FUNDAMENTALS OF DEWATERING
FINE PARTICLE SLURRIES

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INTRODUCTION

Sludges and slimes do not often dewater at the desired rates and as a result their handling is a serious problem for many industries. The problem is particularly acute whenever certain clay minerals are present in these waste products. A prime example of this is the phosphatic slime that is generated during the mining and processing of the phosphate rocks. Other examples of slow settling suspensions include red mud, acid mine drainage sludge, and coal slimes. Large amounts of these slimes are generated annually (Table 1) and in view of the loss of mineral matter in it and the environmental hazards created by them, it is imperative that methods for dewatering slow settling suspensions be devised. It would prove fruitful in this regard to have a proper understanding of the fundamentals of the dewatering or the subsidence behavior of these slurries. However, while sedimentation theories have been adequately developed to cover the two extremes of slurry concentrations, very little is known on the basic aspects of sedimentation of slurries of intermediate concentration range that is of interest here. Thus we have theories for very dilute suspensions based on Stoke's law and for consolidated beds based on models developed for flow through porous media sedimentation or dewatering behavior of concentrated suspensions or slurries has not been adequately modelled. Close examination
of the actual behavior of such a slurry during dewatering has enabled us to develop a
phenomenological model which is described here. A systematic attempt was also made
as a part of this study to identify the characteristics of the minerals that are
responsible for the slow subsidence* behavior of such slurries. This has been
reviewed by us (12, 13) and is briefly summarized below

SEDIMENTATION MODELS

Sedimentation models can be developed on the basis of different properties of
the dewatering system (See Table 2). While in some operations such as thickening,
the solids concentration of the pulp is the criterion, in others such as effluent
treatment, it is the clarity of the supernatant that is of major concern.
Sedimentation of slurries have been modelled in the past mostly on the basis of the
changes in the solids concentration of the slurry as a function of time in batch
sedimentation processes and is represented usually as height of the slurry/super-
natant interface vs sedimentation time (See Figure 1). The simplest sedimentation
curve is produced by a suspension of uniform size and is characterized by a linear
region indicative of constant settling rate followed immediately by a region of
zero settling. Settling stops abruptly since the bed, if settled unhindered, is
totally incompressible at this point. On the other hand, if the slurry is made of
compressible material such as clay, settling can continue for ever at a decreasing
rate. Sedimentation curve of such systems will not show any constant settling
rate region (14) and is characterized by a reverse S-shape.

Number of investigators have studied the sedimentation of clays, even though
none has developed a model to accurately describe it (15-18). The peculiar

*Sedimentation of network slurries are adequately called as subsidence in this
paper.
sedimentation behavior of the clays is the result of the tendency for clays to floculate. Michaels and Bolger (19) were among the first two to take the floculation properties of the sedimenting material into account in the formulation of a sedimentation model. They considered the basic unit to be a floc rather than the individual particle. At low shear rates, the flocs group into large clusters called aggregates, and the aggregates in turn form an extended three-dimensional network. Three different types of settling curves are obtained in this case, one for each solid concentration region. Figure 1 illustrates these three types also.

For very dilute suspensions, flocs can be considered to settle individually on the basis of Stoke's law and the following expression based on Richardson and Zaki equation for the group settling of uniform, spherical particles describes this adequately.

\[ v_i = \frac{\nu_i}{a} \]  

(1)

Where \( v_i \) is the settling rate of slurry/supernatant interface, \( v_a \) is the Stoke's velocity of single aggregates and \( \varepsilon \) is the void fraction. Assuming the average diameter of the aggregate \( d_a \) to be independent of the clay concentration and invariant during settling, equation (1) can be rewritten as

\[ v_i(0) = \frac{g(\rho_s - \rho_w)\bar{a}^2}{18\mu_w C_{as}} (1 - C_{as} \phi_s)^{4.65} \]  

(2)

Where \( v_i(0) \) is the initial settling rate, \( g \) is the gravitational acceleration, \( \rho_s \) and \( \rho_w \) are densities of solids and water respectively, \( \mu_w \) is the viscosity of the water and \( \phi_s \) is the solid volume concentration. \( C_{as} \) is the ratio of volume concentration of aggregate to solid. The above model has been tested with some success for kaolin (19) and TiO_2 (20) but it proved inadequate for the case of alum mud (20).

