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## Initial Particle Growth Effect on Settling of a Flocculating Slurry

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### Abstract

In this study we found unusually high settling velocities in freshly precipitated, undisturbed ferric hydroxide floc. Even though during our operation the overflow from the reactor-clarifier did not meet suspended solid effluent discharge standards, we were confident that we could devise operating procedures that would produce satisfactory effluent. For example, we conducted all our studies without the use of polyelectrolyte addition. Such additives would surely remove the small particles which were causing the suspended solids to exceed standards. Of most importance is to develop the discovery of the increased settling velocities with freshly precipitated flocs. It would seem reasonable to first quantify the power-energy picture so that floc size was predictable from known energy inputs. From this relationship we should proceed to determine the optimum energy-floc size combination which would produce the desired overflow concentrations. The potential here is to be able to increase the solids application rate for any reactor-clarifier, thereby increasing the throughput of the device without the need for additional capital investment. In addition, when designing new equipment, smaller vessels at less cost could be used.

### INTRODUCTION

During the course of the verification of a mathematical model of sedimentation in a flocculating slurry, we conducted extensive studies on the settling behavior of ferric hydroxide slurries in quiescent and upflow

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situations (1). The relationship between settling velocity and solids volume fraction was found to be predictable and reproducible for all slurries with the notable exception of slurries of freshly precipitated floc. Ferric hydroxide that was allowed to settle immediately after precipitation without disturbance settled as much as 10 times faster than the same suspension settled if the floc were disrupted by stirring or pouring prior to settling. The slurries settled rapidly because the undisturbed ferric hydroxide precipitate particles were as much as 5 times larger than remixed particles.

The initial formation of large particles of ferric hydroxide appears to be a chemical effect which occurs in a manner similar to the way crystals are formed. As ferric hydroxide precipitates out of solution, the particles appear to grow into each other so that large, intermeshed particles form. The precipitate particles are loosely bound and are of irregular shape. The mechanism that forms the large particles is associated with the precipitation process, and therefore is not present after precipitation is complete. Just as broken crystals will not weld together, disrupted ferric hydroxide particles will not coagulate again after precipitate formation is complete. The binding of those composite particles is not due to van der Waals forces, as binding of this sort would still be operative after precipitation is complete.

In the sections that follow, we discuss the experimental conditions that led us to the initial particle growth effect and present the data we have collected on large particles. Also, we speculate on what areas of study should be explored to make use of the initial particle growth effect.

## BACKGROUND

Whether the emphasis features clarification or thickening, the standard wastewater treatment process and characterization studies for solids-liquids separation mask the initial particle growth effect on sedimentation. The removal of metals by precipitation and subsequent clarification is initiated by pH adjustment during a rapid mixing step. The metal hydroxide slurry is then transferred to a clarifier or to a flocculation basin. In either case the particles are disrupted and allowed to re-form before settling. Data required for clarifier design are collected from a sedimentation column of depth equal to that of the proposed basin. The column is filled with the treated waste, and the particles are thoroughly mixed to insure an even particle distribution at the commencement of the test. Per cent removal of solids at any given depth is determined for a series of samples taken at various time intervals. Similar data are recorded at several depths in the column. The data are then used to determine detention time for any given depth and per cent removal. In both the typical

clarifier unit and the wastewater characterization studies, the floc particles are disrupted before sedimentation.

Basins designed as sludge thickeners also remove re-formed particles that have been disrupted by pumping to the basin. The design parameter of primary importance is the empirically determined relationship between slurry concentration and settling velocity. The metal precipitate is thickened or diluted to prepare a series of slurries within the range of concentrations that settle with a distinguishable interface between slurry and supernatant. The precipitate slurry may be mixed and poured several times during the test procedure.

We detected an initial mixing effect on particle size and settling velocity in a model verification study of ferric hydroxide in a reactor-clarifier system. In a reactor-clarifier the processes of mixing, precipitation, flocculation, clarification, and sludge removal are combined into a single unit. The separation mechanism combines aspects of both clarification and thickening.

The reactor-clarifier configuration used in our study is illustrated in Fig. 1. The ferric sulfate was brought in at the top of the center reaction cone, at which point lime was added. As the water flowed downward through the inner cone, some mixing occurred at the top of the cone. The water then flowed upward through the sludge blanket, and solids were removed by settling and by entrapment in the blanket. The clarified effluent flowed over peripheral weirs at the top of the unit, and the thickened sludge was withdrawn from the bottom of the unit.

