

A Study of Settling Tendencies of A. P. I. Reference Clay Minerals in Sea Water

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1. Introduction

Whitehouse et al^{1), 4)} reported the differential settling tendencies on various kinds of A. P. I. clay minerals in saline water changing the chlorinity. They explained that settling tendency depends highly on the chlorinity. More different research on the behavior of the clay particles in sea water should be oriented to the problem under the sea water. This remains still for us as the further study. A few papers are available on the solubility²⁾ and the chemical base exchanges of clay minerals³⁾ with consideration of the effect of saline water. In this regard, this paper describes an outline of the basic study on settling tendencies of A. P. I. reference clay minerals of illite (I), kaolinite (K), and montmorillonite (M) in three different waters i.e. real sea water, dilute sea water and distilled water. The settling of clay mineral fractions in sea water is the main area of the study, the results obtained by the experiment carried out with other waters were used for data comparison. In this experiment, 0.5g clay mineral was contained in 100cc water to make an easy detection of the settling height of clay mineral fractions in the suspension, because it was difficult to measure exactly the settling of slurry both too rich and too poor than the above mentioned clay mineral content.

Experiment on settling is not being standardized for the present time. The author defined newly the settling velocity (V) and the settling ratio (R). That is, R was determined by the settling height and V derived from R . As a result, R and V changed according to the salinity and the kind of material, they varied exponentially with time. Thus R was found to be reached each minimum uniform value after a certain time passed. The results deduced the new experimental equations on R and V , and the latter was nearly equal to the velocity in the literature¹⁾. Consequently, the results obtained here can be considered as the possibility of the application to other suspensions, as a whole, to have a clue of an analytical approach in studying the settling mechanism. This paper

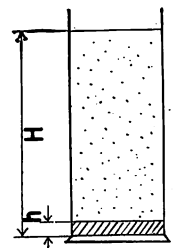


Fig. 1

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deals essentially with the settling ratio of clay mineral fractions in sea water. Further, in the observations on the influence of a moving sea water, as the slightly different settling tendencies were noticed between still water and rolling water, these will be reported in the later section.

2. Methods and Samples

(a) Determinations of Settling Ratio and Settling Velocity

Standard clay mineral fragments were too big for experiments. So, each clay mineral was crushed into powder by the crusher for approximately 30 minutes. Then a 100 mesh sieve was used to accept the clay powder of 0.2mm under. Clay minerals were put in 100cc cylinders containing several kinds of water.

The samples for data analyses were 0.5g/100cc. Also used 1g/100cc, 2g/100cc and 2g/1000cc, but in this paper these are not mentioned. 0.1g/25cc samples were used only for a comparison between still water and rolling water. Selected frequency of the vibrator was 100 cycle/minute horizontally.

Settling rates of clay minerals are in general determined by pipet analysis method, densitometric method, balance method and nephelometric-spectrometric procedure. These methods are concerned with equivalent diameter of clay fractions, i. e. size of falling particles. Consequently falling velocities are limited by the size of the clay fractions. Settling rates mentioned above are based upon Stokes' law. From this point of view, falling velocity is closely related to the settling velocity.

The following is a definition of settling ratio (R) as a function of accumulative settling height of clay fractions. In the cylinder of arbitrary section as shown in Fig.1,

$$R = \frac{V_T - V}{V} = \frac{H - h}{h} \quad (1)$$

in which, V : Settling volume (cm³)

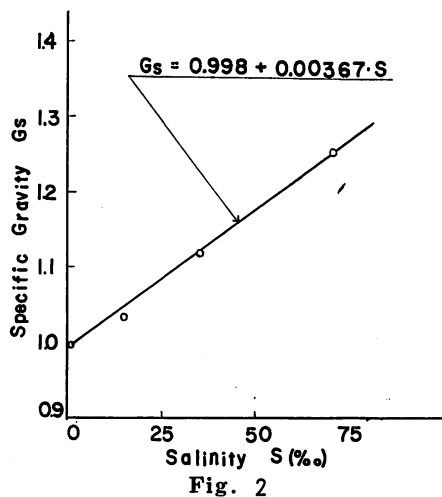
V_T : Total volume of suspension (cm³)

h : Settling height (cm)

H : Total height of suspension (cm).