Slurries of intermediate concentrations often appear like a small, bulky aggregate and they can be considered to settle as a coherent network. The settling will be determined in this case essentially by the balance between the gravity
forces \( f_g \), support force \( f_u \) exerted by the underlying material, the wall support force \( f_w \) and frictional force \( f_f \) for the flow of fluid through spaces between the aggregate. At equilibrium:

\[
f_u + f_w + f_g + f_f = 0 \tag{3}
\]

\[
f_u = \frac{\pi}{4} d^2 c \sigma_c \tag{4}
\]

\[
f_w = \pi D_c \Delta H \sigma_y \tag{5}
\]

\[
f_g = \frac{\pi}{4} D_c^2 \Delta H g \left( \rho_s - \rho_w \right) \phi_s \tag{6}
\]

\[
f_f = \frac{\pi}{4} D_c \Delta H \mu_w \nu_1 \tau^2 S^2 \tag{7}
\]

where \( D_c \) is the diameter of the container, \( \sigma_c \) and \( \sigma_y \) are the compressive load that exists at the boundary between a control constant density zone of length \( \Delta H \) and the underlying compressed zone, \( \sigma_c \) is the yield stress of the slurry, \( \kappa \) is the Kozeny's shape constant in the Kozeny - Carman equation, \( \tau \) is the tortuosity factor, and \( S \) is the specific surface area. From equations 3 to 7, the following expression results relating settling of the slurry to the container diameter, yield diameter, \( D_y \) and yield height, \( H_y \):

\[
v_i = v_i^\infty (0) \left( 1 - \frac{D_y}{D_c} - \frac{H_y}{H_c} \right) \tag{8}
\]

where

\[
v_i^\infty (0) = \frac{g \left( \rho_s - \rho_w \right) \phi_s \varepsilon^3}{\kappa \mu \tau^2 S^2} \tag{9}
\]

\[
D_y = \frac{4 \sigma_y}{g \left( \rho_s - \rho_w \right) \phi_s} \tag{10}
\]

\[
H_y = \frac{\sigma_c}{g \left( \rho_s - \rho_w \right) \phi_s} \frac{H_c}{\Delta H} \tag{11}
\]

The above expression has been tested for kaolin suspensions and the results suggested that the container diameter has a negligible effect on the settling of flocculated slurries provided that it is not as small as \( D_y \). Our results (21) for
phosphatic slime, however, showed a definite effect of the container diameter on the settling rate (See Figure 2). This effect and other features that are characteristic of the slow settling sludges can however be explained well using our phenomenological model.

**Phenomenological Model**

The observed behavior of the slurry during dewatering is schematically shown in Figure 3. There are four stages that are distinctly exhibited by the slurry during this time:

(I) Almost immediately after mixing is stopped, all rotational movements created during the suspension terminate

(II) In a few minutes, coarser size particles and small air bubbles trapped in the solidified slurry move through it creating tears. Water seeps up through these tears and forms lenses of water.

(III) Additional tears develop leading to channels connecting various lenses, and finally opening up at the slurry-water interface to permit water to exit. The slurry/supernatant interface now subsides rapidly and water along with entrained particles can be seen sprouting through in the form of microvolcanoes. Liquid also seeps up along the container walls. The effect of the container diameter that was discussed earlier can in fact be explained by taking into account wall area/unit mass of slurry available for water seepage.

(IV) Continuous compression of the slurry during this dewatering process finally causes the contraction of the channels which in turn reduces the rate of additional dewatering.

According to this model, dewatering is dependent essentially upon the availability of seepage paths for the water and in the present system such paths are proposed to be essentially the result of the heterogeneity of the system. This hypothesis was tested by determining the effect of the addition of coarser particles to the slurry and the generation of microbubbles in it. If
the hypothesis is valid, such procedures should enhance the dewatering of the slurry.