Because a sludge blanket that settles as a zone is maintained in a reactor-clarifier, the slurry-supernate interface settling velocity, of importance in thickener operation, was the parameter of most importance to us. Thus our work followed the path of a thickener study, beginning with the measurement of the settling velocities of various dilutions of ferric hydroxide slurry.

The model, previously presented in a series of articles by Wilson et al. (2-5), consists of a set of differential equations describing sedimentation in a flocculating slurry. Our first experimental objective was to verify the model for quiescent settling while refining our selection of parameters relating to particle size and density. We assumed that slurry properties determined from quiescent tests would be applicable in the upflow situation. Our second objective was to verify the model of the reactor-clarifier during steady-state flow.

Quiescent studies showed the model predictions to be in close agreement with measured setting velocities (6). If the ferric hydroxide was formed in the feed tank and pumped to the clarifier, the measured blanket velocities agreed with the model predictions in the upflow mode. However,

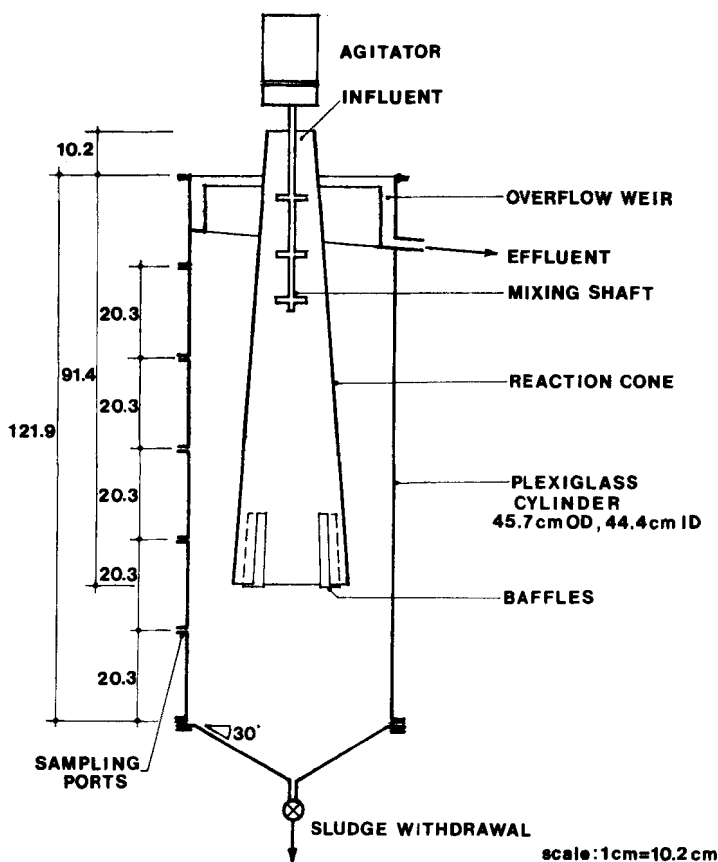


FIG. 1. Schematic of the reactor-clarifier.

when the ferric hydroxide was formed in the top of the clarifier reaction cone, the model predicted blanket rise velocities that were 5 times as great as the observed velocities. Investigation of the discrepancy in settling behavior showed us that ferric hydroxide particles grow to a large size during behavior showed that ferric hydroxide particles grow to a large size chemical precipitation if not disturbed. Hence settling velocities of these large particles are much greater, and the blanket rise is consequently much slower.

## EXPERIMENTAL WORK

Although the occurrence of the initial particle growth effect came to our attention in the reactor-clarifier system, a simple way to observe the phenomenon is by precipitation in a shallow glass vessel such as a Petri

