SEDIMENTATION OF STRUCTURED SUSPENSIONS, I

Introduction and some General Statements

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The first paper of our series on sedimentation of structured suspensions begins with summarizing the most important results available in literature. The principal types are presented by describing some characteristic processes. Then, based on the results, a model consisting of three sections, namely sedimentation, filtering and shrinking is drawn up. Finally the objectives of further investigations are outlined.

Introduction

Investigations on sedimentation of structured suspensions performed at the Institute of Colloid Chemistry during the last ten years made it necessary to review the results obtained from a uniform point of view. It seemed also justified to deal with the results to be expected in the series of articles beginning with this paper.

Preliminaries. Review of literature

The problem of sedimentation of extremely dilute suspensions seems to be practically resolved on the basis of Stokes' and Navier's conception and its further development. The question concerning more concentrated suspensions seems more problematical, even if dynamically independent spherical particles, settling individually, are considered. The most widely used approximations for this case were elaborated by STEINOUR as well as by RICHARDSON and ZAKI. These authors, like others, taking into account the upward streaming of the displaced medium and the effect on the settling process of the density and viscosity of the suspension, generally gave relations for determining the sedimentation rate of rigid monodisperse spheres as a function of the "free" volume (relative volume of the medium, *i.e.* porosity ε) and the classical parameters (radius or diameter of the sphere, difference in density, and viscosity of the medium). These relations are generally complicated functions

of ε, because the influence of hydrodynamical interactions, as well as the density and viscosity of the suspension also depend on ε. According to STEINOUR [1], for non-flocculated spherical suspensions in the range $0.5<\varepsilon<0.7$, the relation

$$Q = v_S \frac{\varepsilon^3}{1-\varepsilon} \tag{1}$$

is valid, where Q is the settling rate of a suspension of porosity ε, *i.e.* of volumetric density $(1-\varepsilon)$, consisting of spherical particles, and v_S the settling rate of the particles in a corresponding, infinitely dilute suspension according to Stokes. RICHARDSON and ZAKI [2] calculated with the following relation:

$$Q = v_S \varepsilon^{4.65}. \tag{2}$$

In comparetively more dilute, monodisperse suspensions, as long as ε can be considered as constant in the upper zone, the settling velocity of the interface between the slurry and the supernatant is constant, the beginning of the settling curve can be considered as linear (see later). In intermediate concentrations, technically in the shrinking zone, ε changes with the height of the zone during sedimentation. In this case, some authors [3, 4] assume as an empirical approximative solution that the sedimentation rate dV/dt is a linear function of the difference between the instantaneous volume V and the ultimate volume V_∞

$$-\frac{dV}{dt} = k(V - V_\infty), \tag{3}$$

where k is the velocity sonstant. Integrating with the initial condition that at $t=0$ $V(0)=V_0$, the following exponential formula

$$V(t) = V_\infty + (V_0 - V_\infty)e^{-kt} \tag{4}$$

is obtained.

In heterodisperse suspensions of rather low concentration, if interactions between the particles can be neglected, the particles of different sizes will fall individually with different velocities, according to Stokes' law. The settling suspension does not give a sharp interface and the weight of the sediment increases with time according to the classical analyses. In suspensions occurring in practice, the interactions (adhesive forces) between the particles cannot be neglected. In this case the formation of larger or smaller aggregates (orthokinetic coagulation) is to be expected, by which the sedimentation process becomes much more complex. Kinetics and mechanism of this process has been first dealt with in detail by TUORILA [5] and MÜLLER [6]; subsequently ANDERSSON [7] elaborated a theory, taking into account the hydrodynamical effects between the settling particles. The probability of collision and adhesion of the particles depends on the sign and the value of the resultant of the attractive and repulsive forces between the particles. These can be calculated on the base of Deryaghin—Landau—Verwey—Overbeek's (DLVO) theory. This was taken into account by JOVANOVIČ [8] in his recent calculations concerning more dilute suspensions containing individually settling aggregates.