Settling heights of clay suspensions were measured by micrometer at the time intervals of 3, 6, 10, 15, 20, 30, 45, 60, 90 in minute. By the above definition, a large ratio makes for small settling quantities.

Settling velocity (V) may be defined from (1) as follows:



$$v = \frac{dh}{dt} = \frac{d}{dt} \left(\frac{H}{1+R} \right) \quad (2)$$

in which, t: Time (minute).

(b) *Samples Employed*

1) Clay Mineral	The Place of Production	A. P. I. No.
Kaolinite (K)	Lewistown, Montana	17
Montmorillonite (M)	Santa Rita, New Mexico	30
Illite (I)	Fithian, Illinois	35
2) Water	The Place of Production	Salinity
Real Sea Water	{Off shore of Monastery	33.95(%)
Dilute Sea Water	{Beach, California	16.97
Distilled Water	Laboratory, (U. C. Berkeley)	0

Fig. 2 shows the relationship between the salinity and the specific gravity. In the figure, the water of salinity of 70% was not used for experiments.

3. Results and Discussions

Experimental results of settling ratios are described in Fig. 3(a) to Fig. 3(c). As is evident from the figures, within the limits of this experiment, settling ratios of the clay minerals except montmorillonite varied considerably with the kind of water employed. In distilled water, a smooth rate of increase of settling quantity appeared after a certain time passed, while in real sea water, considerable quantities were settled within the time regardless of any clay kind. In dilute sea water, the tendency was very similar to the case of the real sea water. In each sample, a great quantity of sediment was observed in the first 10 minutes. After 20 minutes, similar settling tendencies arose in each type of clay. It was noted that the settling ratio in the first stage (within 10 minutes)

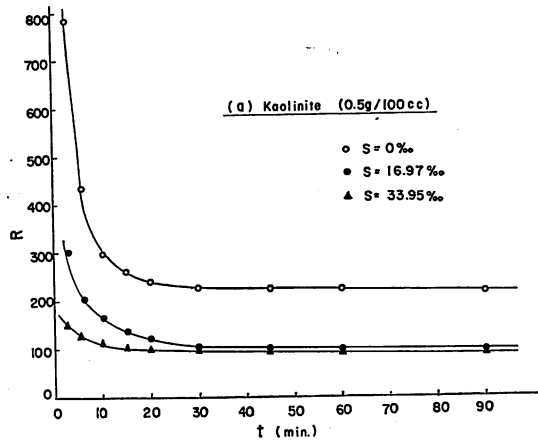


Fig. 3 (a)

showed very large value. This settling ratio was largest in distilled water because the increase in settling quantities was slight. Montmorillonite didn't have a special response to sea water as seen in Fig. 3 (b). This is considered due to the reason why the montmorillonite particles were too fine than the other clay particles. Whithin the experimental time, settling ratio of montmorillonite in the salinity of 33.95% was only a little less than the salinity 0. In general, the settling ratio of montmorillonite was fairly small compared with other clay minerals. Illite and kaolinite showed a high response to sea water. However,

their settling tendencies in respect of time closely resembled one another.

From these figures, one can see that the change of R depends on t , i. e. time effect becomes small as R increases. Then R tends to reach gradually its minimum value (R_{min}) as t increases. In the case of fixed clay mineral content, time is still necessary to reach a certain settling height. After all clay suspensions will be reached "colloid state" of which settling ratio is R_{min} , and it is thought that the settling will not occur any more.

According to the figures of settling ratio (R) vs time (t), the relation may be recognized in the straight lines of best fit in the Log-Log diagram. Showing this in an equation, one can get as :

$$\text{Log}(R - R_{min}) = \text{Log } k - n \text{Log } t \quad (3)$$

In which "k" is a constant to be determined from the kind of clay minerals and the salinity of suspensions, also "n" is an exponent with respect to time, which is determined from the diagram.

