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Theory of Clarifier Operation. VI. The Precipitation Process in Reactor-Clarifiers

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Abstract

A mathematical model is developed for the effect of the rapid-mix step on floc settling velocity in reacter clarifier operation. Data on ferric hydroxide flocs are consistent with the model. The most important parameter is the duration of the rapid-mix step; the longer this is, the more slowly does the floc settle. This is thought to be due to the finite rate at which the precipitation reaction causes the supersaturated solution to decay to equilibrium. Some applications are suggested, and the results of some pilot scale studies are reported.

INTRODUCTION

Reactor-clarifiers are widely used for removal of metals from metal finishing wastewaters. They are similar to standard upflow clarifiers except that the addition of chemicals and the precipitation of solids takes place within the clarifier, as shown in Fig. 1. Rapid mixing, flocculation, and sedimentation take place in the same unit. EPA has designated these clarifiers as recommended for the metal finishing industry (*1*). We developed a mathematical model for the time-dependent operation of upflow clarifiers (*2, 3*) and tested it with ferric hydroxide flocs. We found good agreement

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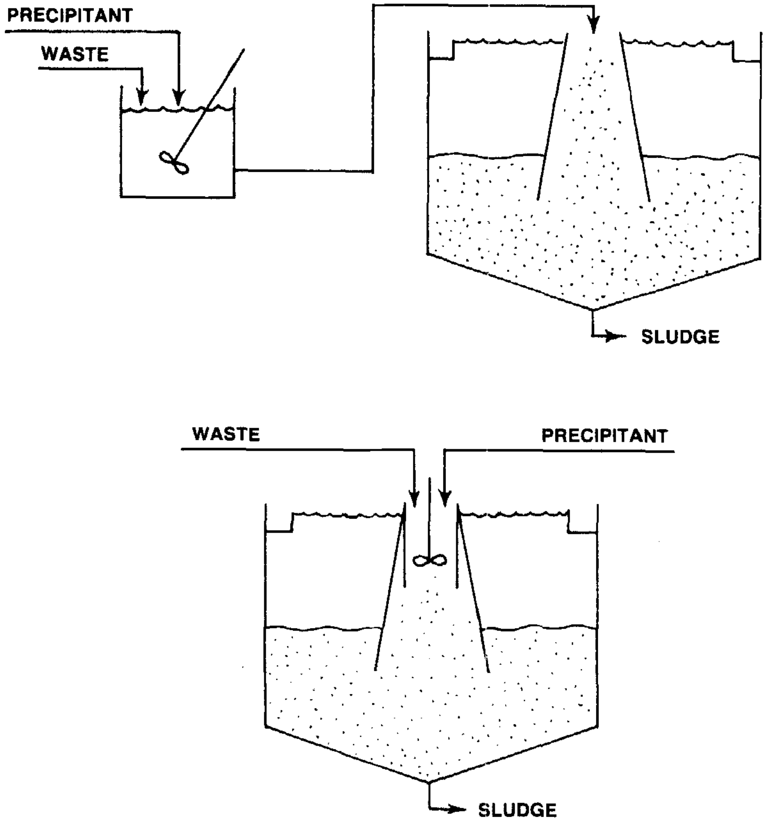

FIG. 1. Schematic representation of two types of upflow clarifier. Top: Standard upflow clarifier preceded by rapid mix. Bottom: Reactor-clarifier.

between theory (parameters assigned on the basis of liter cylinder tests with exhaustively mixed floc) and experimental results from a pilot scale reactor-clarifier only if the floc used in the pilot plant had also been exhaustively mixed. Graves (*4*) then showed that freshly precipitated, relatively undisturbed ferric hydroxide flocs formed extremely large, fragile aggregates which settled several times faster than exhaustively stirred floc. She also noted that such flocs, once disrupted by mixing, did not reaggregate; the binding forces holding the aggregates together are evidently not simply van der Waals forces.

Our model (*3*) for upflow clarifier operation requires the determination of two parameters by liter cylinder test studies. These are the effective radius of the particles, r, and a parameter α which occurs in a formula for the effective viscosity of the slurry. Graves's work demonstrated that one must not assume that values of r and α determined in liter cylinder tests were appropriate for flocs formed in our reactor-clarifier. It is our purpose here to demonstrate that these parameters are determined primarily by the duration of the rapid mix, and to develop formulas relating their numerical values to the duration of the rapid mix. These then permit the extension of our mathematical model for upflow clarifier operation to the operation of reactor-clarifiers. We shall find that the duration of the rapid-mix step should be as short as possible consistent with adequate mixing of the reagents. A chemical mechanism accounting for these observations will be proposed, and a simple modification of ordinary clarifiers to improve their performance will be described.

We have been particularly interested in $Fe(OH)_3$ flocs precipitated from ferric sulfate solutions because these simulate the rinsewaters from steel pickling operations. These acidic wastewaters contain from 200 to 5000 mg/L of iron, initially mostly Fe(II), which then is oxidized to Fe(III) in the presence of dissolved oxygen (*5*). The reaction of ferric sulfate with sodium hydroxide to produce ferric hydroxide floc can be summarized as

$$Fe_2(SO_4)_3 + 6NaOH \rightarrow \underline{2Fe(OH)_3} + 3Na_2SO_4$$

Actually, the process is much more complex. Stumm and Morgan (*6*) reviewed the chemistry of iron precipitation. They note that the hexa-aquo ferric ion, $[Fe(H_2O)_6]^{3+}$, readily donates protons to solvent water molecules or other bases and is converted into ferric hydroxo complexes. These tend to polymerize, as illustrated by the reaction

$$2[Fe(H_2O)_5(OH)^{2+} \rightarrow [Fe_2(H_2O)_8(OH)_2]^{4+} + 2H_2O$$

This dimer is able to undergo further hydrolysis and condensation, leading eventually to hydroxo polymers of colloidal size and ultimately to insoluble hydrous ferric oxide precipitates. One would expect the reaction rates of large hydroxo polymers to be relatively slow because of their high molecular weights and correspondingly low diffusion constants.

The minimum solubility of ferric iron and the isoelectric point of ferric hydroxide occur at about pH 8 (*7*). The precipitate is positively charged in acidic or neutral solution; in alkaline media it is negative.

Rapid mixing of treatment chemicals and wastewater can be done by baffled chambers, mechanical mixers, air agitation, and injection of chemicals ahead of pumps or into in-line blenders. Although much research has been devoted to flocculation (or the agglomeration of flocs brought about by slow mixing), less has been done on rapid mixing and its effects on subsequent flocculation and sedimentation. Most of the available work deals with the desirability of adding chemicals in a rapid mix prior to flocculation, and with the development of broad guidelines for the rapid-mix operation.

Camp (*8*) precipitated $Fe(OH)_3$ flocs using a rapid mixer with various velocity gradients, finding that the floc size decreases with increasing velocity gradients; similar observations have been made by Tekippe and Ham (*9*), Stump and Novak (*10*), and ourselves (*4*). Letterman, Quon, and Gemmel (*11*) studied turbidity removal by alum coagulation, and noted the existence of an optimum rapid-mix period, indicating that the early conditions of floc formation are important, and that the function of the rapid-mix operation is more than simply to disperse the coagulant. These authors, Argaman and Kaufman (*12*), Kawamura (*13*), and Leentvaar and Ywema (*14*) have noted that velocity gradient (G value) alone is not adequate to describe the effects of the rapid-mix step. Vrale and Jordan (*15*) suggested that the discrepancy between chemical dosages determined by jar tests and those actually required for plant operation might be due to the varying efficiencies of rapid mixing. Letterman, Quon, and Gemmel (*11*) developed an empirical model for optimizing the mixing parameters for an existing facility; coagulant dose, G value, and rapid-mix time were combined in an equation based on experimental results. Since the model includes no methodology for scale-up, its utility for design work is limited.

EXPERIMENTAL WORK

We prepared synthetic wastewaters from technical grade ferric sulfate (Ferri-Floc, $Fe_2(SO_4)_3 \cdot 7H_2O$, marketed by Cities Service Co.). Its properties are given in Table 1.

A 50% by weight solution was prepared by dissolving 14.2 kg of ferric sulfate in 14.2 L of tap water, mixing for at least 2 h, and then adding 400 mL of 0.2% Jaguar 1080 polymer (Stein, Hall and Co.) to facilitate the removal

TABLE 1
Properties of the Ferric Sulfate Used

Molecular weight	526
Bulk density	50–60 lb/ft^3
Water-soluble iron expressed as Fe	21.5%
Water-soluble Fe^{3+}	19.5%
Water-soluble Fe^{2+}	2.0%
Insolubles total	4.0%
Free acid	2.5%
Moisture at 105°C	2.0%

of insolubles. The resulting solution was allowed to settle for 24 h and then decanted. It contained about 160 g/L of Fe(III). This was then used as a stock solution for preparing simulated wastewaters.

Iron concentrations were determined by atomic absorption analysis with a Perkin-Elmer Model 305B atomic absorption spectrometer at 249.2 nm and using an air-acetylene flame. All samples were acidified with concentrated nitric acid to a pH of 2 before analysis. Samples being analyzed for dissolved iron were passed through a membrane filter (0.45 μm) prior to acidification. Standards for calibration were prepared according to the usual procedures (*16*).

Two different analyses for quantifying ferric hydroxide precipitates were performed. The direct measurement of the volume occupied by the floc, the settleable solids volume fraction (SSVF), was the more directly relevant of the two tests in terms of the mathematical model. One-hundred milliliter samples of suspension were allowed to settle for a 24-h period in a graduated cylinder so that most of the inter-particle water could escape the settled solids. The SSVF was taken as the volume of suspended solids divided by the original volume of the suspension. Total suspended solids tests were also performed to determine the solids composition of the reactor-clarifier sludge blanket and effluent. These tests were done in duplicate with bitumen crucibles and glass fiber filters according to Section 208D of *Standard Methods* (*16*).

pH was frequently measured in order to adjust the addition of NaOH to maintain an pH optimum for Fe(III) precipitation. A Fisher Model 600 pH meter calibrated with Fisher buffers was used. A General Radio Co. Type 1531 Strobotac was used to measure the rate of rotation of the turbine impellers used to provide mixing in the reactor-clarifiers.

The optimum pH for $Fe(OH)_3$ precipitation was determined by jar tests. Solutions containing 500 mg/L of Fe(III) were brought to various pH's with 1.0 *N* NaOH. After 10 min of rapid mixing (100 rpm), 15 min of flocculation (10 rpm), and 30 min of settling, samples of supernatant were taken for analysis. Total and dissolved Fe were determined; the results, shown in Fig. 2, indicate that the optimum pH is about 7.9.

Titrations were made to determine the volume of NaOH solution required to produce the optimum pH; 0.500 *N* NaOH was used. The NaOH dosage curve was linear with a correlation coefficient of 0.997; it is shown in Fig. 3.