Effect of Addition of Coarse Particles

The effect of the presence of coarse particles was tested by mixing the slime with sand tailings. The results given in Figure 4 show that the addition does indeed enhance the settling rate significantly. The proposed seepage mechanism itself was tested by conducting experiments using particles with a wide range of properties, and the results are presented in Figure 5. Evidently, increase in the specific gravity of the additive produced no measurable effect on subsidence suggesting that the observed effect is not due to any increase that could have occurred in the weight of the slime network. It is noted that cassiterite, the heaviest mineral, was not as effective as the other lighter minerals.

This was confirmed to be due to the fact that the heavy cassiterite particles had broken through the slurry even before it gelled and were not thus available for creating the tears for water seepage. Interestingly, silicone coated glass beads also broke through the slurry similarly, producing no effect on the subsidence. Since glass beads without silicone coating did enhance the settling, the above effect must be attributed to the hydrophobic nature of the silicone coated surface. Evidently polar interactions between the particles and the aqueous medium are helpful in causing entrapment of the particles in the slurry. Indeed irregular quartz particles are more effective than even the uncoated glass beads suggesting that in addition to the hydrophilicity of the surface, the morphology of the particles also plays a governing role in determining the subsidence rate. The effect of graphite and molybdenite might have resulted from the presence of some hydrophilic sites on the surface as well as irregular morphology. Indeed it is possible to alter the interactions between the particles and the slurry by means of chemical additives, particularly polymers (22-24). Polymers can affect the aggregation and therefore dewatering
by modifying the structure of flocs and aggregates as well as by enhancing
bridging of particles to clay and thereby trapping of particles in the slurry.
Principles of polymer adsorption and flocculation have been reviewed in detail
recently (25, 26). Addition of polymers in proper dosages can indeed cause
flocculation, the extent of adsorption and flocculation being dependent upon
polymer properties such as molecular weight, functional group distribution, and
charge density, solution properties such as pH, ionic strength and temperature
and mineral properties such as surface charge and porosity. While polymers in
proper dosages can be expected to enhance the initial settling, the final solid
content can often be low due to entrapment of large amounts of water inside bul-
ky flocs. In such cases, restructuring of flocs and aggregates by mechanical
means becomes a necessary part of the process to achieve the desired solid con-

Effect of Air Bubbles

Settling rates of slurries which were subjected to suction, are compared in
Figure 6 with that obtained for control samples. It can be seen that generation
of bubbles due to suction does enhance the subsidence considerably. The bubbles
were found to alter the physical features of the slurry such that water seepage
was possible at an enhanced rate. It appears that any means for the generation of
tiny bubbles might prove useful for enhancing the subsidence particularly when
in combination with other techniques These observations do closely support
the proposed mechanism of enhanced subsidence

IDEALIZED PHENOMENOLOGICAL MODEL

Enhanced settling of materials that has a tendency to form a network struc-
ture is a complex process because it is governed by a combination of several me-
chanisms, each predominating in a different concentration range. The complex
nature of this sedimentation is illustrated in Figures 7 and 8 (27). Major
stages and their relative durations have been identified in these Figures. The phenomenological equation is derived considering the fact that a slurry with an internal structure subsides according to the action of two interrelated processes namely gravitational expulsion of water from the slurry and internal resistive forces that oppose the movement of water. While the rate of expulsion of water itself depends upon the amount of water contained below the interface in the suspension, the resistance depends upon the amount of water which has already passed through the interface. This can be expressed as:

\[ \frac{\mathrm{d}w}{\mathrm{d}t} = c + k\phi(W)\psi(1-\xi(W)) \quad (12) \]

Where \( W \) is the fraction of recoverable water remaining in the slurry at time \( t \); \( k \) is general rate coefficient and \( \phi, \psi, \) and \( \xi \) are general functions. \( c \) is the value of constant settling rate and takes into account the fact that there may be initial incompressible settling, preceding the development of resistance. The form of this equation that is applicable for various stages can be obtained by examining the nature of subsidence and the type of water (interaggregate, interfloc and intrafloc) that is involved in dewatering during each stage.