The experimental results obtained in the way described above are shown in Fig. 4 (a) to Fig. 4 (c). As is indicated in these figures, one can estimate the time for R_{min} when $R - R_{min} = 1$, also can estimate the value of k when $t = 1$ although that was not measured in the experiment by using these diagrams. In which each k has a different value, i. e. k for sea water is fairly small, and the slope of the line is a little

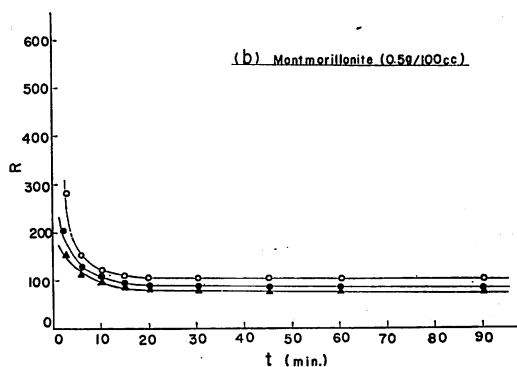


Fig. 3 (b)

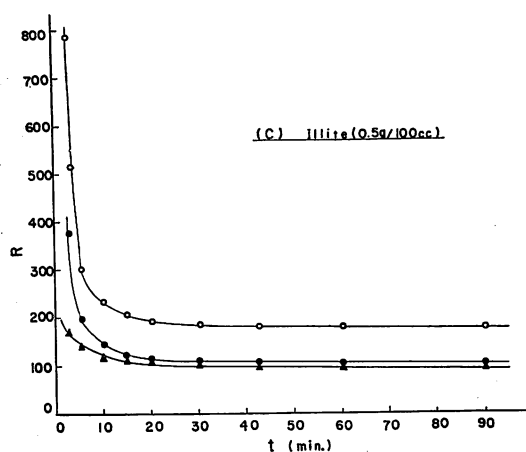


Fig. 3 (c)

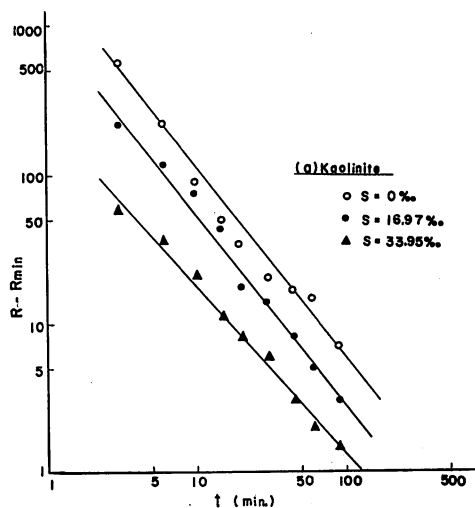


Fig. 4 (a)

gentle than the other water's one. Every time of R_{min} was settled around $t=100$ minutes. As previously referred, it is to say that rate of sedimentation and flocculation of clay particles in sea water is fairly high compared with other waters.

From (3), R is given in the following form.

$$R = R_{min} + k \cdot t^{-n} \quad (4)$$

in which, n is a constant to be determined from a kind of material and salinity, and its value surpasses the unit.

Since (1) and (4) are equivalent, k in the above equation is

$$k = t^n \left(\frac{H}{h} - 1 - R_{min} \right). \quad (5)$$

By using eqs. (2) and (4), settling velocity can be written in the form of

$$V = \frac{d}{dt} \left(\frac{H}{1 + R_{min} + k \cdot t^{-n}} \right). \quad (6)$$

Integrating the eq. (6), settling velocity may be concluded in the following form.

$$V = \frac{H}{k} \frac{n \cdot t^{-(n-1)}}{\left\{ \left(\frac{1 + R_{min}}{k} \right) t^{n+1} + 1 \right\}^2} \quad (7)$$

If we put $1 + R_{min} = C_1$ and $n \cdot k \cdot H = C_2$ because they are constants, we get consequently following equation.

$$V = n k H \left\{ \frac{1}{(1 + R_{min})^2 t^{(n+1)} + 2 k (1 + R_{min}) t + k^2 \cdot t^{(1-n)}} \right\} \\ = C_2 \left(\frac{1}{C_1^2} + \frac{t^n}{2 C_1 k} + \frac{t^{2n}}{k^2} \right) t^{-(n+1)} \quad (7)'$$

Fig. 5 shows an example of the $V-t$ relations in sea water obtained by the eq. (7)'. In the first 10 minutes, settling velocities for each clay suspension are fairly high. In general, settling velocities for clay minerals employed here within 90 minutes follows the form of $M > I > K$. On the other hand, Whitehouse et al showed that the settling velocities for three A. P. I. clay minerals were in the form of $I > K > M$. They took the relation of weight vs.