The most complex cases — occurring most frequently in industrial practice — are those of comparatively more concentrated suspensions, in which the interactions

between the particles have also to be taken into account. Despite their heterogeneity, these suspensions mostly settle with a sharp interface; their particles are in more or less aggregated state. (The respective literature is not quite uniform and consequent in using the terms "coagulation" and "flocculation"; therefore we use the most general term*). This type of sedimentation was studied first in the case of kaolin suspensions by COE and CLEVENGER [9], who dealt with the concentration zones formed in the settling suspension, and pointed to the fact that the upward streaming of the displaced liquid in the sediment is actually a case of streaming through pores. Taking into account the results of POWERS [10] concerning concentrated, flocculated cement suspensions, STEINOUR [11, 12] gave the following relation:

$$Q = \frac{0.123 v_S}{(1-W_i)^2} \frac{(\varepsilon - W_i)^3}{1-\varepsilon} \tag{5}$$

where W_i is the volume of the so called "immobilized" liquid, which does not take part in the streaming through the pores. According to STEINOUR, in heterodisperse systems

$$v_S = \frac{2g(\varrho_s - \varrho_f)}{\eta \sigma^2} \tag{6}$$

where g is the gravity acceleration, ϱ_s the density of the suspended material, ϱ_f that of the liquid, η the viscosity of the medium and σ is the specific surface of the particles relative to their volume. For spherical particles of radius r, $\sigma = 3/r$, and v_S is in accordance with Stokes' relation. Equation (5) is very similar to the sedimentation formula of POWERS [10]:

$$Q = \frac{0.2}{\sigma^2} \frac{g(\varrho_s - \varrho_f)}{\eta} \frac{(\varepsilon - W_i)}{1-\varepsilon}. \tag{7}$$

It has to be mentioned that, in POWERS' formula, the specific surface is determined from gas permeability instead of the definition used by STEINOUR. The quantity of the immobilized water was taken into account in some cases, namely in filter-beds containing clay, by KOZENY [13] and CARMAN [14].

A partly different model was used by MICHAELS and BOLGER [17] in their investigations on sedimentation of flocculated kaolin suspensions. These authors, starting from the types of settling curves described already by SMELLIE and LA MER [16] (see Fig. 1), treated more dilute and more concentrated suspensions separately. They assumed a more complex structure to exist in more dilute suspensions too; the units of sedimentation are aggregates consisting of flocs formed by the primary kaolin particles. In dilute suspensions the aggregates, considered as spherical, settle individually, and produce a sharp interface. The settling curve begins with a linear part (Fig. 1, curve *a*). The model of MICHAELS and BOLGER is thoroughly connected with earlier X-ray absorption investigations of GAUDIN and FUERSTENAU [17], by which they

* To distinguish this case of sedimentation from other types, it is designed as "subsidence" in English literature. The expression "collective sedimentation" is also used.

verified the existence of a sedimentation zone of constant density. The sedimentation rate Q_0 can be characterized by the slope of the linear part of the settling curve; it is a function of Φ_A (volume concentration of the aggregates). MICHAELS and BOLGER applied the relation of RICHARDSON and ZAKI

$$Q_0 = v_{SA}\varepsilon_A^{4.65} \tag{8}$$

where v_{SA} is the settling rate of the aggregates according to Stokes, $\varepsilon_A = 1-\Phi_A$. With respect to the material balance,

$$Q_0 = \frac{g(\varrho_s-\varrho_f)d_A^2}{18\eta C_A}(1-C_A\Phi)^{4.65} \tag{9}$$

where d_A is the mean diameter of the aggregates, $\Phi = 1-\varepsilon$ the volume ratio of the solid component and $C_A = \Phi_A/\Phi$, *i.e.* the quotient characterizing the "looseness" of the aggregate (the ratio of the immobilized liquid). The above relation permits to determine d_A and C_A by a graphic method, which can be applied in the range of Φ in which v_{SA} and C_A are independent of Φ.