In the first stage, called lenticular stage \((H(0) \text{ to } H(t_1))\), gel structure develops in the suspension, but there is negligible interface settling. \( c \) in equation (12) is zero. Coarse particles and air bubbles move through the suspension forming channels. Water seeps up through the channels and forms lenses. Thus, at the end of this stage, the suspension consists of solids grouped into a loose network of aggregates made up of flocs with lenticular water filled fissures interspersing throughout the network structure.

During the next stage, called reticular stage \((H(t_1) \text{ to } H(t_2))\), lenses become interconnected such that continuous filaments or reticules of water intersperse the loosely connected floccular aggregates. As channels open up at the interface, interaggregate water is expelled from the sedimenting mass slowly at first, then more rapidly and gradually slowing as aggregates make contact with
each other. This can be written as
\[
\frac{dW_a}{dt} = -k(1-W_a)W_a \tag{13a}
\]
and
\[
H(t) = (H_0-H(t_3)) \left\{ 1-1/(1+r \exp (-s(t-t_1))) \right\} + H(t_3) \tag{13b}
\]

\(W_a\) being the fraction of interaggregate water at time \(t\) and \(r\) and \(s\) being rate coefficients. The equation is based on the fact that the rate of expulsion will depend upon the amount of water present in the suspension and on the degree of bridging which provides a growing resistive force which itself is proportional to the water that has already escaped.

In the vermicular stage \((H(t_2))\) to \(H(t_3)\) the aggregates establish closer contacts reducing the water filaments into a narrow vermiform structure. The bridging allows forces to be transmitted through the mass and subsidence proceeds at a decreasing rate as the water in the structure is expelled and continues until the channels close. Equation 13 will describe this stage, but the exponential expression is a better fit.

\[
\frac{dW_a}{dt} = -k \exp \alpha W_a 
\]
\[
H(t) = H(t_2) - b \ln \left( t/t_2 \right) \tag{14b}
\]
\(\alpha\) and \(b\) being constants. This equation represents a moderating rate of water expulsion as compared with the fast flow rate during the latter part of the reticular stage.

When all the water in the macrochannels between aggregate has been expelled the end of the vermicular stage is reached and further dewatering takes place due to the consolidation of flocs (floccular stage: \(H(t_3)\) to \(H(\infty)\)). Water is now removed from the microchannels between flocs and at a slower rate from within the flocs. These processes determined by gravitational and viscous forces follow first-order kinetics
\[
\frac{dW}{dt} = -kW_f \tag{15a}
\]
and:

\[ H(t) + m \exp(-p(t-t_3)) + n \exp(-q(t-t_3)) + n(t) q < p \]  

Where \( W_f \) is interand intra flocs water at time \( t \), \( m \) and \( n \) are respectively coefficients referring to fast and slow parts of the floccular region, and \( p \) and \( q \) are corresponding rate coefficients.

At the end of intrafloc processes, the system approaches an equilibrium between gravitational, frictional, and electrical forces with viscous forces approaching zero. During this stage the plot of suspension height versus time asymptotes to a constant value.

The phenomenological model was tested by first determining various rate coefficients then comparing the resultant curves with experimental curves. As can be seen from Figure 9, the model fits the experimental results satisfactorily. To develop a full understanding of this type of subsidence, it is however essential to identify the major physical and chemical factors that determine the slow settling behavior and then to arrive at a fundamental interpretation for all the parameters including the rate coefficients.

MODEL SLOW SETTLING SLURRY

Slow settling behavior of the slimes is generally attributed to clays and clay type minerals, but not all clays produce slimes of the phosphatic type. To identify characteristics of clay responsible for problematic features, experiments were conducted with components of phosphatic slimes, and mixtures of these components.