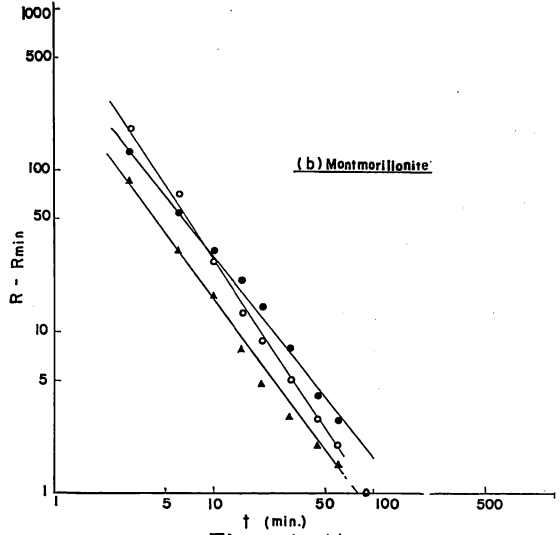


Fig. 4 (b)

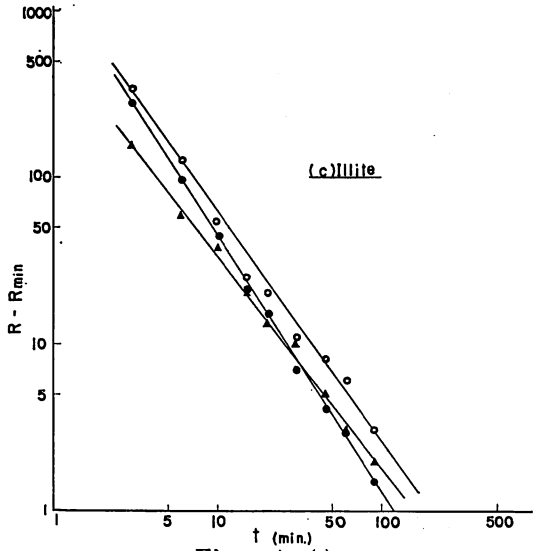


Fig. 4 (c)

settling velocity. Their result don't partially correspond to the experimental result as M is replaced with each other. This is considered due to the differences of the experimental methods i.e. clay content, sea water, temperature and the size of vessel containing the clay suspension and the difference of clay powder fineness. However, settling velocity in this experiment ($10^{-3} \sim 10^{-2}$ cm/min) shows

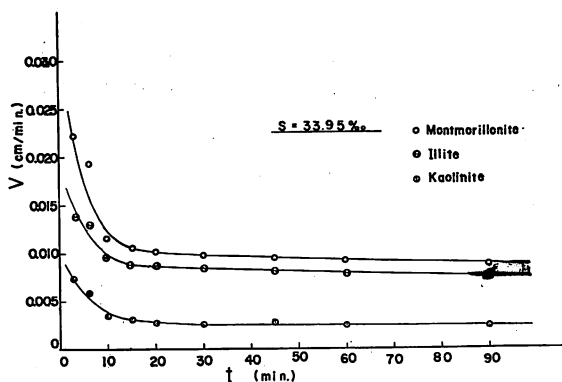


Fig. 5

reasonable agreement with their results. That is, the equation deduced here in the limit of the clay content about 0.5g/100cc means generally sufficient.

4. Observation on Suspensions in Rolling Waters

For the investigation of wave action effect, 0.1g/25cc samples were employed in the rolling machine (100 cycle per minute). From the experiments, high settling velocity was observed when rolling commences. Settling almost ceased within 30 minutes. The amount of settling in sea water nearly doubled in still water. Most of these increases were due to flocculent precipitation. No special settling tendency was observed in each type of clay in rolling water except montmorillonite which kept muddy state a little longer than the other two materials. This suggests that off shore deposit has a highly developed flocculent structure and that clay suspensions are rather easily flocculated by the introduction of a rolling motion. The main reason of this tendency is considered that the flocculated sediments consisted of particles attracted to one another to form loose arrays, and that shear strength between the particles will be thus decreased by the rolling motion in one direction.