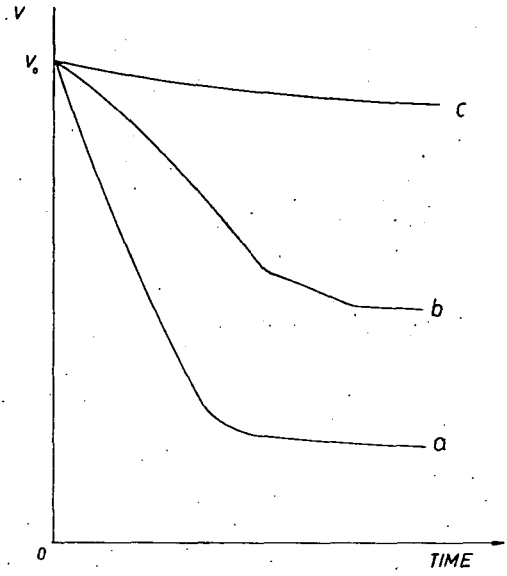

Fig. 1. Three general types of settling curves according to MICHAELS and BOLGER [15]

The behaviour of suspensions of intermediate concentration, the settling curves of which were of type *b*, was interpreted by MICHAELS and BOLGER using a network model of the aggregates. They found the central part of the curve to be linear; the corrected maximum settling rate, characterized by the slope of the straight, independent of the dimensions of the settling system, is

$$Q_1' = \frac{g(\varrho_s-\varrho_f)\Phi d_P^2}{32\eta}(1-C_{AF}\Phi_F). \tag{10}$$

In this equation d_P is the mean pore diameter in the network, $C_{AF} = \Phi_A/\Phi_F$, and Φ_F is the volume ratio of the flocs forming the aggregates relative to the volume of the suspension. The characteristics of the flocs can be determined by studying the sediment volume in detail. The corrections suggested in [15] can be obtained by studying the sedimentation of suspensions starting from different levels and in vessels of different size.

The above investigations on flocculated suspensions were, withouth exception, performed with aqueous suspensions. Simultaneously with the results of MICHAELS and BOLGER, as well as somewhat later, one of the present authors published results on the sedimentation rate of structured suspensions in organic media [18, 19] and described analogous sedimentation curves. Later on, we extended the evaluation method of MICHAELS and BOLGER to systematically coagulated aqueous kaolin

suspensions [20]. In a recent publication on suspensions of organophilic bentonite [21] the curves of type *b* were formally approximated by a hyperbolic tangent function with four parameters

$$V(t) = P\tanh(Nt+R)+S \tag{11}$$

where P, N, R and S are parameters of the function. In the same paper we presented a better fitting approximation by the function

$$V(t) = \frac{V_0+V_\infty\left(\frac{t}{t'}\right)^n}{1+\left(\frac{t}{t'}\right)^n} \tag{12}$$

where V_0 means the volume at $t=0$, $V(t)$ the actual settling volume, V_∞ the ultimate volume at $t=\infty$, and t' is given by the relation $V(t')=1/2\,(V_0+V_\infty)$. The meaning of n will not be considered here.

General description of the phenomenon of structured sedimentation

Suspensions settling with sharp interface may result from homodisperse systems containing particles of the same size, as well as from heterodisperse suspensions of semi-coherent structure. From a practical point of view, the latter are more important, because homodisperse suspensions are far more rarely found. A semi-coherent system can be formed *e.g.* from an aqueous suspension, if the adhesion between the particles is increased by an electrolyte. Namely, the ζ-potential of the electric double layer ensuring the stability of the suspension will decrease by the electrolyte, and thus coagulation may occur. The extent of coagulation can be controlled best by changing the concentration and valency of the ions. Polyelectrolytes can be also used as coagulants. In this case, besides the narrowing down of the double layer, it is very important that bounds of physical or chemical nature between the linear macromolecules and the solid particles may arise and so the particles become connected by the macromolecules. In this way, aggregates of very loose structure are formed.

In the case of suspensions in organic media, it is the lyophility of the particles which has the most important influence on stability. Between particles poorly wetted by the medium, adhesion will manifest itself and the particles become connected. The character of sedimentation both of aqueous and organic suspensions under given conditions will depend on the concentration of the suspension, a certain minimum of concentration being necessary for the forming of semi-coherent structure. At lower concentration a well observable interface will not develope. The concentration minimum necessary for obtaining a sharp interface crucially depends on the dispersity, the shape and interaction of the particles.

As an example, settling curves of aqueous sodium kaolinite suspensions of volume concentrations Φ, containing primary particles of diameter $d<2$ μm, are presented in Fig. 2. The coagulation occurs at a given electrolyte concentration. The aggregates easily disintegrate by mild shaking. In suspensions of different concentrations the following observations can be made during sedimentation.