Information on the suspended solids and SSVF produced when the pH of a solution of known Fe(III) concentration is raised to 7.9 was needed in order to choose the Fe(III) concentrations to be studied. Figure 4 shows the relationship between suspended solids and Fe concentration; Fig. 5 displays SSVF as a function of Fe concentration. The relationship between SSVF

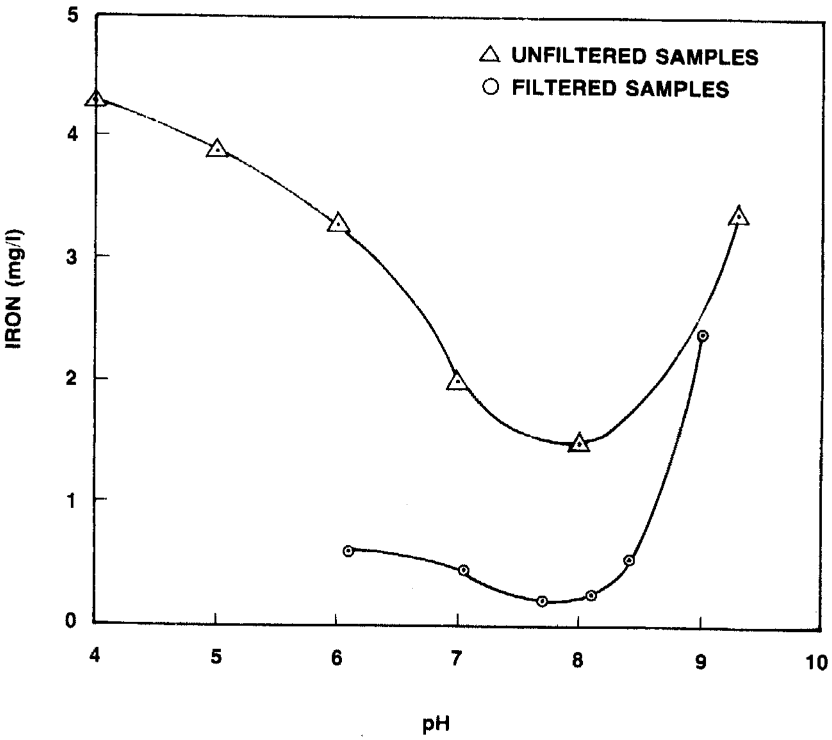

FIG. 2. Determination of optimum pH for $Fe(OH)_3$ precipitation. Supernatant Fe concentration in filtered and unfiltered samples as a function of pH.

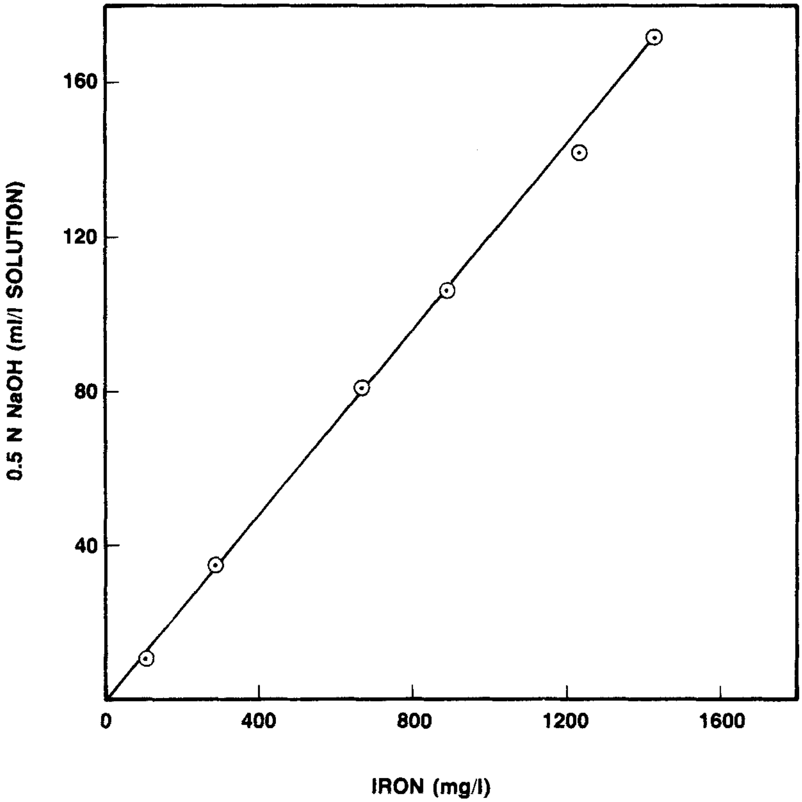

FIG. 3. Dose rate of NaOH required to reach the optimum pH of 7.9.

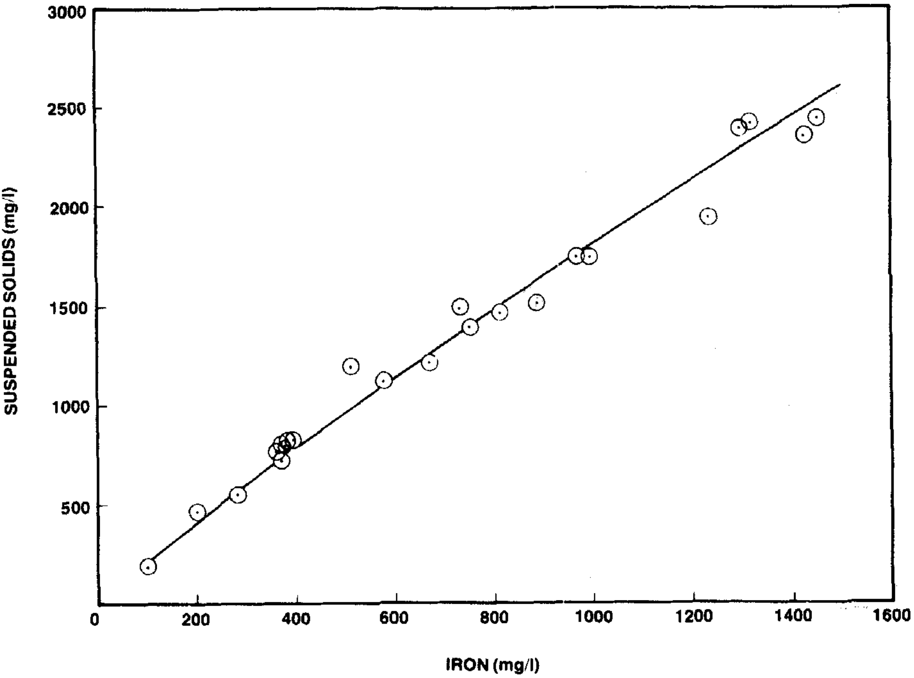

FIG. 4. Suspended solids produced by the precipitation of Fe(III) at pH 7.9.

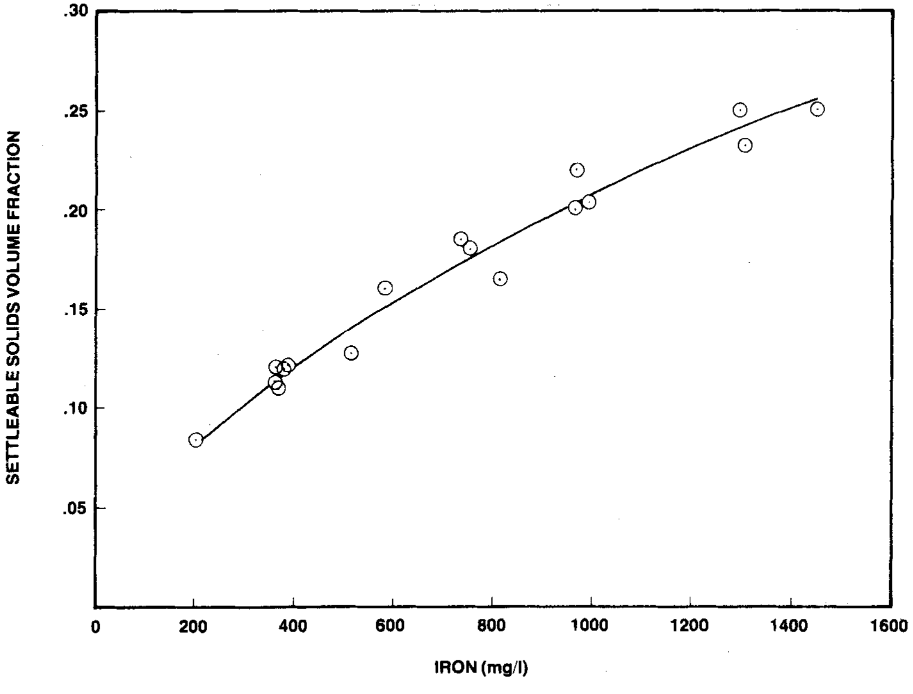

FIG. 5. Settleable solids volume fraction (SSVF) produced by the precipitation of Fe(III) at pH 7.9.

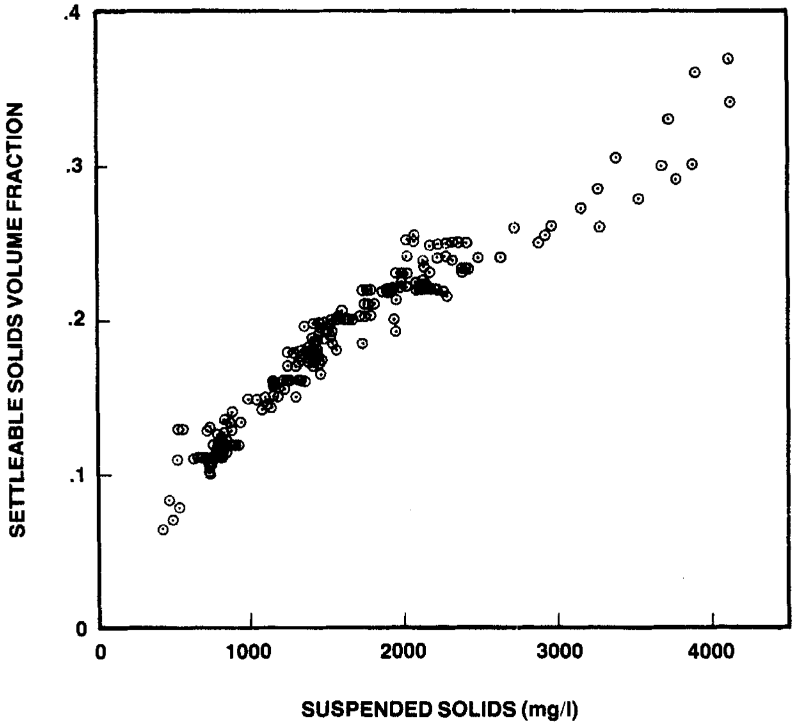

FIG. 6. Relationship between SSVF and suspended solids.

and Fe concentration is also needed to provide input to the mathematical model concerning the influent SSVF produced by a wastewater of known Fe concentration. The relationship between SSVF and suspended solids is shown in Fig. 6.