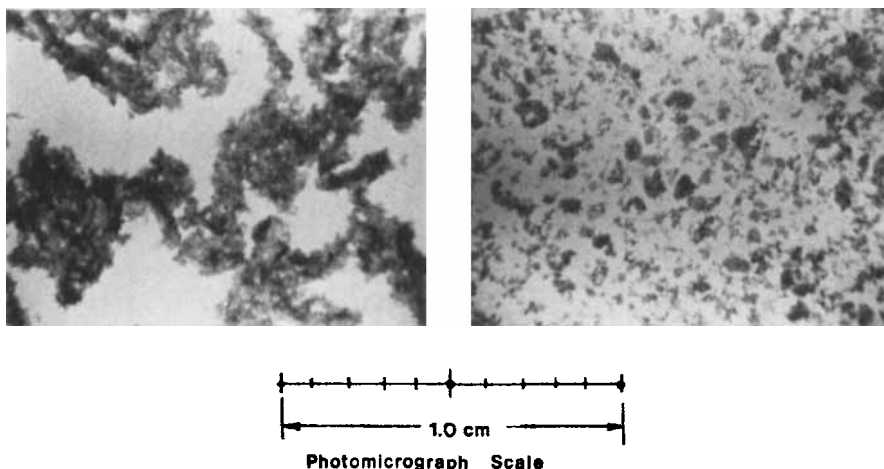


FIG. 2. Particle size difference due to amount of agitation during chemical precipitation. Left: Nondisrupted particles, rotation stopped. Right: Completely agitated particles, rotation continued.

dish. While gently rotating a dish of ferric sulfate, we added a few drops of NaOH. The floc particles grew into each other as they precipitated out of solution. If the gentle rotation was continued for more than 20–30 s, the particles broke up into smaller, more uniform particles. In Fig. 2, particles magnified 10 times are shown in one dish where the rotation was stopped when the particles were large and in a second dish where the rotation was continued. The particles that had not been disrupted had an average diameter of about 0.3 cm, with some particles as large as 0.5 cm. Particles in the thoroughly agitated solution ranged from about 0.03 to 0.1 cm in diameter, and showed no tendency to coagulate.

The effect of particle size on quiescent settling velocity was shown by comparing the results of thickening tests with settling tests of freshly formed floc. The thickening tests were done in slowly stirred (0.1 rpm) 1-L cylinders with dilutions of slurries that had been precipitated with either lime or NaOH at either pH 6 or 10. The slurries were poured into the cylinders, and the height of the interface was plotted with time. Settling velocity was taken as the straight line portion of that plot. The relationship between settling velocity and concentration was an exponential function, as shown in Fig. 3, with only slight variation according to precipitant and pH.

Settling tests were conducted with fresh floc by adding lime to ferric sulfate in the 1-L cylinders. Floc particles formed in the wake of the falling

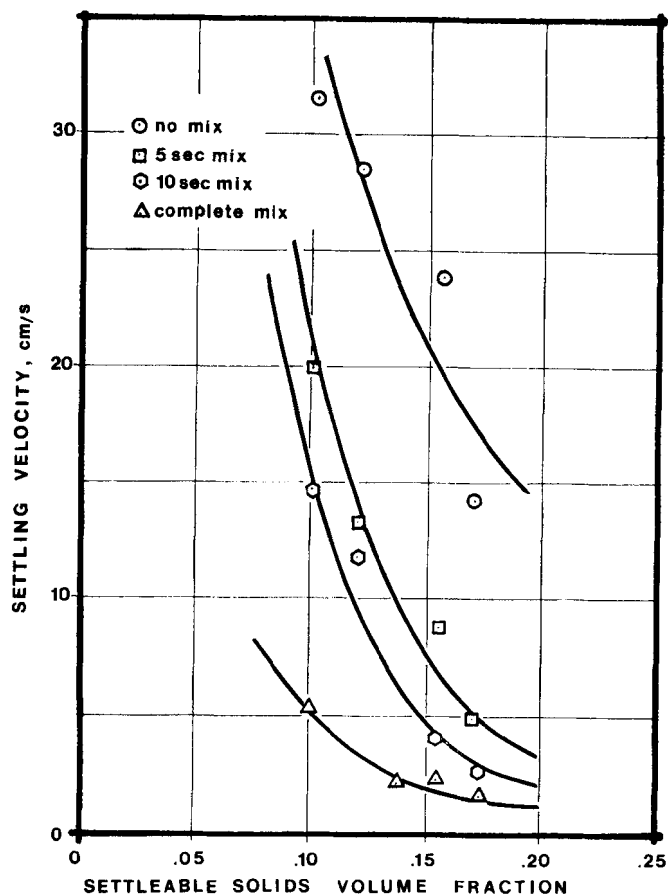


FIG. 3. Effect of initial air mix time on the settling velocity and solids concentration relationship.

lime, filling the cylinder with large, fluffy floc particles. Several concentrations of suspension were made and tested. Settling velocities of these preparations were as much as 10 times greater than those of remixed floc.