5. Summary

This paper represented the partial results of all experimental runs of settling ratio (R) and settling velocity (V) for A. P. I. reference clay minerals in sea water by the new definition. Equations on R and V were introduced experimentally as follows:

$$R = R_{\min} + k \cdot t^{-n}$$

$$V = \frac{H}{k} \cdot \frac{n \cdot t^{(n-1)}}{\left\{ \left(\frac{1 + R_{\min}}{k} \right) t^n + 1 \right\}^2}$$

Although the equations don't indicate directly the influence of salinity, but the settling velocity would seem to give a clue of investigating the sedimentary structure of clays in sea water. For instance, kaolinite and illite in sea water

presented a considerable settling height as salinity increases, while in distilled water their settling heights were small. This is considered that the reaction force between clay particles varied with the magnitude of salinity. In other words, this behavior shows the changes of void ratio which shows a random structure of sedimented clay fractions if the ratio is large. Therefore, shear strength of such clay structure would be decreased as salinity increases. This is concluded that high settling velocity of clay particles in sea water should introduce flocculation system of the clay, and subsequently low shear strength of the clay with such a structure should be come out.

As is provided in the former section, the flocculation of the suspension occurred more readily in rolling water. To make clear the relationship between salinity and settling velocity, many more experiments will be needed to confirm the above results and definitions and to provide additional details.

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Appendix

As the another method for solving the settling velocity and the settling ratio, a following equation will be made because R is reached its minimum value Rmin when t increases

$$\frac{dR}{dt} = -k(R - R_{min}) \quad (8)$$

Integrating this, we get

$$R = R_{min} + C \cdot \exp(-kt) \quad (9)$$

If $t=1$, then $R=R_1$ thus,

$$R_1 = R_{min} + C \cdot \exp(-k)$$

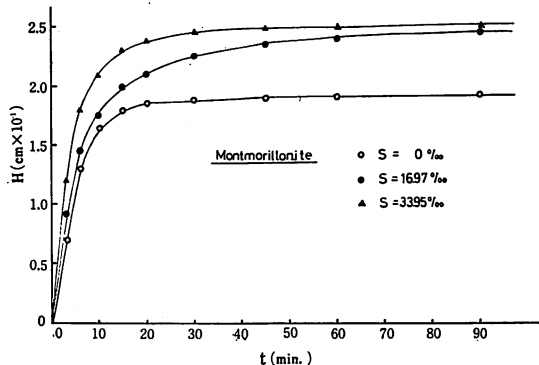


Fig. 6

$$\therefore C = (R_1 - R_{\min}) \exp(k) \quad (10)$$

Therefore, eq. (8) might be written in the following general form.

$$R = R_{\min} + (R_1 - R_{\min}) \exp\{-k(t-1)\} \quad (11)$$

Using eq. (1), settling height will be expressed as follows:

$$h = \frac{H}{R_a + R_b \cdot \exp\{-k(t-1)\}} \quad (12)$$

in which $R_a = 1 + R_{\min}$ and $R_b = R_1 - R_{\min}$.

It is possible to put $R_a = R_{\min}$ since 1 is very small compared with R_{\min} . Therefore, settling velocity may be concluded here in the form of

$$V = k \cdot h \cdot \frac{R_b \cdot \exp\{-k(t-1)\}}{[R_{\min} + R_b \cdot \exp\{-k(t-1)\}]^2} \quad (13)$$

Of course, one may put $R_1 = R_{\max}$ if $t \rightarrow 0$. In the above equations, k depends highly on the type of clay, and which might be solved experimentally. Namely, k is determined by curve fitting in h - t relationships like Fig. 6. k is also solved by changing the equations of (8) and (10) as below.

$$\left. \begin{aligned} k &= - \frac{1}{R - R_{\min}} \frac{dh}{dt} = \frac{\tan \alpha}{R_c} \\ \text{or } k &= \{\log(R_c/R_b)\} / (1-t) \end{aligned} \right\} \quad (14)$$

in which $R_c = R - R_{\min}$ and α = inclined angle of the curve. In this way, though we could get another type of equations on R and V , which are fairly rough compared with the former ones. In any case, more detailed and accurate experiments are necessary to ensure this kind of phenomenon.