Measurements of SSVF were used to estimate the floc density needed in the model. The floc was assumed to consist of water entrained in geothite, FeO(OH). The calculation of floc density is as follows:

$$\begin{aligned}(\text{floc mass}) &= (\text{geothite volume}) \times (\text{geothite density, 4/28 g/mL}) \\ &\quad + (\text{floc volume} - \text{geothite volume}) \times (\text{water density})\end{aligned} \tag{1}$$

For example, precipitation from 100 mL of solution containing 1400 mg/L of Fe produces floc having a settled volume of 25 cm^3. The 0.14 g of Fe in the solution yields 0.22 g of geothite (density = 4.28 g/mL) with a volume of

0.052 cm^3. The floc mass, calculated as above, is 25.17 g; division by the settled floc volume gives 1.0068 g/cm^3 as the floc density.

Bench Scale Reactor-Clarifier Study

The bench scale apparatus was built of Plexiglas. The outer body of the clarifier was constructed from a 41.7 cm long, cylindrical section with an o.d. of 30.48 cm. Four sample ports were located at 10 cm intervals along the side of the cylinder.

Simulated wastewater and 0.5 *N* NaOH were introduced at the top of a rapid-mixing cylinder mounted inside the large cylinder. The rapid-mixing cylinder consisted of a 22.8-cm long tube with an internal diameter of 8.89 cm. The submerged volume, available for mixing, was approximately 1300 mL. A plastic grid, 1.2 cm deep with 0.44 openings per cm^2, was secured to the bottom of the mixing cylinder as a baffle between the zone of mixing and the more quiescent regions of the clarifier. Mixing was provided by a Chemineer ELB agitator with a 6.35-cm six-bladed turbine. Wastewater was delivered from a 120-L Nalgene tank through a calibrated Dwyer rotometer by a Gorman-Rupp centrifugal pump. The O.5 *N* NaOH, also delivered through a Dwyer rotometer, was pumped from a 50-L Nalgene tank with a Cole-Parmer peristalic pump.

The ferric hydroxide was precipitated in the rapid mixer; it then flowed through the grid baffle and out into the main body of the clarifier to form a blanket where solid–liquid separation occurred. The clarified effluent flowed up and over a weir 2.5 cm high by 2.5 cm wide, positioned at the top of the unit. The total volume of the reactor-clarifier was 23 L.

In a typical run, simulated influent was prepared in the 120-L container by diluting the stock iron solution with tap water to the desired iron concentration. A titration was performed on a 1.00-L sample of the influent to ascertain the volume of 0.50 *N* NaOH needed to produce the optimum pH for ferric hydroxide precipitation. The volume of NaOH determined from this titration was compared to the volume specified by the NaOH dosage curve developed during the titration studies. This procedure served as a check on the intended iron concentration of the influent. The desired NaOH flow rate was then calculated from the volume of NaOH required to precipitate the Fe from a liter of the wastewater and the proposed wastewater flow rate.

Prior to the run the reactor-clarifier was filled with tap water so that steady-state operation could be approached quickly without having to take into account the solids precipitated while the reactor was being filled. The run was initiated by adjusting the mixer to the desired speed and beginning the flows of influent and NaOH. A timer was used to determine the flocculation time—the time from the beginning to the end of the run during which the flocs had the opportunity to agglomerate in the sludge blanket.

After a significant sludge blanket had developed and the desired flocculation time had elapsed the run was terminated. The flows were shut off, the mixer stopped, and 125-mL samples of the sludge blanket were taken from the sample ports to be analyzed for SSVF and total suspended solids. The height of the sludge blanket was recorded with time, as the solids in the clarifier settled slowly to the bottom of the unit, to calculate the zone settling velocity of the suspension.

Over 60 runs were made with the bench scale reactor-clarifier to explore the effect of various experimental parameters on the size and settling velocity of precipitated ferric hydroxide. Table 2 lists the variables investigated. For each of the influent Fe concentrations, runs were made using from two to four different mixer speeds at each of the wastewater flow rates. The flocculation time was also varied and the temperature of the reactor during the precipitation reactions was measured.

Detailed data from the bench scale reactor-clarifier experiments are given in Ref. *17*. The SSVF of the sludge blanket is reported for the purpose of correlating it with the settling velocity measured during each run. In most of the experimental runs, enough mixing was present in the clarifier to produce a homogeneous sludge blanket such that the SSVF's measured at the different sample ports were equal. Occasionally these samples gave different SSVF results. In this case the SSVF taken from the sample port nearest to the top of the sludge blanket was used for the settling velocity correlation.

Settling velocity was correlated with impeller rpm, Reynolds number, and energy input in an effort to test the suggestion put forth by Graves, Schnelle, and Wilson (*4*) that precipitated flocs are gradually disrupted in a rapid mixer. All these attempts failed to give a satisfactory explanation for the relationship between settling velocity and SSVF in the reactor-clarifier experiments.

TABLE 2
Variables Investigated with Bench-Scale Reactor-Clarifier

rpm	157	234	309	392	474	633
G (s^{-1})[a]	300	540	820	1170	1560	2400
Influent Fe (mg/L)	400	600	800	1000	1200	1400
Waste flow (L/min)	1.0	1.75	2.5			
Flocculation time (min)	7.5 →	29.8				
Temperature (°C)	22.0 →	24.5				

[a] Details of the calculation of G values appear in Ref. *17*.

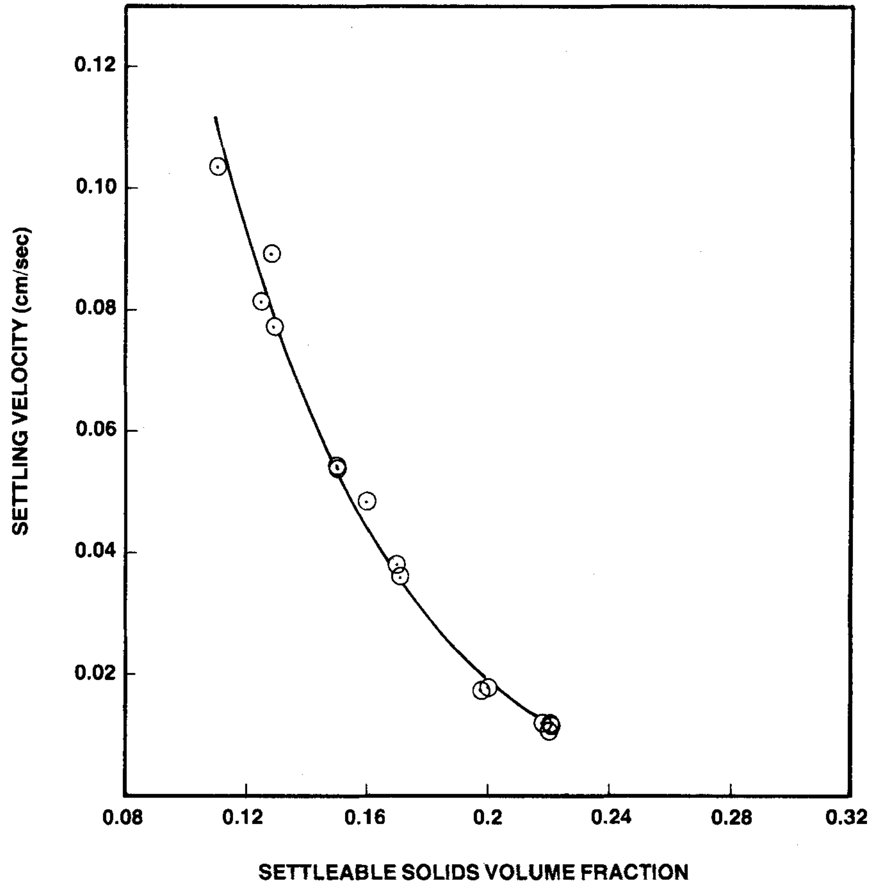

FIG. 7. Data and model predication of settling velocity versus SSVF for rapid mix duration $\bar{t}$ = 0.447 min. $r = 0.082$ cm, $\alpha = 18.3$.

Ultimately we found that one of the simplest of all the possible correlations yielded the best results. The experimental data were segregated according to the rapid-mixer retention time used during each run. Figure 7 is a plot of the zone settling velocity as a function of the SSVF for flocs produced with an average rapid-mixer retention time $\bar{t}$ of 0.447 min. The individual runs were made using different influent Fe concentrations, impeller speeds, and flocculation times. The weak dependence of settling velocity on impeller speed and flocculation time is indicated by the absence of scatter in the plot. Similar results for runs with average retention times of 0.681 and 1.17 min are presented in Figs. 8 and 9. On comparing these three figures we see that

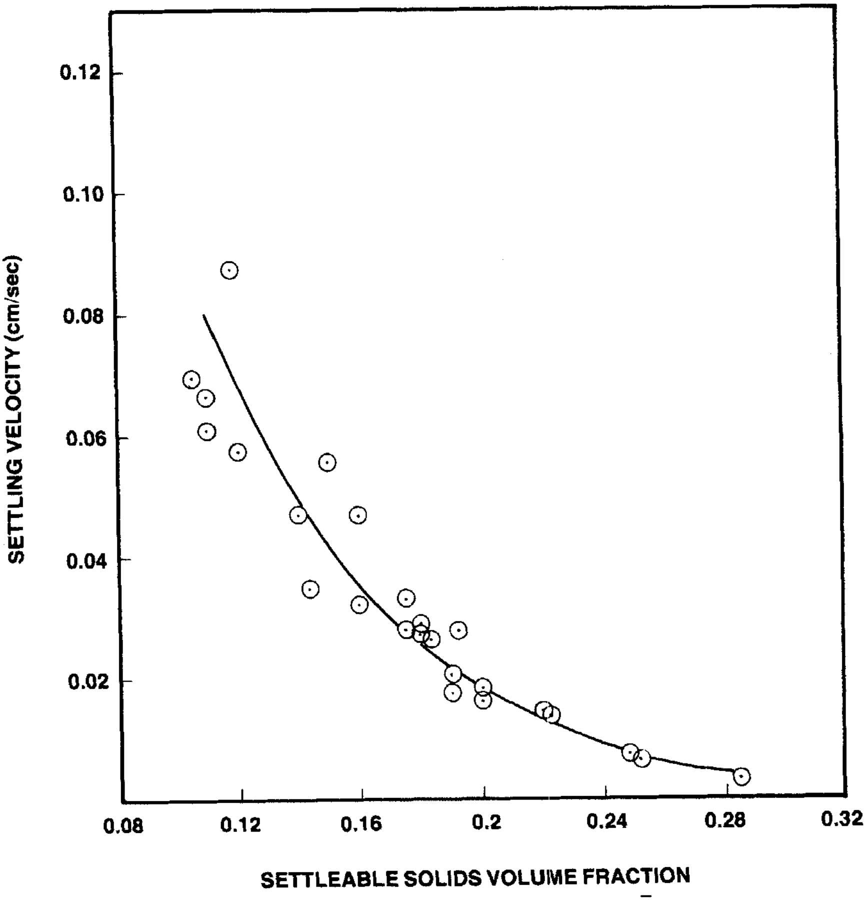

FIG. 8. Data and model prediction of settling velocity versus SSVF for $\bar{t} = 0.681$ min. $r = 0.06$ cm, $\alpha = 15.7$.