At low concentrations, for a short time (some minutes) after shaking, practically no change can be observed in the system. Then the flocs appear simultaneously with the sharp interface which begins to sink rather quickly. Besides the settling, an upward streaming of the medium, carrying part of the flocs with the stream, can

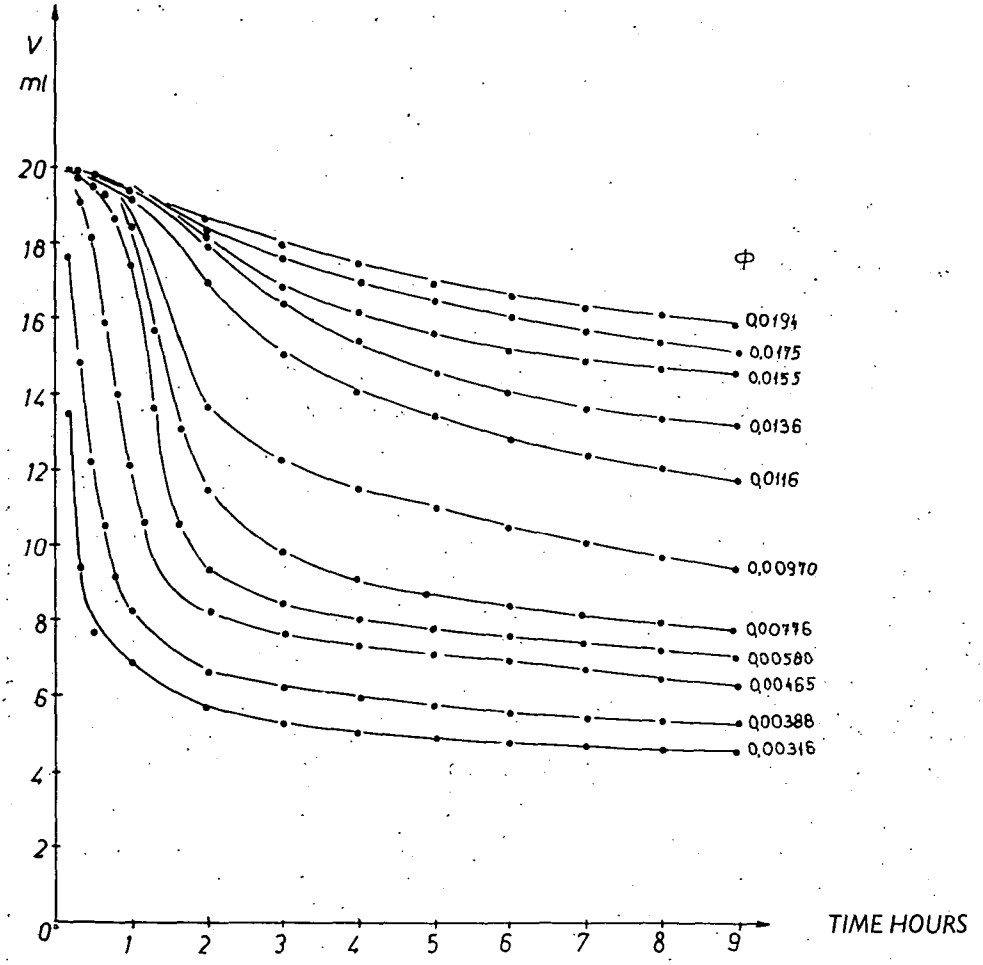

Fig. 2. Settling curves of sodium kaolinite suspensoins of different volume concentrations Φ, containing 19 mmole $CaCl_2$/l

be observed and the interface becomes diffuse. The perceptible upward streaming of the liquid ceases when the suspension becomes more concentrated due to the settling, and the sedimentation itself turns slower. Then the interface becomes sharper, more distinguished. In suspensions of intermediate concentration there is also a short time during which no change can be observed, then the sharp interface appears, but its sinking is slower. Meanwhile, visible inhomogenities (gaps and gross flocs) appear in the originaly homogeneous suspension. When this formation of

gaps can be observed in the whole suspension, fast sedimentation begins (Fig. 3). At the same time, the upward streaming of the medium can be observed and the interface becomes somewhat diffuse. The settling of the suspension progressing, the sediment formed becomes more compact and the process slows down. The visible upward streaming of the medium ceases, the interface between the sediment and the supernatant becomes sharper.

