would be obtained. Additionally, the requirements for treatments for initiating or accelerating destabilizing mechanisms can be better elucidated.

In the real world however, we recognize that multiple collisions occur in concert with the various interactions established between the electrostatic forces of repulsion and attraction. Yong (1) has shown that the dispersion stability of the solids suspension which follows from the fact that surface active solids interact in the fluid medium via collision and electrostatic forces can be viewed in terms of the water-holding capability of the solids. At a zero osmotic pressure (i.e. zero midplane potential), the volume of water associated with each solid or floc is at its maximum value. This volume of water can be computed from theoretical considerations using the DLVO model, as mentioned in the preceding, where the energy-separation distance calculations will give the most likely equilibrium interparticle spacing and void ratio of the system. Since real slurry systems will not have ideal particle arrangements, and since local agglomeration will indeed occur, one can resort to control experiments designed to measure the equilibrium water-holding capacity of specific types of minerals (or solids).

In performing equilibrium suspension experiments, the rationale established considers that if each solid, or if each floc "holds" onto a specific volume of water as its "equilibrium" shell of water (defined as the suspension volume), consistent with the balance of internal and external energies, the total stable dispersed state of the suspended solids would be equal to the sum of the suspension volumes of the individual component solids. In the experiments conducted by Yong and Sethi (10) to determine the equilibrium (suspension) volume of water associated with specific minerals, the values obtained (Table 4) show good correspondence with those computed on the basis of the theoretical interaction model, - provided that proper accounting is given to the presence of the potential determining anions. As seen from the extreme right hand column of Table 4 the methods for determination of the suspension volume for the various mineral required suspension/setting experiments in long settling columns, left in a controlled temperature-humidity chamber for periods of from 18 to 36 months. The suspension volumes measured do not require any preferred orientation of solids, and can be used in comparing theoretically predicted equilibrium solids concentrations with actual measured values for the slurry samples studied.

TABLE 4 Suspension Volume for Various Minerals and Method of Their Determination

Sample No.	Mineral	Suspension Volume	Void Ratio	Specific Gravity	Method of Determination
1	Kaolinite	1.3	3.44	2.65	settling of pure kaolinite in $NaHCO_3$ for 18 months.
2	Illite	3.1	8.15	2.65	settling of kaolinite:illite (40:60) in $NaHCO_3$ for 18 months
3	Montmorillonite	21.5	57.0	2.65	settling of Na-montmorillonite for 36 months
4	Amorphous Fe_2O_3	20.5	82.0	4.00	settling of Fe_2O_3+ kaolinite:illite for 18 months

Table 4 Continued

					containing 4.5% Fe_2O_3.
5	Gibbsite	1.0	2.65	2.65	estimated from kaolinite experiments.
6	Mica	3.0	7.95	2.65	estimated from illite experiments
7	Quartz	0.14	0.37	2.65	estimated from Theory of Mixture
8	Others*	0.42	1.12	2.65	assumed

* Includes feldspar, calcite, ankerite, siderite and pyrite.

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NOTATIONS

$C(f_o)$ = collision term

$\bar{f} = f_o$ = average of f

$\underline{F}$ = average force

k = Boltzmann constant

κ = Debyre-Hukel reciprocal length

m = mass of particle

m' = *submerged mass of particle in liquid*

n = number density of particles

N = total number of particles

$\underline{r}$ = position vector

t = time

T = absolute temperature

$\underline{u}$ = velocity

$\underline{u}_o$ = mean value of $\underline{u}$

$\underline{u}'$ = fluctuation value of $\underline{u}$

$\underline{v}$ = average velocity

V = Stokesian velocity

$\hat{z}$ = unit vector

ϵ = dielectric constant

η = viscosity

τ = relaxation time of interparticle collisions

ψ = potential

R, a = radius of interacting spheres or particles

Ω = total volume of the system

η_o = viscosity of the pure fluid

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