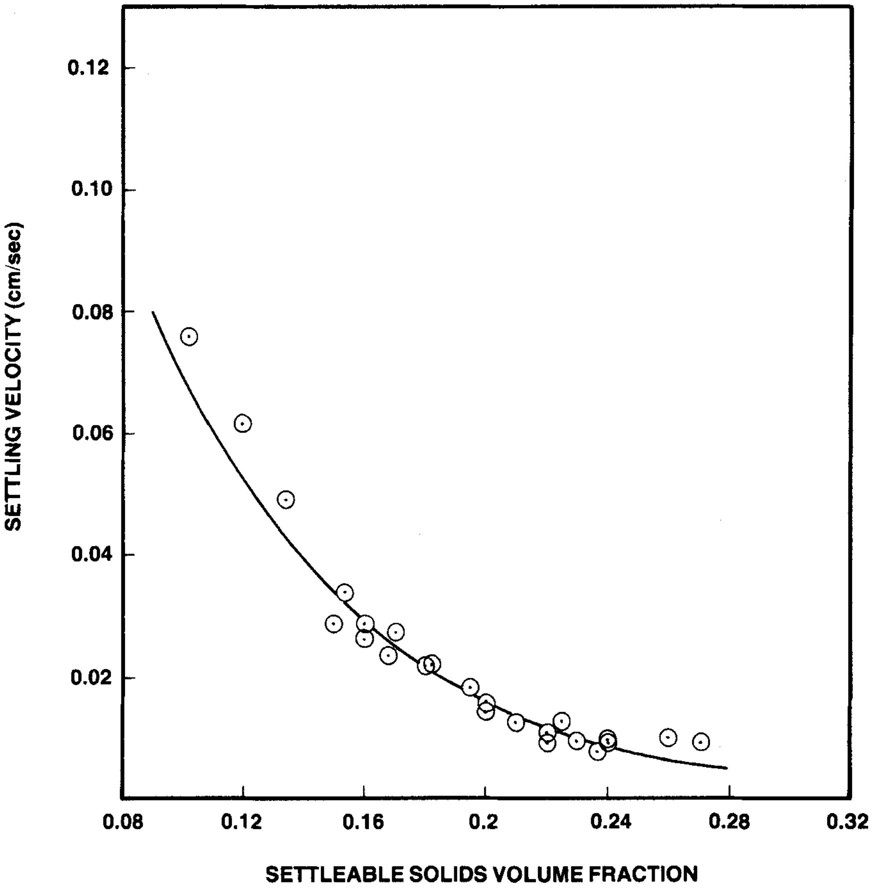

FIG. 9. Data and model prediction of settling velocity versus SSVF for $\bar{t} = 1.17$ min. $r = 0.047$ cm, $\alpha = 13.9$.

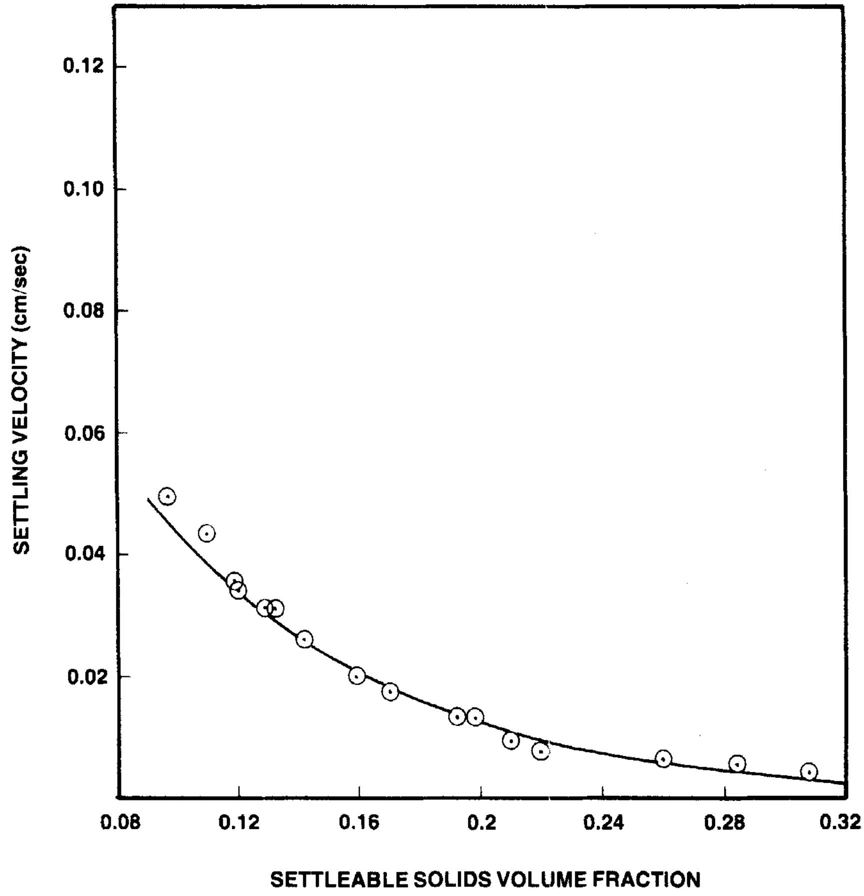

FIG. 10. Data and model prediction of settling velocity versus SSVF for exhaustively mixed floc, $\bar{t} = \infty$, $r_\infty = 0.033$ cm, $\alpha_\infty = 11.7$.

as the rapid-mixer retention is increased the settling velocity of a slurry with a given SSVF decreases.

A series of liter cylinder settling velocity tests were performed in order to determine the settling behavior of ferric hydroxide flocs produced during an essentially infinite rapid-mix retention time. A batch of concentrated ferric hydroxide was prepared and mixed for 30 min. Liter cylinders containing different solids concentrations were made using supernatant from the original batch as dilution water. The zone settling velocities of the suspension were measured using the standard technique, including slow stirring of the settling flocs. The results of this experiment appear in Fig. 10. As expected, the settling velocities were lower than those measured for flocs generated in a rapid mixer.

As mentioned above, our upflow clarification model has two adjustable parameters; these are the effective particle radius, r, and a parameter describing slurry viscosity, α. These two parameters appear in Eq. (2), which results from the combination of a settling velocity equation from Fair, Geyer, and Okun (*7*) and an equation for slurry viscosity used by Graves (*4*).

$$u = \frac{2g\Delta\rho r^2}{9\mu_0 \exp[\alpha c]} \left[1 + \frac{1}{4}\left(\frac{\rho_{sl} r u}{2\mu_0 \exp[\alpha c]}\right)^{1/2} + \frac{0.34\rho_{sl} r u}{12\mu_0 \exp[\alpha c]} \right]^{-1} \tag{2}$$

where u = settling velocity (cm/s)
g = gravitational constant (980 cm/s^2)
μ_0 = viscosity of water (P)
ρ_{sl} = slurry density
$\Delta\rho$ = floc density − water density
c = SSVF

This equation forms the basis for the calculation of settling velocity in the mathematical model. When used to describe upflow-clarifiers, the parameters r and α are constants derived from experimental data. However, when used to describe reactor-clarifiers, r and α become variables dependent upon the rapid-mix operation. The model developed here specifies values for the effective particle radius and the viscosity parameter as functions of the rapid-mixer retention time, apparently the most important of the rapid-mix parameters.

The model is developed by fitting Eq. (2) to the infinite retention time data and to the data collected for each of the three rapid-mix retention times. Fitting Eq. (2) to the experimental data involves the adjustment of r and α and results in the production of four pairs of values for these parameters, each pair being specific to a given rapid-mix retention time. Empirical equations, one for r and one for α, are then developed to predict their values for any retention time.

Fitting the settling velocity equation to experimental data is most easily done by first using settling data for slurries having low SSVF values to calculate r, since if c is small, u is only weakly dependent on α. One assumes initially a first approximation for α; for ferric hydroxide 10 is satisfactory. Having calculated r at low slurry SSVF's, one then uses this value of r and settling data at high SSVF's to calculate α. The values of r and α were selected in this way to yield settling velocities in agreement with experimental data for the four sets of runs displayed in Figs. 7–10. We shall refer to these as the experimental values of r and α.

Two empirical equations, (3) and (4), were developed to describe the variation of r and α with the rapid-mixer retention time:

$$r = r_\infty \exp[K_1/t] \tag{3}$$

where r = effective particle radius (cm)
r_∞ = effective particle radius produced after an infinite rapid-mixer retention time (cm)
K_1 = empirical coefficient (min)
t = rapid-mixer retention time (min)

$$\alpha = \alpha_\infty \exp[K_2/t] \tag{4}$$

where α = slurry viscosity parameter
α_∞ = slurry viscosity parameter produced after an infinite rapid-mixer retention time
K_2 = empirical coefficient (min)
t = rapid-mixer retention time (min)

In both equations, as the retention time approaches infinity, the argument in the exponential approaches zero,making r and α assume the values used to fit the settling velocity equation to the data generated using flocs produced under an infinite rapid-mix retention time.

The values of r and α determined by fitting Eq. (2) to the experimental data are plotted as functions of the inverse of the rapid-mix retention time in Figs. 11 and 12. The values of K_1, K_2, r_∞, and α_∞ were determined by a least-square regression analysis performed on the log forms of Eqs. (3) and (4). The experimental values for r and α and the values for these variables calculated from Eqs. (3) and (4) are listed in Table 3.

The curves in Figs. 7 through 10 plot the settling velocities calculated by Eq. (2) using the values of r and α produced by regression analysis on the original estimates of these variables. The correlation coefficients between the observed and calculated settling velocities in these figures are given in Table 4.

Equations (2), (3), and (4) may be combined to calculate the predicted settling velocity for each of the experimental runs. A comparison between the predicted and observed settling velocities is presented in Fig. 13. The high correlation coefficient, 0.973, between the observed and predicted settling velocities indicates that these equations making up the rapid-mix model successfully describe the effect of rapid mixing on the settling behavior of ferric hydroxide precipitates.

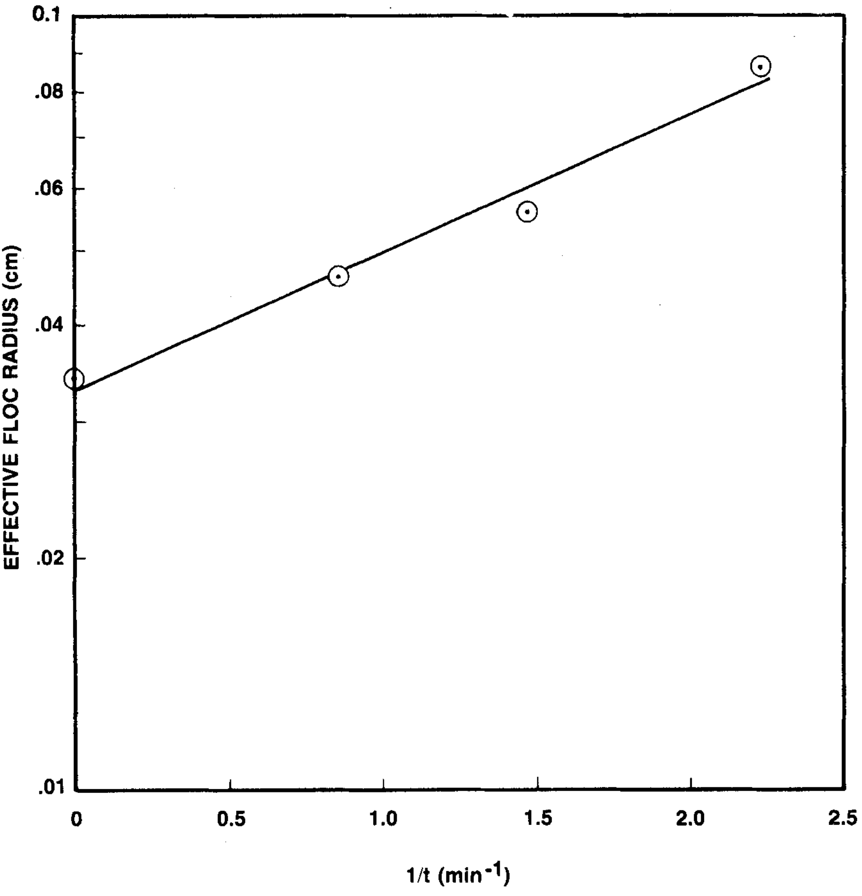

FIG. 11. Experimental and calculated values of effective floc radius, r, as a function of $1/\bar{t}$.