Three types of minerals were used to arrive at the following model systems:

- **clay minerals** - montmorillonite, attapulgite, kaolin. These three minerals are major components of phosphatic slime
- **asbestos minerals** - amphibole, chrysotile. These fibrous minerals were included to determine the role of such a mineral feature
- **sand** - quartz. This is also a component of the phosphatic slime, but it is neither fibrous nor clay type
Single, binary, ternary, and quarternary mixtures of the above minerals were tested for the following eight basic characteristics of the phosphatic slime:

1. an initial period of gelling
2. slow subsidence with continuously varying settling rate
3. minimum segregation of mineral constituents during subsidence
4. a bulky sediment
5. presence of fissures and channels during subsidence
6. water exiting as microvolcanoes
7. a sharp slurry/supernatant interface
8. a clear supernatant

Subsidence behavior of the typical single, binary and ternary systems are shown in Figure 10 along with that for phosphatic slime. It was found that none of the constituent minerals themselves or their binaries resembled the industrial slime with respect to the above eight characteristics. From the various combinations of montmorillonite, kaolinite, attapulgite, quartz, chrysotile and amphibole studied only the montmorillonite-attapulgite-kaolinite ternary and the montmorillonite-attapulgite-kaolinite-quartz quarternary showed the major slow settling features of the phosphatic slime. The role of the montmorillonite and the fibrous attapulgite particles was particularly evident since the absence of either mineral made the behavior of the slurry most different from that of the phosphatic slime. It is evident that the morphology of the minerals does play a major role in determining the dewatering rate.

The experiments conducted as a function of pH showed the supernatant to be clear only when the solution pH was such that the minerals were oppositely charged. Apparently favorable electrostatic interactions that can induce attachment of the colloidal mineral matter to the subsiding mass are required to produce a clear supernatant. Thus while the settling rate and the solid content is dependent essentially upon the size and morphology of the mineral components, the clarity of the supernatant is governed by the surface charge properties which can in turn be
controlled either by adjusting the solution properties such as pH and salinity or by addition of polymers or other chemicals that can adsorb on various component minerals.

CONCLUDING REMARKS

Much work has been done on the dewatering of sludges such as phosphatic slime, acid sludge, coal slime and red mud, and yet very little is established on the basic reasons for their slow settling behavior. Also settling of these slimes have not been adequately modelled.

In our study, the mechanism by which enhanced dewatering of phosphatic slime occurs has been identified based on the actual observation of the phosphatic slime during subsidence. Also a phenomenological model developed to describe during various stages is successfully tested for this system. To conduct any fundamental studies on these slurries, it is most useful to have a reproducible known model slurry and a mineral mixture that closely resembles the phosphatic slime in its subsidence behavior has been formulated towards this purpose. Clearly, there exists now a need to systematically study the effect of relevant physical and chemical factors on the dewatering of the model slurry and problem slurries, and from the results to identify the reasons for the pertinacious behavior of these slurries inorder that adequate technology can be developed for their dewatering.

ACKNOWLEDGEMENT

The support of the Particulate and Multiphase processing program of the National Science Foundation (CPE-80-11013) is gratefully acknowledged. Contributions of Prof. C.C. Harris, Dr. D.R. Nagaraj, Mr. G.C. Sresty, and Mr. E.L. Smith, Jr. with the author (Ref12,21,27 & 28) used in this review are also acknowledged.
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17. ibid., 1957, 566.


Table 1

<table>
<thead>
<tr>
<th>Waste</th>
<th>Million Tons per Year</th>
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<tr>
<td>phosphatic slime</td>
<td>40-50</td>
</tr>
<tr>
<td>Mud</td>
<td>8-10</td>
</tr>
<tr>
<td>Acid Sludge</td>
<td>0.5</td>
</tr>
<tr>
<td>Slimes</td>
<td>10.</td>
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</tbody>
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Others: Potash, Clay fines, Uranium tailings, drilling mud waste, paper and pulp effluent, TiO₂
Table 2. **Major Criteria in Dewatering**

<table>
<thead>
<tr>
<th>Solid concentration of sediment</th>
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<tbody>
<tr>
<td>Volume of sediment</td>
</tr>
<tr>
<td>Settling rate</td>
</tr>
<tr>
<td>Supernatant clarity</td>
</tr>
<tr>
<td>Cake yield strength</td>
</tr>
<tr>
<td>Cake moisture</td>
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LIST OF FIGURES

1. Typical batch sedimentation curves for pulps of various solid concentrations (19).

2. Diagram illustrating the effect of container diameter on the slurry/supernatant interface height, after 8 hours of subsidence; -37μm slimes; Initial height of the slime column, 17.8 cm.