If the initial concentration of the suspension is further increased, then no period of fast sedimentation can be observed.

The picture of sedimentation in organic media is qualitatively similar if the particles are poorly wetted by the liquid, *e.g.* in the case of kaolin suspended in acetone (see Fig. 4).

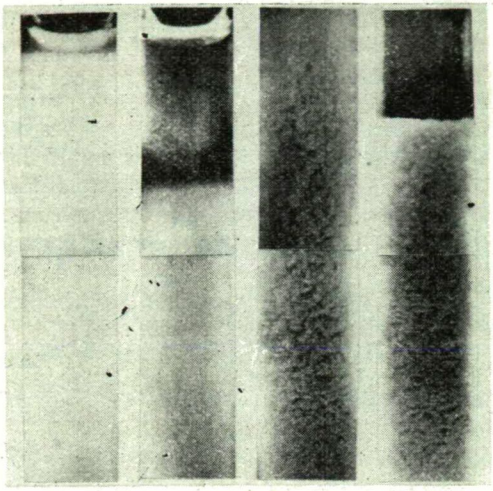

Fig. 3. Sodium kaolinite suspension in different phases of sedimentation. $\Phi=0.00388$, electrolyte concentration 50 mmole NaCl/l. *a* and *b*: upper part of the tube, *a:* at $t=5$ min; *b:* at $t=15$ min; *c* and *d*: lower part of the tube, *c:* at $t=22$ min; *d:* at $t=30$ min.

Three-section model

If the purpose is only numerical fitting of the settling curves, then several empirical formulas (*e.g.* the hyperbolic tangent function mentioned above) are available. In certain cases the different parameters calculated by this fitting may be used for characterizing the suspensions; it is, however, evidently difficult to find connections between these parameters and the structure of the suspensions.

In the following a model for describing the process is given. Though this model permits the evaluation of the curve only by sections, we hope that later we shall be able to obtain a unified equation by improving this model.

Let a suspension of volume V_0 and mass M, susceptible to sedimentation, be prepared in a test-tube of cross-section F. Let the shape of the settling curves measured at different concentrations $\Phi=M/V_0\varrho_s$ be corresponding to those of Fig. 1. Let $h(0)=h_0=V_0/F$ be the height of the interface at the time $t=0$, $Q=-dh/dt$ the sinking velocity of the interface plane, and $\varepsilon=1-\Phi$ the proportion of the free liquid.

In the case of comparatively low concentrations, the settling curve is similar to curve *a* in Fig. 1. At higher concentrations the sigmoid curve, characteristic for the sedimentation of structured suspensions, can be observed (see Fig. 1, curve *b*). For very high concentrations, the curve *c* shown in Fig. 1 is characteristic. It is important to observe that the values $h_\infty=h(\infty)$, pertaining to a series of increasing concentrations $\Phi_1<\Phi_2<\Phi_3$, often increase proportionally to M.

The particles may form aggregates already in dilute suspensions and, as this process involves "inclusion" of some liquid, a porosity $\varepsilon_A(<\varepsilon)$ will be characteristic for this system.