In addition, some suspensions were subjected to limited amounts of air mixing during precipitation before velocity measurements were taken. Air mixing was applied to each suspension for 5 to 60 s after chemical addition. The results of 10-s, 5-s, and no mix tests are shown in Fig. 3, along with the completely mixed floc results. Mixing tends to reduce particle size and to decrease the settling velocity of a suspension. As the chemical mix time is increased, suspensions approach the settling velocity of remixed floc. Apparently floc comes to the same effective particle size

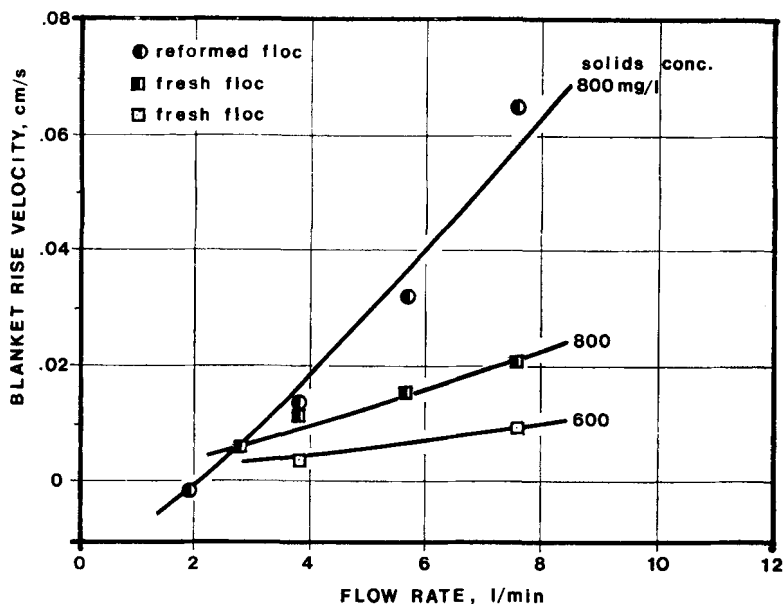


FIG. 4. Sludge blanket velocity of re-formed floc and fresh floc in the reactor-clarifier as a function of flow rate at several solids concentrations.

if it has been subjected to one mix time that exceeds about 30 s or if it has been repeatedly disrupted and re-formed.

Although the quiescent studies showed ferric hydroxide to be very sensitive to the amount of initial mixing, the large particle effect was quite evident in the steady-state flow studies that we conducted in the laboratory reactor-clarifier. The scale of this system was such that feed rates varied from 1.0 to 7.6 L/min through the 200-L vessel. In the mode of operation for which the system was designed, the ferric sulfate and lime were pumped to the top of the inner reaction cone where precipitation occurred.

Under these operating conditions, which resulted in minimum floc agitation, the system accepted a much higher loading rate in terms of solids concentration or in terms of hydraulic loading rate than we had expected. Blanket rise velocities for two fresh floc solids concentrations and several feed rates are shown in Fig. 4.

To demonstrate the effect of strong agitation of the floc, we changed the mode of operation. Ferric sulfate was mixed with lime in the feed tank, and the ferric hydroxide precipitate was pumped to the inner cone of the reactor-clarifier. This operation caused the floc to be thoroughly mixed and disrupted. The results, plotted in Fig. 4, were very similar to those expected on the basis of the quiescent tests. Suspensions of comparable

solids concentrations rise as much as 3 times faster when re-formed floc is fed through the system than do suspensions of fresh, little-disturbed floc. The reactor-clarifier is able to handle much higher applications of fresh, undisturbed solids than of re-formed solids.

## DISCUSSION

We have shown that the initial particle growth effect can be influential in the operation of reactor-clarifiers. In order to model a system in which the large particles form, we need to correlate the amount of mixing during chemical precipitation with size of particles in the sludge blanket. From the air mix tests in 1-L cylinders, we have recorded settling velocities for a series of suspensions of 0.10 SSVF (settleable solids volume fraction) (800 mg/L SS, suspended solids). Either the mix time or the air flow rate was varied while the other parameter was held constant. The power input was assumed to be equivalent to the rate of energy dissipation by water displacement as the air bubbles rose to the top of the cylinder. The total energy was calculated from the mix time.

Figure 5 is a plot of settling velocity versus mix time at a constant power input of 181 ergs/(cm<sup>3</sup>)(s). From this plot we can see that the settling velocity is strongly dependent on mix time for mix times less than about 30 s. Figure 6 shows that if the mix time is constant, the settling velocity decreases with increasing input power until it levels off at about 0.05 cm/s when the power input is 360 ergs/(cm<sup>3</sup>)(s).