TABLE 3

Experimental and Calculated Values of r and α[a]

$\bar{t}$ (min)	$1/\bar{t}$ (min^{-1})	r_{expt} (cm)	r_{calc} (cm)	α_{expt}	α_{calc}
0.447	2.237	0.086	0.082	19.0	18.3
0.681	1.468	0.056	0.060	15.0	15.7
1.170	0.855	0.046	0.047	13.7	13.9
∞	0	0.034	0.033	12.0	11.7

[a] Correlation coefficients for $r = r_\infty \exp [K_1/\bar{t}]$ and $\alpha = \alpha_\infty \exp [K_2/\bar{t}]$ were 0.991 and 0.981, respectively; $K_1 = 0.4063$ min and $K_2 = 0.1999$ min.

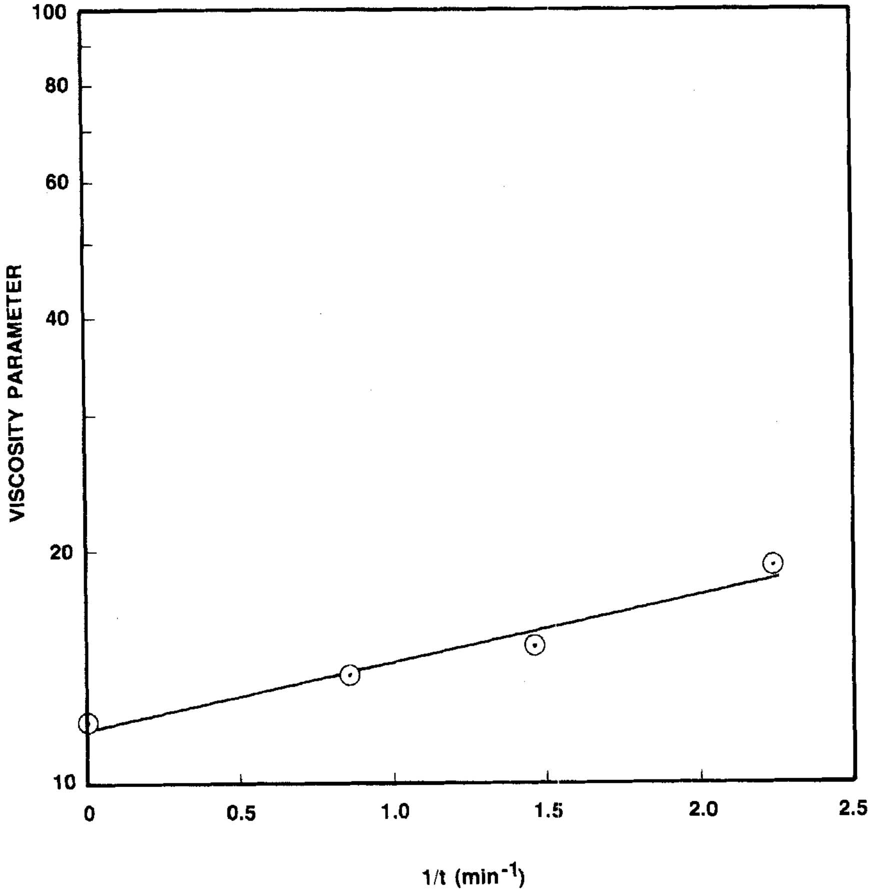

FIG. 12. Experimental and calculated values of the viscosity parameter α as a function of $1/\bar{t}$.

TABLE 4
Values of r and α Used to Fit the Settling Velocity Equation to Experimental Data and the Corresponding Correlation Coefficients, R, between Observed and Calculated Settling Velocities

$\bar{t}$ (min)	r (cm)	α	R
0.447	0.082	18.3	0.988
0.681	0.060	15.7	0.951
1.170	0.047	13.9	0.975
∞	0.033	11.7	0.994

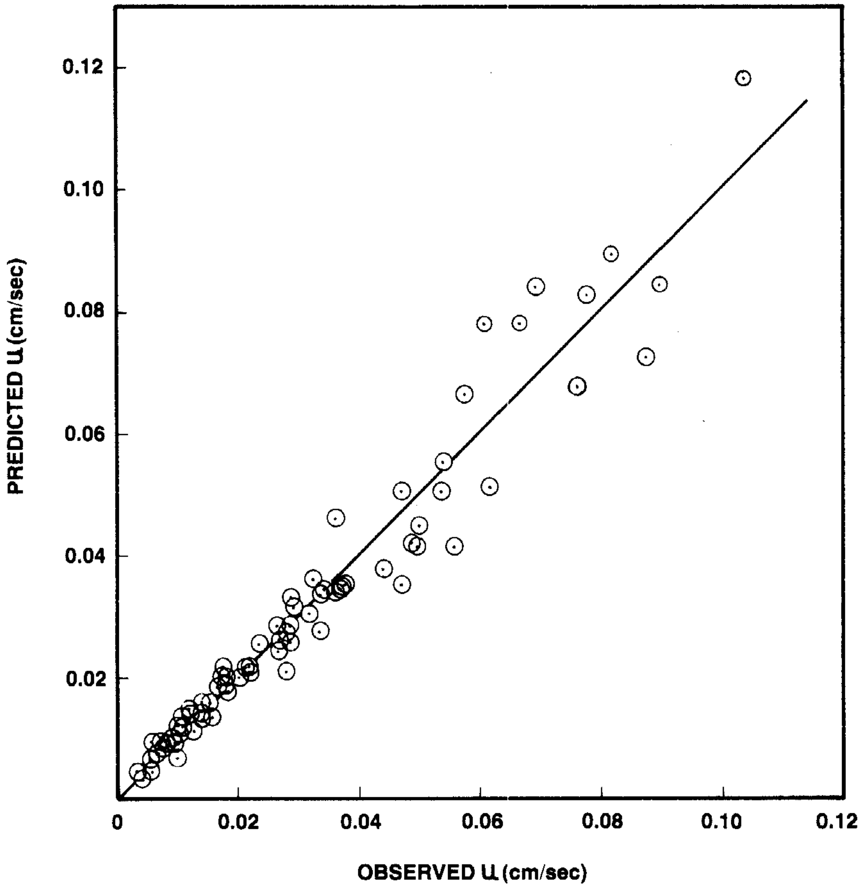

FIG. 13. Model predictions of settling velocities versus observed settling velocities for all runs made. The correlation coefficient is 0.973.

Pilot Scale Reactor-Clarifier Study

(a) Experimental

The pilot scale reactor-clarifier system was constructed by Graves (*18*) and Schroeder (*19*) and used in earlier studies (*3, 4*). A rapid-mixing cylinder, geometrically similar to the rapid mixer used in the bench scale apparatus, was made from sheet metal and installed in the top of the reactor cone. The cylinder was 35.9 cm long by 13.97 cm i.d., with a mixing volume of 5.4 L. A 10.1-cm 6-bladed turbine impeller provided mixing.

Simulated wastewater (ferric sulfate solution) and 0.5 *N* NaOH were delivered to the rapid mixer for the precipitation of $Fe(OH)_3$. The wastewater was prepared in a 1000-L Nalgene tank equipped with a mixer; it was pumped to the rapid mixer through a calibrated rotometer. The NaOH solution was pumped from a 50-L Nalgene container through a rotometer by a peristaltic pump. The precipitates formed in the rapid mixer flowed through a grid baffle fastened to the bottom of the mixing cylinder and into the reactor cone. This sheet metal cone is 13.98 cm i.d. at the top, 25.4 cm i.d. at the bottom, and extends 85.9 cm down into the clarifier. The precipitate leaving the bottom of the cone flowed past baffles and out into the main body of the clarifier, where a sludge blanket formed and solid–liquid separation took place.

The outer body of the clarifier was made from a Plexiglas cylinder 122 cm high, o.d. of 45.7 cm, and a wall thickness of 0.635 cm. Five sample ports were placed at 20.3 cm intervals up the side of the clarifier. A funnel-shaped sheet metal cone was attached to the bottom of the cylinder and equipped with a valve for sludge withdrawal. Clarified effluent left the unit by a peripheral weir located at the top of the clarifier.

The most convenient method for testing our methematical model with the pilot plant was to feed the pilot plant a solids or hydraulic overload and then to measure the rate of rise of the top of the sludge blanket. This blanket rise velocity could then be compared with the theoretically predicted value.

As in the bench scale study, the reactor-clarifier was initially filled with tap water so that a run could be initiated without the complication of a large amount of solids precipitated under unknown mixing conditions while the clarifier was being filled. Simulated wastewater and 0.5 *N* NaOH were prepared as before. Samples of the influent were analyzed for Fe, and were also titrated, as before, to determine the proper ratio of flow rates of precipitant and wastewater. Runs were initiated by establishing the desired flow rates of waste and NaOH solution and turning on the mixer. Since the bench scale study had shown that floc characteristics were independent of mixer speed, all pilot scale runs were made with the impeller rotating at 234 rpm, corresponding to a velocity gradient of 300/s.

A timer was started after a substantial sludge blanket had formed in the reactor, and the height of the blanket was recorded as a function of time. Effluent samples were taken near the conclusion of the run for determinations of dissolved iron and total suspended solids. Samples of the sludge blanket were taken from the sample ports and the underflow valve for determination of SSVF.

(b) Results

Two series of runs were made with the pilot scale reactor-clarifier, the first using influent containing approximately 1000 mg/L Fe and the second using influent containing about 400 mg/L of iron. In both series runs were made at a number of different flow rates, thereby producing blanket rise velocity data for flocs formed under a variety of rapid-mix retention times. Blanket rise data for the 1000 mg/L series are shown in Fig. 14; data for the 400 mg/L series are in Fig. 15.

The upflow clarifier model developed by us earlier (*3*) is combined with Eqs. (3) and (4) to give us a model for reactor-clarifier operation. Equations (3) and (4) predict the effective particle radius and the viscosity parameter for flocs precipitated under a given retention time in the rapid mixer of a reactor-clarifier.