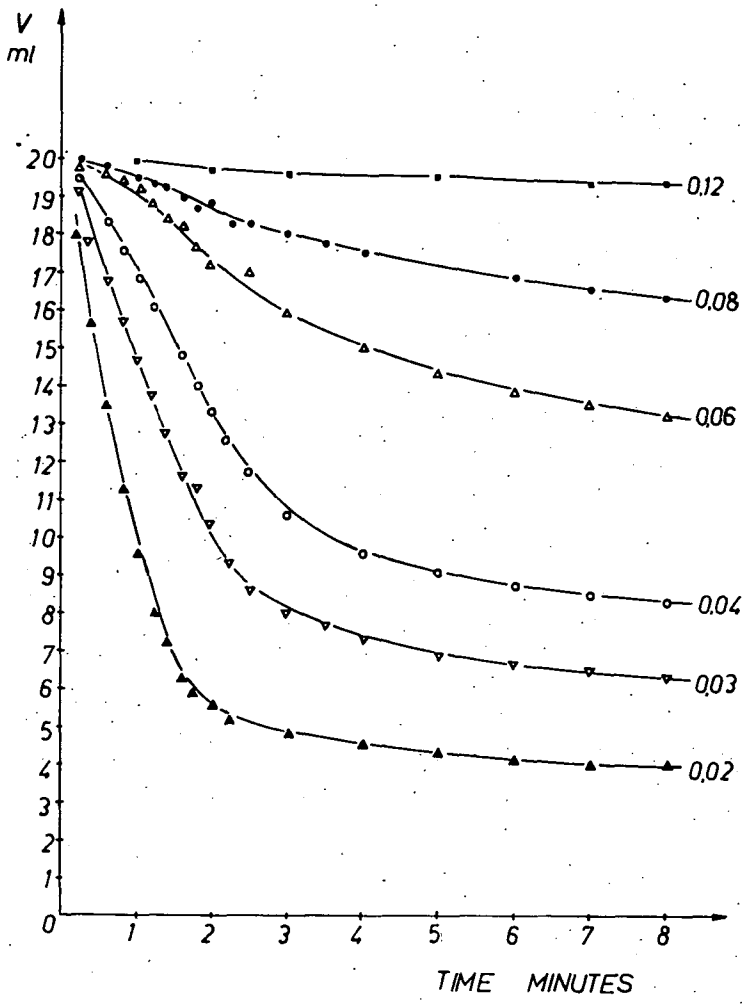

Fig. 4. Settling curves of non-fractionated kaolin suspensions of different volume concentrations Φ in acetone

Let us suppose that, in a certain concentration range (Φ_1, Φ_2) of the suspension, the aggregates form a semi-coherent structure. This condition can be characterized by a porosity $\varepsilon_s(<\varepsilon_A)$. The structure is not rigid; it "shrinks" under the influence of its own weight and, after a certain time, it "breaks down".

In the case of a given system, there is always a critical concentration Φ_2 above which coherent structures are formed. The sedimentation of such suspensions should be designed as "compression".

Based on this model, the types of settling curves shown in Fig. 1 can be interpreted as follows:

a) If $\Phi < \Phi_1$, then a state characterized by the porosity ε_A is formed. The settling rate is constant and proportional to the Stokes settling rate v_S of solid particles. The proportionality factor ε_A is a function of the porosity

$$Q = v_S f_1(\varepsilon_A). \tag{13}$$

In the settling phase, Φ is practically constant. The volume of the sediment settled at the bottom of the test-tube increases until the "quick" period of sedimentation is finished. The sediment volume is first proportional to $(1-\varepsilon_A)$, but it does not remain constant, because the sediment shrinks. For the shrinking a formula analogous to Eq. (3), or other similar relations can be applied:

$$Q = k(h - h_\infty). \tag{14}$$

b) If $\Phi_1 < \Phi < \Phi_2$, then a structure characterized by ε_s is formed. According to our assumption, this structure is similar to a coherent, soft filter bed and for the settling rate the equation

$$Q = v_S f_2(\varepsilon_s) \tag{15}$$

will be valid.

At the end of the "filtering" characterized above, the structure "breaks down", and the sedimentation of the aggregates proceeds according to Eq. (13); then the shrinking described by Eq. (14) can be observed.

c) If $\Phi > \Phi_2$, then only "compression" is to be observed; this can probably be described by Eq. (14).

From the above three cases, the curve of type *b*, shown separately in Fig. 5 is the most common. The ordinates delimiting the different parts of the curves (separating the sections of filtering, settling and compression) are h_1, h_2 and the corresponding abscissas are t_1, t_2. Under otherwise identical conditions it is always possible to find a concentration Φ for which t_1, is maximum. At this concentration the semi-coherent structure will be the most stable.