The settling velocity versus the total energy input, the product of power and mix time, is plotted in Fig. 7. The data combine both the air flow rate and the air mix time variations shown previously. Settling velocity consistently decreases with energy input until the energy input reaches 5000 ergs/cm<sup>3</sup>. At this point the settling velocity is approaching that for completely remixed floc. Figures 5, 6, and 7 suggest that some form of power calculations will provide a basis for particle size predictions. However, the measurement techniques are not refined enough to make quantitative predictions at this time. We leave this area for future research work.

Another aspect of the initial particle growth effect is that many small particles are formed as well as the large particles. Supernatant suspended solids were measured for two slurries and are reported in Table 1. Aliquots of each slurry were made by three primary mixing techniques; complete mix, 10-s mix with air at 5 cm<sup>3</sup>/s, and no mix. Supernatants of the well-mixed slurries were sampled after the slurries had settled to one-half their original volume.

solids in suspension after 2 min. Some of these solids continued to settle,

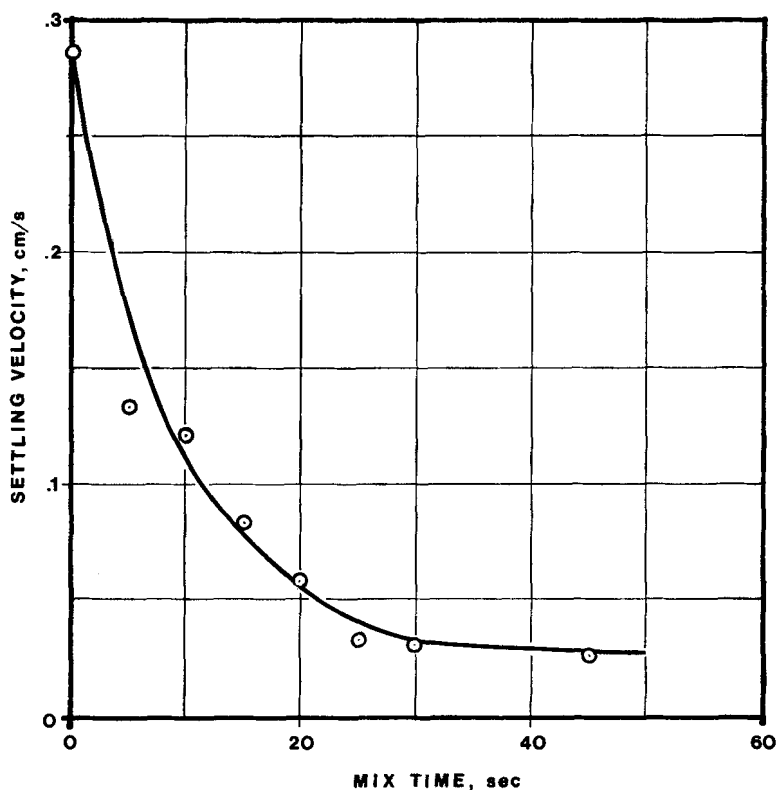


FIG. 5. Settling velocity as a function of mix time at a constant power input of 181 ergs/(cm<sup>3</sup>) (s).

TABLE 1

Suspended Solids in Supernatants of Quiescently Settled Suspensions  
After Varied Initial Mix Times

Elapsed Settling Time	Supernatant Suspended Solids (mg/l) [Percent of suspension in parentheses]		
	Complete Mix	Ten-Second Mix	No Mix
Suspensions of 1070 mg/l SS or 0.085 SSVF			
2-6 min	28.9 (3%)	97.8 (9%)	386 (36%)
15 min	29.6 (3%)	81.8 (8%)	132 (12%)
60 min	24.3 (2%)	42.5 (4%)	81.4 (8%)
Suspensions of 1770 mg/l SS or 0.120 SSVF			
2-6 min	—	106 (6%)	439 (25%)
15 min	17.6 (1%)	70.1 (4%)	206 (12%)
60 min	—	47.9 (3%)	95.1 (6%)

NOTE: The slurries were precipitated with lime at pH 6.