The mathematical model requires the input of a number of parameters, all of which are readily evaluated. These, given in Table 5, include some computer program parameters, the various dimensions of the clarifier, and physical quantities relating to water and to the ferric hydroxide precipitates. The equations for the effective particle radius and the viscosity parameter were calibrated with data from the bench scale experiments; r and α for each run were calculated using the rapid-mix retention time for that run.

The computer results were very sensitive to the value of the SSVF, which was one of the least precise of our experimental measurements. The measurement of the total iron concentration of the influent was both more rapid and more precise than the 24-h SSVF determination. We therefore used the influent iron concentration and the curve in Fig. 5 to determine SSVF values.

The model predictions of blanket height as a function of time for the two sets of runs are shown in Figs. 16 and 17. For the runs with 1000 mg Fe/L influent, the model predicts a constant blanket rise velocity throughout each run, as seen in Fig. 16. However, for the runs with 400 mg Fe/L influent, the model predicts that the sludge blanket rise velocity will gradually increase

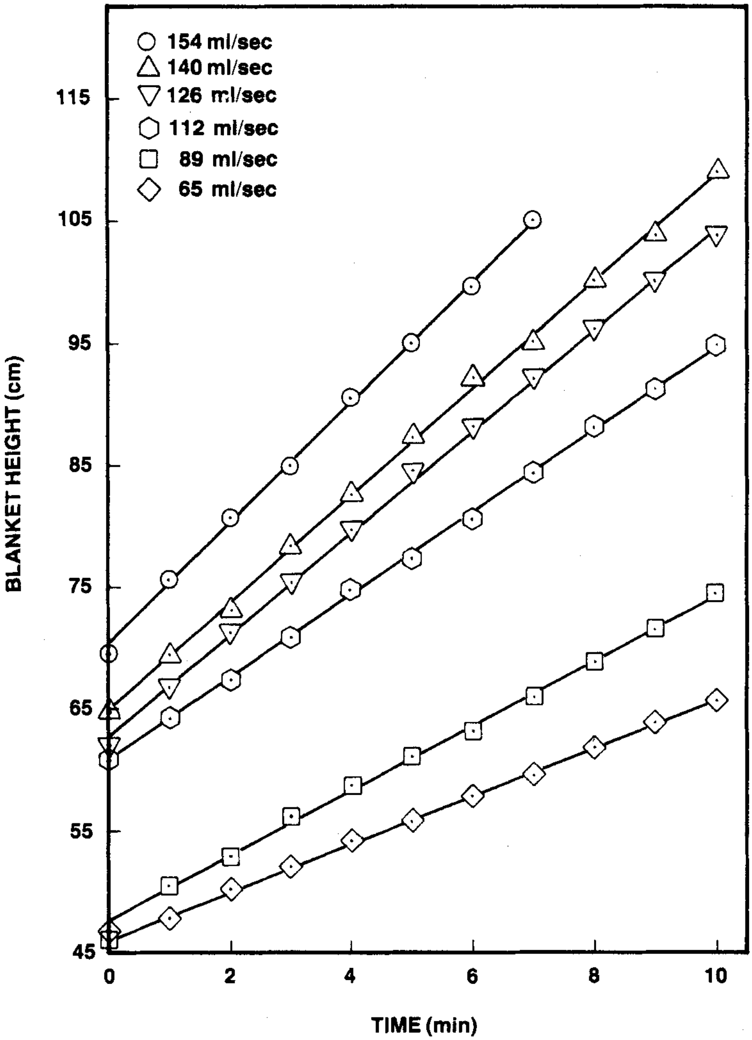

FIG. 14. Blanket height as a function of time at various flow rates. Influent iron concentration = 1000 mg/L.

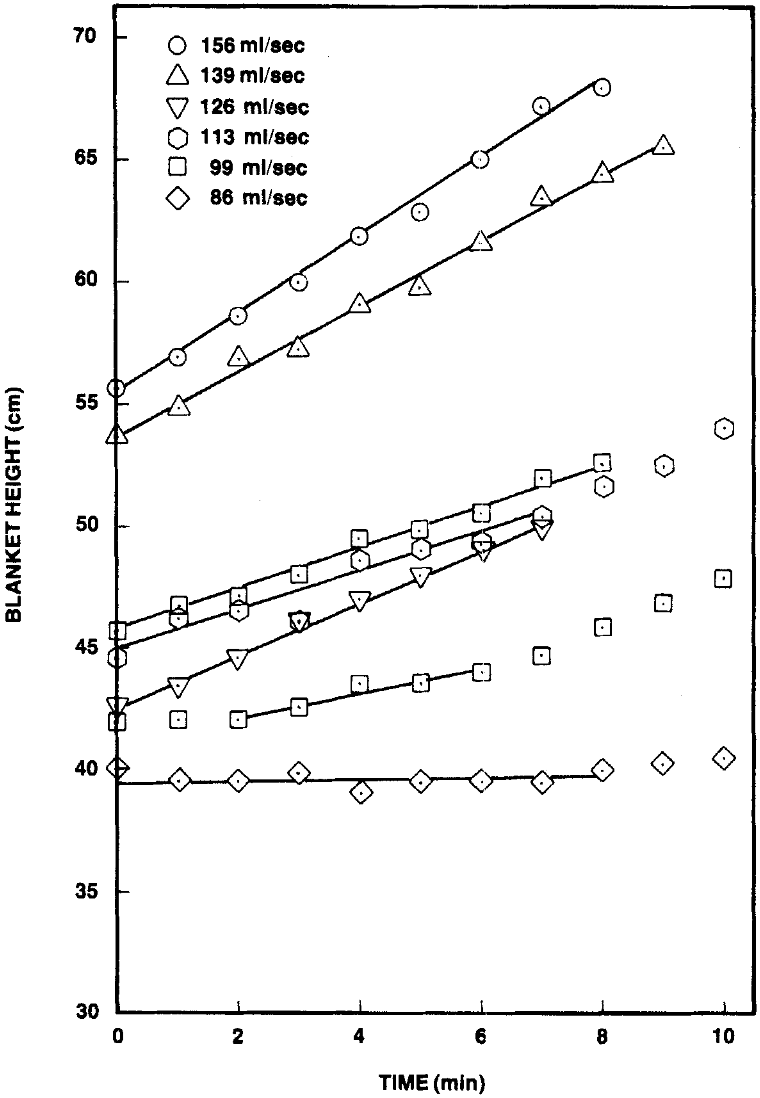

FIG. 15. Blanket height as a function of time at various flow rates. Influent iron concentration = 400 mg/L.

TABLE 5
Model Parameters for the Pilot Scale Reactor-Clarifier[a]

Parameter	Value used
Integration time increment	1.0
Operation time	840 s
Number of slabs	30
Print command	60
Radius of casing	22.6 cm
Upper radius of feed cone	6.99 cm
Lower radius of feed cone	12.7 cm
Height of clarifier	121.9 cm
Height of feedplane	40.5 cm
Viscosity of water	0.01 g/cm·s
Density of water	1.0 g/cm^3
Density of flocs	1.0068 g/cm^3
Sludge wasting rate	0.0 mL/s
Influent flow rate	−mL/s
Effective floc radius	$r = r_\infty \exp [K_1/t]$
Viscosity parameter	$\alpha = \alpha_\infty \exp [K_2/t]$
Influent SSVF	$\mathrm{SSVF} = a\ \mathrm{Fe}^b$

[a] Variables in the equations for *R*, *S*, and Col were determined in the bench scale study. $r_\infty = 0.033$ cm, $K_1 = 0.4053$ min, $\alpha_\infty = 11.7$, $K_2 = 0.1999$ min, a = 3.67×10^{-3}, $b = 0.583$ where Fe is influent iron concentration in mg/L.

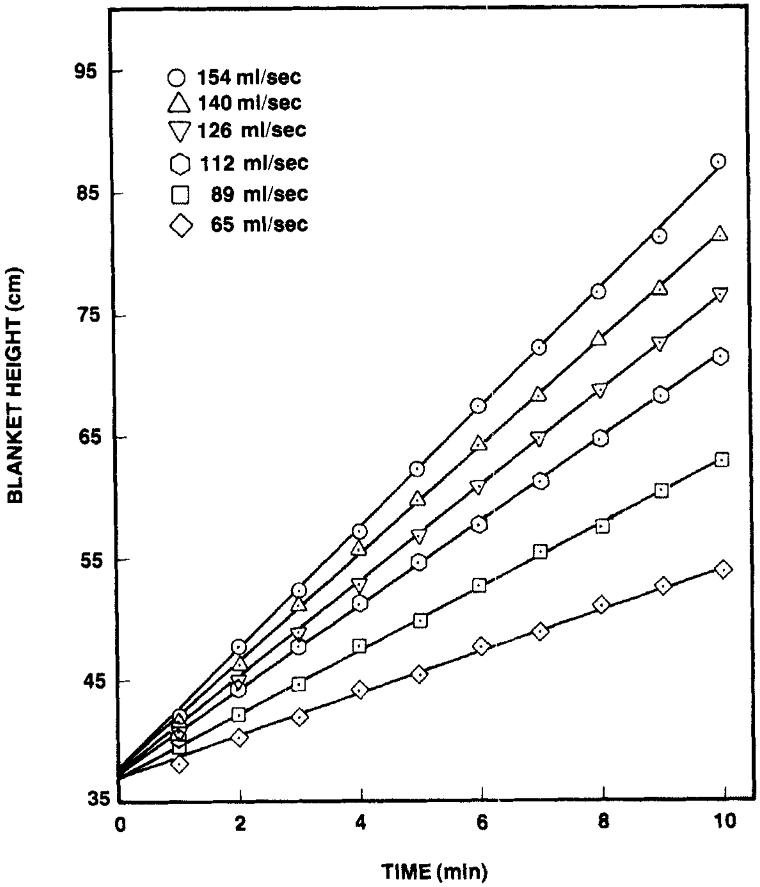

FIG. 16. Model predictions of blanket height as a function of time for various flow rates. Influent iron concentration = 1000 mg/L.