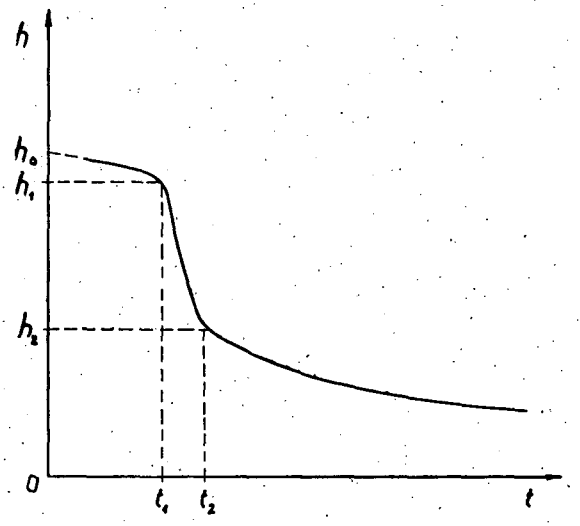

Fig. 5. Characteristic sections of a settling curve of type *b*

As a conclusion, this model indicates two critical points on the settling curve. Experimental investigation of the environment of these points is very important from a theoretical point of view. It is to be expected that by an exact description of these environments and of the deviations from the sections supposed to be linear in the model, it will be possible to find a formula permitting uniform characterization of the general settling curve. It seems that "fitting" of the values Q given by Eq. (13)—(15) might lead to such a formula if it were possible to express the respective variables as functions of the porosity. It seems favourable that an analogy between f_1 and f_2 can be found.

Some further conceptions

In our opinion, for the description of sedimentation, and of course also of the shrinking of more or less structured systems, a uniform method of description should be used. This follows chiefly from the conviction that the state of the system studied changes under the influence of external and internal forces, and the sedimentation in a given system can be considered as a motion due to gravitation. Of course, it cannot be sufficient to take into account only the external gravitational forces, as the formation of any structure points to the presence of considerable internal forces, too. Therefore it seems that a detailed investigation of the nature of these internal forces would lead to the desired result. In principale, the internal forces involved in the formation and preservation of the structure can be described with the means of modern physics. The units forming the system are, however, so different and their interactions so complex that this way does not seem practicable.

Up to now the efforts to give a complete description of the process do not seem to have been succesful. The above conception suggests, however, that a uniform way of description must exist. It is possible that the phenomenological aspect of the problem will become clear only after dividing the problem into parts and investigating these parts separately. But also in this case, a subsequent step, coordinating the description of the different parts, must exist. Namely, if a phenomenon can be approximated by dividing it into three partial processes, each of which is characterized by a parameter, then it can be tried to give a uniform description containing three parameters. Taking into account the necessary initial condition, four characteristic data will be needed. Similar efforts led to the formula given in Eq. (12), which satisfies the requirements mentioned above.

Comparing Eqs. (3) or (4), describing the shrinking phase, with Eq. (12) and approaching the latter for high values of t, the relation

$$V = V_\infty + (V_0 - V_\infty) \frac{1}{1 + \left(\frac{t}{t'}\right)^n} \tag{16}$$

can be obtained. The term e^{-kt} in Eq. (4) also tends to zero, though not in the same way, but similarly to $\left[1 + \left(\frac{t}{t'}\right)^n\right]^{-1}$. To decide the question as to in which way the factor of $(V_0 - V_\infty)$ approaches zero, further and more exact measurements will be necessary.

If our purpose is to give a complete phenomenological description of the process, a more general method has to be applied, because the movement in a complex system cannot be described by a single rate value. Therefore, it has to be supposed that the sinking velocity in the bulk of the settling system changes from point to point. Our objective should therefore be to find the equation of motion describing the field of velocity with the initial and boundary conditions determined by the experiment. The objective outlined earlier in this paper is only a part of this more general program, as its aim is only to describe the motion of the interface between the pure medium and the suspension.

Besides carrying out the total phenomenological program drawn up in the above, it will be necessary to raise the question of the microscopical interpretation of the phenomenon. This does not exclude the possibility of trying to find methods (see the three-section model), which describe directly the events occuring in the suspension. It will be certainly necessary to follow both ways.

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СЕДИМЕНТАЦИЯ СТРУКТУРИРОВАННЫХ СУСПЕНЗИЙ, I

Введение и некоторые общие положения

М. Гилде, Ф. Санто, К. Варга, Ф. Й. Гилде

В серии работ, посвященных исследованию седиментации структурированных суспензий, в данной статье рассматриваются основные положения по литературным данным. Представлены основные типы происходящих явлений. На основании литературных данных, создана модель из трех составляющих: оседания, фильтрации и уплотнения. Намечены пути дальнейших исследований.