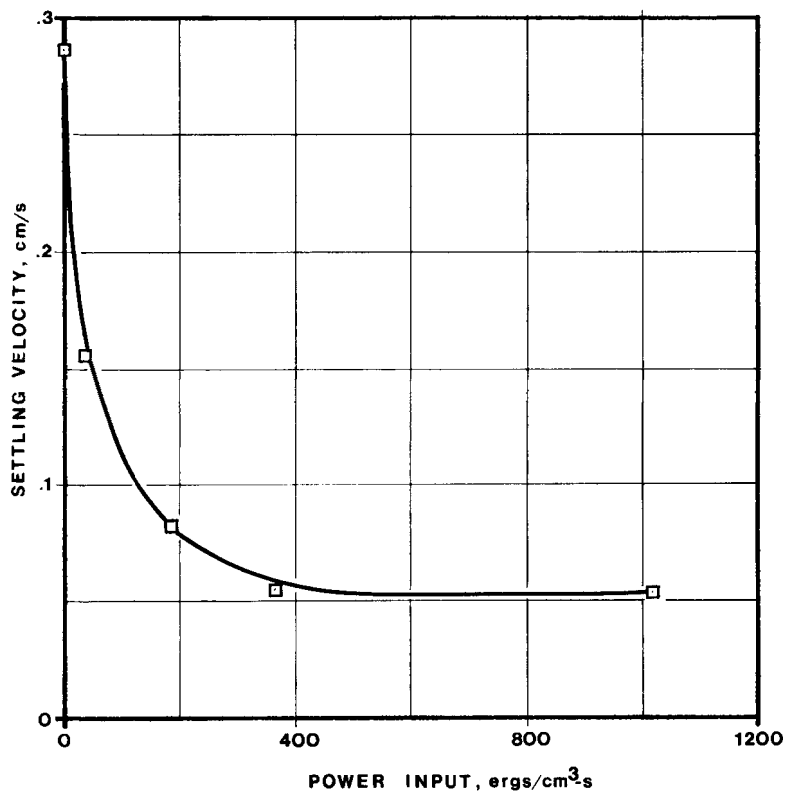


FIG. 6. Effect of power input on settling velocity at a constant mix time of 15 s.

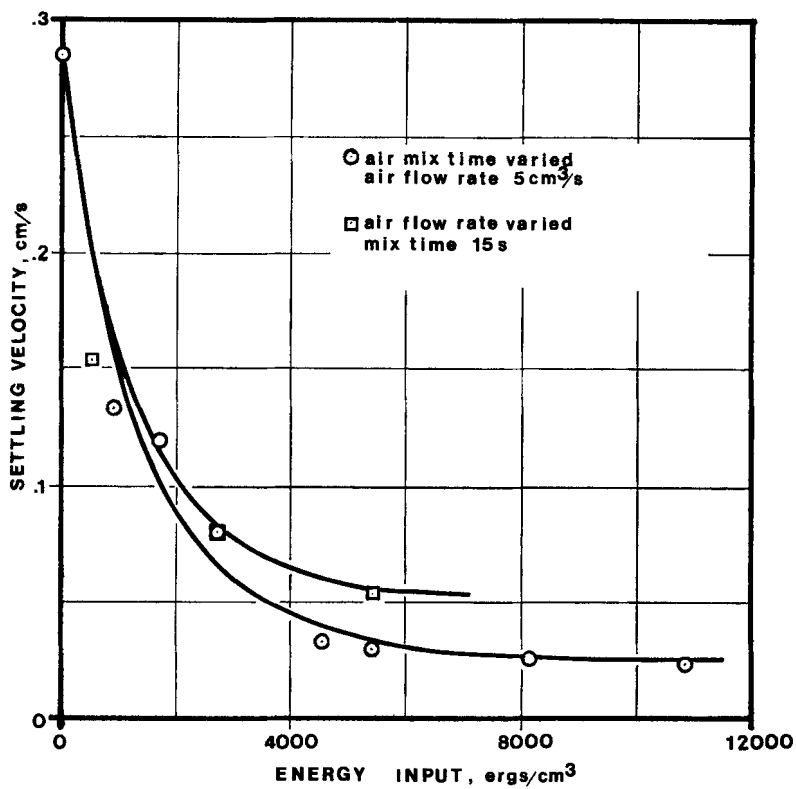


FIG. 7. Effect of initial mixing on the settling velocity as a function of energy input.

so that after 15 min the solids were reduced to 12% and by 1 h only 6–8% remained. Ten seconds of mixing improved the supernatant considerably. After 2 min, 6–9% remained, and solids were reduced to 3–4% during 1 h of settling.

The results indicate that the large particle settling leaves a less than satisfactory supernatant, but that most of the particles will settle eventually. Before practical application of limited mixing can be made, experimentation will be necessary to determine the relationship between particle size and effluent quality.

### Acknowledgments

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