3. Schematic representation of processes that a 2.6% phosphatic slime containing 0.5g coarse particles underwent during subsidence. Observations: 0 min., suspension gels immediately after mixing is stopped; ~10 minutes, moving particles and air bubbles create tears; ~13 min. to ~35 min., water concentrates into lenses around the tears; ~2 hours, channels and microvolcanoes permit enhanced dewatering; ~4 hours, water filaments depleted, channels begin to close and dewatering rate becomes very small (27).

4. Diagram showing the effect of quartz flotation tailings on the subsidence of 2.6% ~37μm phosphatic slime, vertical bars indicate range when larger than symbol (21).

5. Effect of addition of various types of coarse particles on the height obtained for the slurry (2.6% ~37μm phosphatic slime)/supernatant interface at various subsidence times (21).

6. Diagram illustrating the effect of air bubbles generated by suction on the subsidence of phosphatic slime (28).
Batch subsidence curve, H(t) vs. log t plot showing principal regions. The duration of the stages depend upon the characteristics of the solids and the experimental conditions (27).

8. Idealized sedimentation model. A: Reticular stage commences, Aggregates come in contact, water lenses form; B: Reticular stage completes, Aggregates are increasing the number of points of mutual contact; C: Vermicular stage commences, Aggregates are bridged strongly, water filaments interconnected but less intensely than during the previous reticular stage; D: Vermicular stage partially complete; E: Floccular stage commencing, water present only as inter and intrafloc water (27).

9. Diagram illustrating the fit of the phenomenological equation (27).

10. a. Height of the slurry/supernatant interface vs. settling time for single mineral systems (2.5%); the numbers in parantheses indicate the pH values (28).

b. Height of the slurry/supernatant interface vs. settling time for binary systems containing kaolin (K) and chrysotile (Ch), attapulgite (At), amphibole (Am), and quartz (Q). Curve 1 for K: Ch = 1:1 (pH 8.8), 2 for K:At = 1:1 (pH 8.3); 3 for K:Am = 1:1 (pH 6.7 and 8.5), 4 for K:At = 1:1 (pH 7.4), 5 for K:Q = 1:1 (pH 6.4), 6 for phosphatic slimes (pH 8.2), (28)

c. Height of the slurry/supernatant interface versus settling time for binary systems at pH 5 containing Montmorillonite(M) and Attapulgite(At) and Chrysotile(Ch). Curves 1 and 4 for At:M = 4:1, and 6:1 respectively, 2, 3 and 5 for Am: M = 4:1, 5:1 and 6:1 respectively, 6 for Ch: M = 4:1, 7 and 8 for phosphatic slimes at pH 6.2 and 8.2 respectively (28).
d. Height of the slurry/supernatant interface versus settling time of Montmorillonite(M), Attapulgite(At), Kaolin(K), and Quartz(Q). Curves 1, 2 and 4 for M:K:At=1:2:3 (pH 4-8), 1:1:3 (pH ~6) and 1:1:6 (pH ~6) respectively, 3 and 5 for M:Q:At=2:2:2 (pH 3-8) and 1:1:4 (pH ~4) respectively (28)
Henry's Law Constant for Gases in Solutions

**Graph Description**

The graph illustrates the height of the interface (%) over time in minutes under different suction conditions.

- **No Suction**: Diamond marker
- **Suction (~20 mm Hg)**: Circle marker. Continuously using a water aspirator.
- **Suction (~18 mm Hg)**: Square marker. 10 min. every 20 min. using a water aspirator.
- **Suction (~10 mm Hg)**: Triangle marker. 2.5 sec. every 30 min. using a vacuum pump.

**Axes**

- **Y-axis**: Height of the interface (%)
- **X-axis**: Time (min.)

**Legend**

- **NO SUCTION**: Diamond marker
- **SUCTION (~20 mm Hg)**: Circle marker. Continuously using water aspirator.
- **SUCTION (~18 mm Hg)**: Square marker. 10 min. every 20 min. using water aspirator.
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