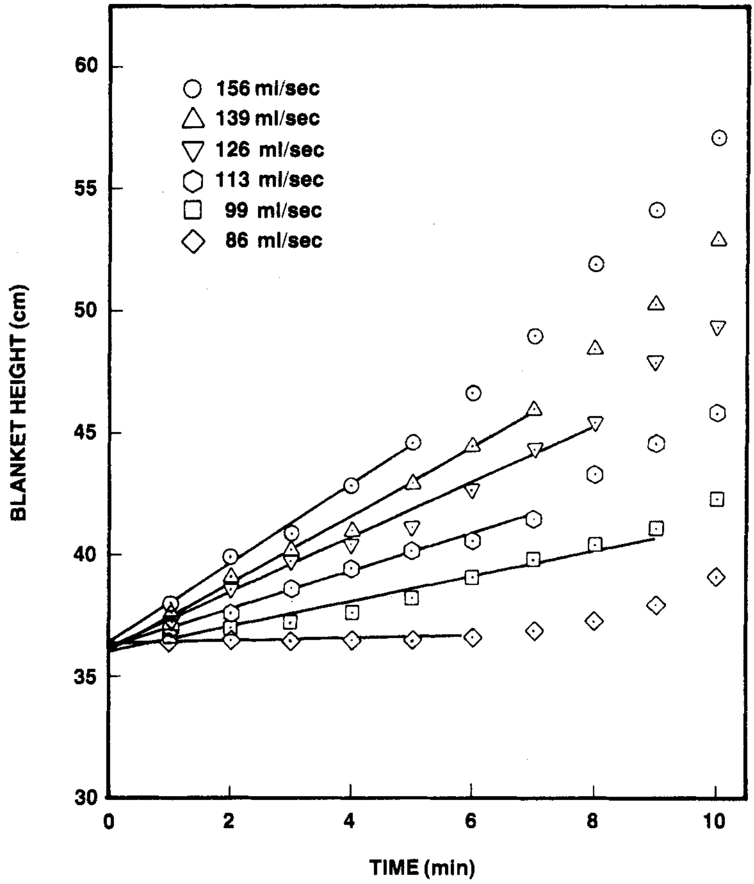

FIG. 17. Model predictions of blanket height as a function of time for various flow rates. Influent iron concentration = 400 mg/L.

during the course of a run. This was apparent in the experimental observations at lower flow rates, too. .It is understood by considering the behavior of dilute solids suspensions. Solids suspensions of low concentrations generally have rather high settling velocities with a rapid transition from hindered settling to thickening once the solids have settled into a slurry of greater concentration. The process is similar in the sludge blanket of the reactor-clarifier. Initially the solids concentration in the blanket is relatively low, and the high settling velocity of the solids nearly overcomes the upward velocity of the wastewater, resulting in a low blanket rise velocity. As solids build up in the blanket the settling velocity decreases, producing a larger

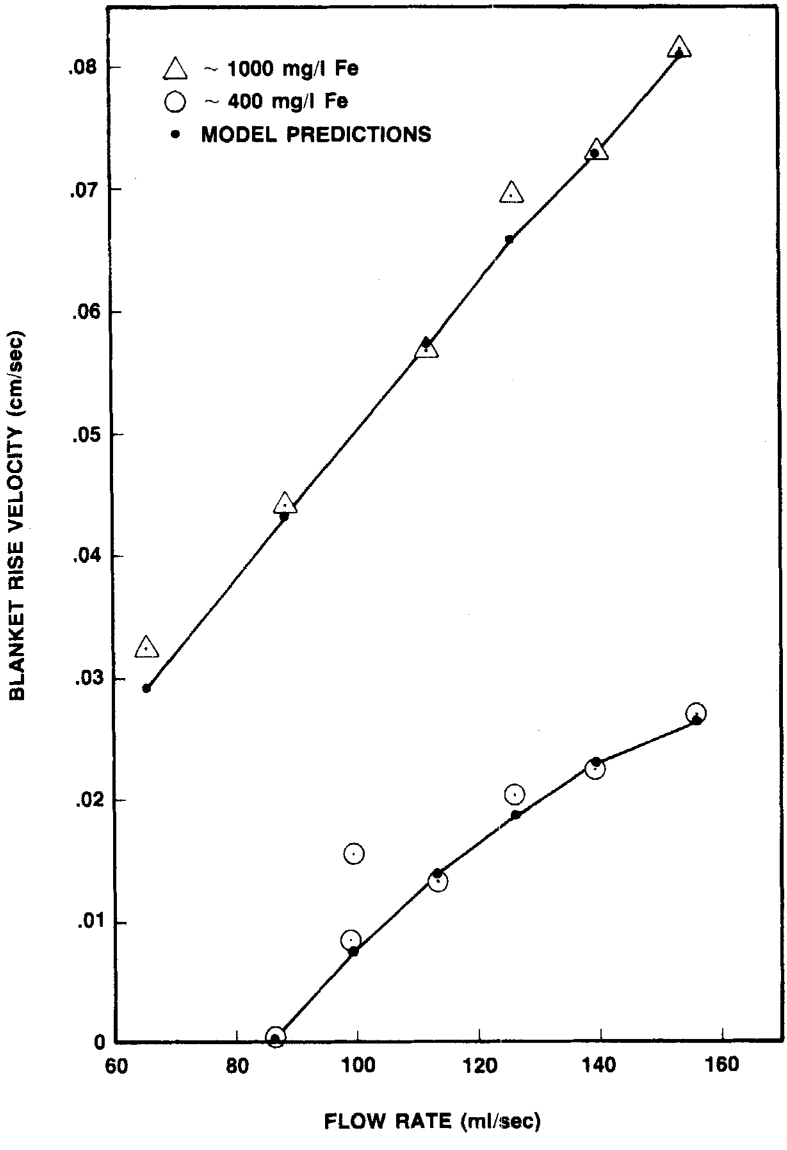

FIG. 18. Experimental results and model predictions of sludge blanket velocity in the reactor-clarifier as a function of flow rate. Influent iron concentrations = 400 (lower) and 1000 mg/L (upper).

blanket rise velocity. This change in blanket rise velocity is not seen in slurries of higher solids concentrations because the change in settling velocity as one makes the transition between hindered settling and thickening is smaller and less abrupt.

The blanket rise velocities calculated from the experimental data and those obtained from the computer model appear in Fig. 18. Agreement was good; the correlation coefficient for the 1000 mg Fe/L series was 0.997, and 0.949 for the 400 mg Fe/L series. The obvious outlier in the 400 mg Fe/L series was due to measurement of the blanket rise velocity too late in the run, after solids build-up in the blanket had enhanced the rate of rise. A second run, for which the rise velocity was measured before a large build-up of solids had occurred, yielded results in good agreement with the model.

Rapid-Mix Bypass Study

As noted above, the difference between the sizes of flocs produced under long and short rapid-mixer retention times is believed to be related to the time required for the polymerization of ferric hydroxide precursers. With relatively long rapid-mix retention times, the Fe(III) in the wastewater has ample time to react with the added OH^- and to complete the complex polymerization reactions in the rapid mixer. The solids so formed are immediately disrupted by the shear produced by the impeller, resulting in the formation of small, slow-settling floc particles. With short rapid-mix retention times the Fe(III) does not have sufficient time to react with the OH^- and to complete the polymerization reactions while in the rapid mixer. Therefore, while some solids are formed and disrupted in the rapid mixer, a portion of the dissolved iron initially in the wastewater passes unreacted or incompletely reacted from the rapid mixer into the relatively quiescent regions of the clarifier where the polymerization reactions continue to take place. When these reactions take place under quiescent conditions, large flocs with high settling velocities are produced, probably by the joining together of smaller floc particles by bridging. Flocs of the order of 2–5 mm across were readily formed in petri dishes under conditions of minimal gentle mixing. Much smaller floc particles (<0.5 mm across) were formed when the flocs were violently mixed during their formation.

This mechanism of floc agglomeration by chemical bridging in transiently supersaturated solutions explains why large, rapidly settling flocs are produced in reactor-clarifiers having short rapid-mix retention times. The mechanism also suggests a method by which the settling velocities of ferric hydroxide slurries may be increased regardless of the type of clarifier used. One expects that large, rapidly settling flocs could be produced through bypassing a small portion of influent wastewater around the rapid-mix operation and letting the bypassed iron react with excess alkalinity in the quiescent regions of the clarifier. The bypassed iron(III) would act like conventional polymeric electrolytes by precipitating on and bridging between existing floc particles, thereby agglomerating them into larger particles.

The proposed enhancement of settling by bypassing of influent was first tested in 1-L cylinders. A series of cylinders, each containing 1000 mL of simulated wastewater containing 600 mg Fe(III)/L, was prepared. A portion of the wastewater, ranging from 10 to 120 mL, was removed from each cylinder and set aside for addition later. Each cylinder then received 72 mL of 0.5 *N* NaOH, the alkalinity required to produce the optimum pH for iron removal in 1.000 L of the waste. The slurries were then mixed for at least 2 min with a high-speed laboratory stirrer. During the last few seconds of mixing, the wastewater which had been withdrawn earlier was added, thus simulating a wastewater bypass around the rapid-mix step. The settling velocities of the slurries were then measured by recording the height of the sludge interface with time. After completion of the settling measurements, the contents of the cylinders were remixed vigorously for at least 1 min and the settling velocities of the flocs were again determined.

As is seen in Fig. 19, a bypass of as little as 10 mL produced a significant increase in settling velocity compared to the re-mixed samples. The trend of increasing settling velocities with increased volume of wastewater bypass is what we would expect in the light of the increasing settling velocities observed with decreasing rapid-mix retention times in the bench scale reaction-clarifier.

These results, in which the settling velocities were more than doubled by the simulated bypass, encouraged us to apply the principle to the pilot scale reactor-clarifier. This was done by determining the relationship between sludge blanket rise velocity and influent flow rate for (a) the pilot plant operated as a simple upflow clarifier with exhaustively mixed floc, (b) the pilot plant operated as a reactor-clarifier, and (c) the pilot plant operated as a simple upflow clarifier with exhaustively stirred floc, but with 10% of the influent bypassing the rapid mixer. The simulated wastewater contained 600 mg Fe/L. The procedure for reaction-clarifier operation has been described above; blanket rise velocities for a number of flow rates were determined. The pilot plant was operated as a simple upflow clarifier by turning off the mixer housed in the clarifier and precipitating the iron in the 1000-L waste storage tank (which was kept vigorously stirred). The slurry was pumped to the clarifier, and blanket rise velocities were determined at several flow rates. The results of these two sets of measurements, together with the results of computer simulations, are shown in Fig. 20. (See Ref. *17* for details.)

Two bypass experiments were made; in each, simulated watewater was

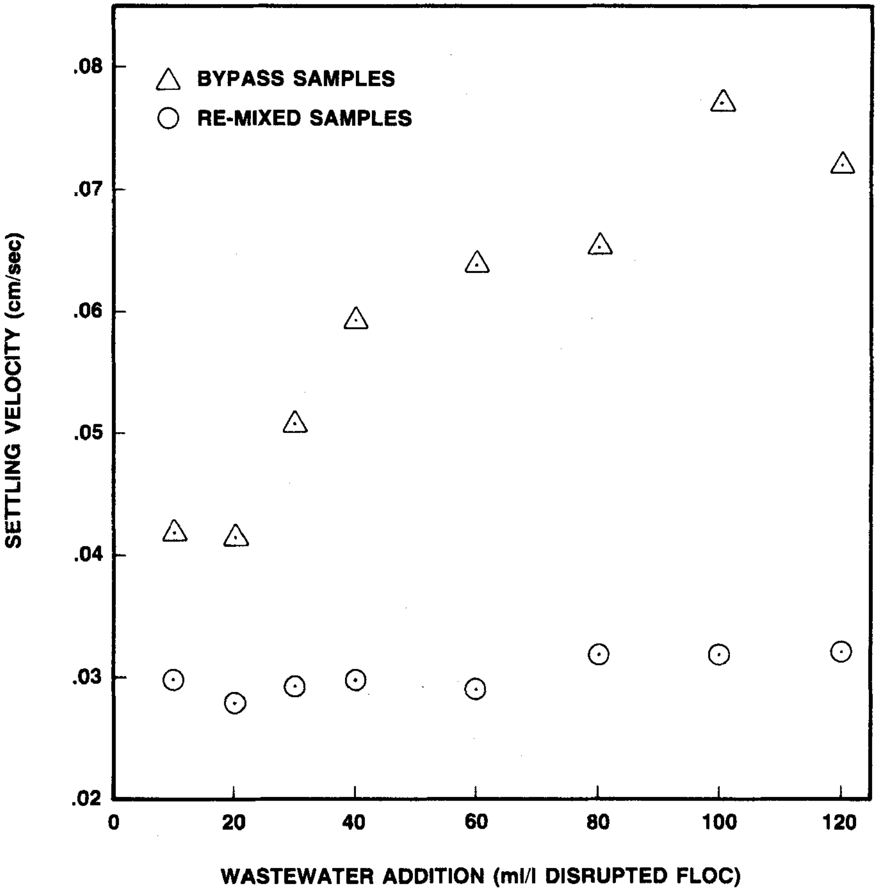

FIG. 19. Settling velocities of slurries receiving a small addition of wastewater after exhaustive rapid-mixing.

prepared in the 1000-L tank. A portion of the solution was then removed and placed in a 30-L tank which had been the reservoir in the NaOH feed system used in the reactor-clarifier runs. This feed system, which included a peristaltic pump and rotometer, was used to deliver bypassed wastewater to the clarifier during these runs. The wastewater remaining in the 1000-L tank received a dose of 0.5 *N* NaOH sufficient to precipitate all the iron originally present, so that the ferric hydroxide was precipitated in the large tank with excess alkalinity.

In the first of the two experiments the bypassed wastewater was introduced at the base of the reactor cone in the feed plane of the clarifier. The results of

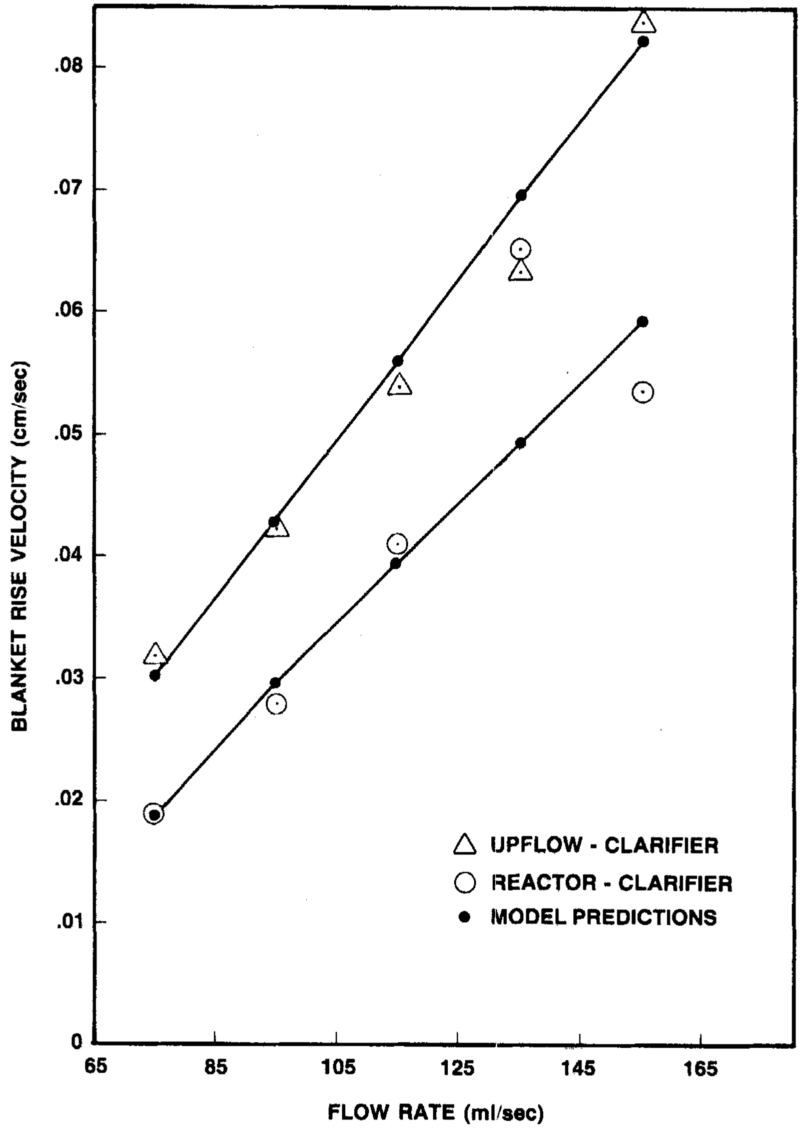

FIG. 20. Experimental results and model predictions of sludge blanket velocity as a function of flow rate for upflow clarifier (upper) and reactor-clarifier (lower) treating the same wastewater.

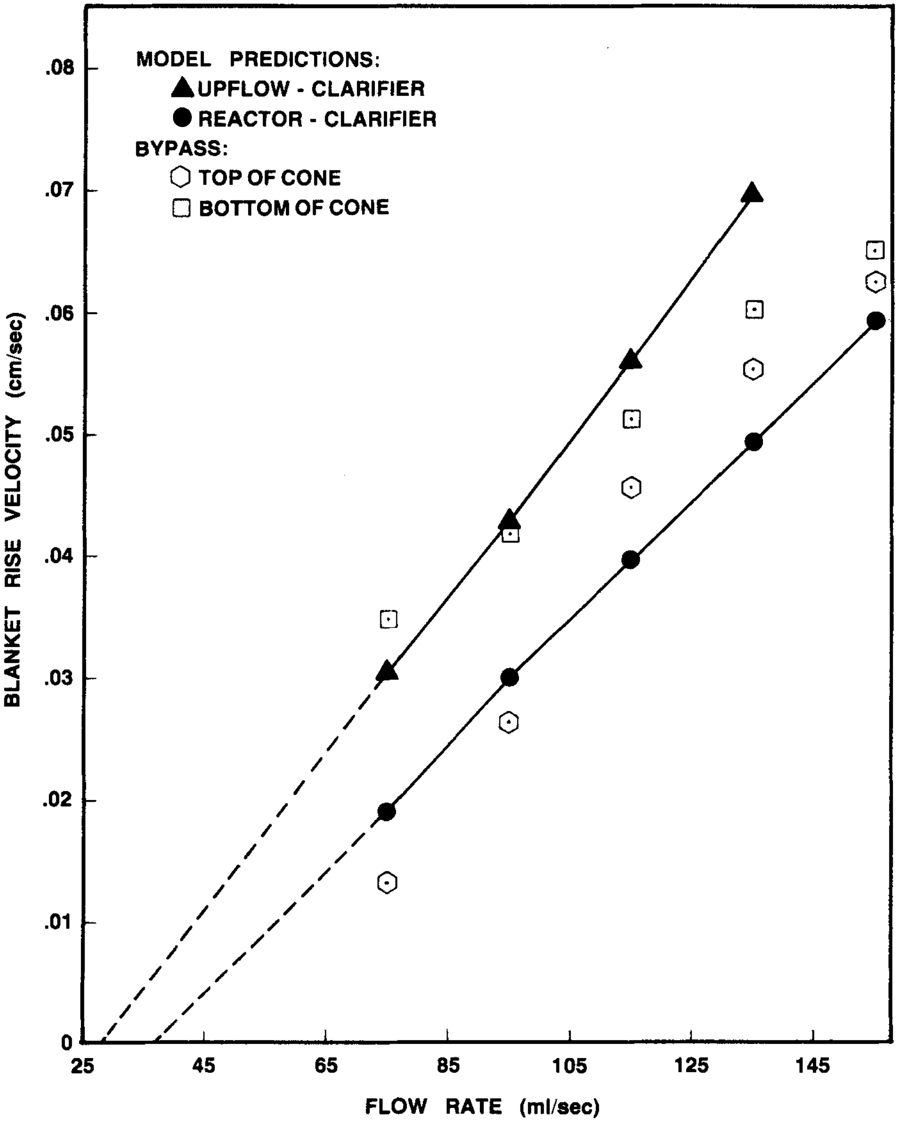

FIG. 21. Sludge blanket velocity as a function of flow rate for an upflow clarifier receiving bypassed wastewater at different locations within the clarifier.

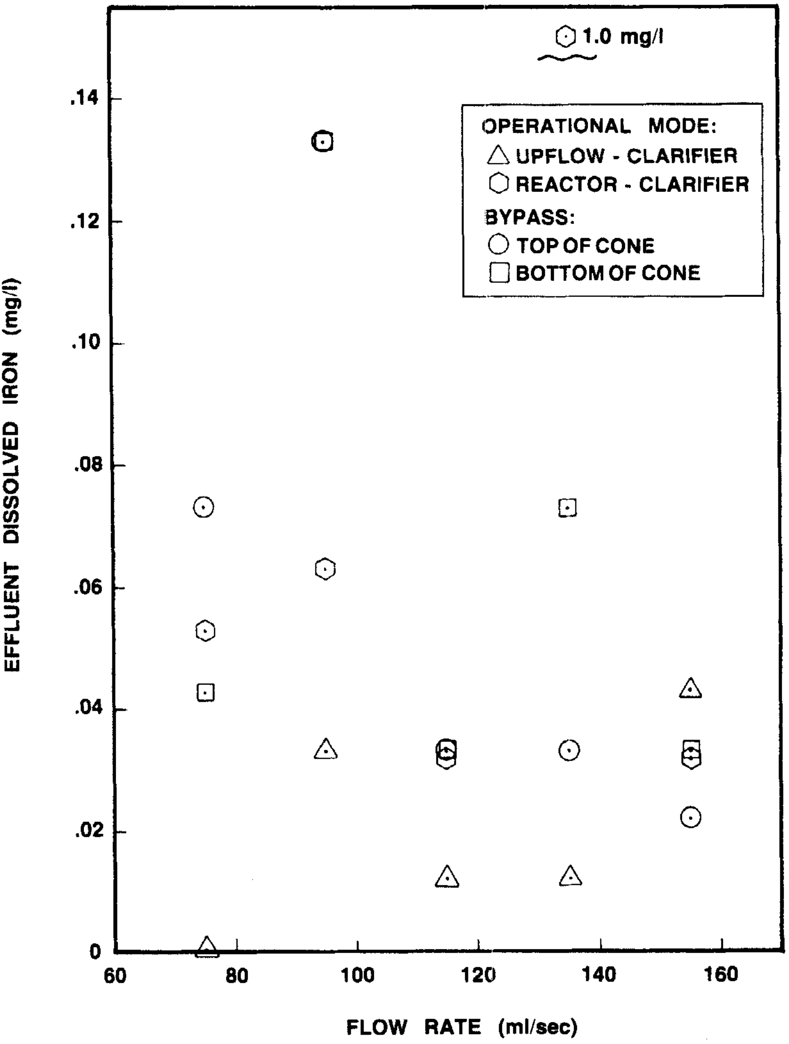

FIG. 22. Effluent dissolved iron as a function of flow rate for two clarifier operational modes and two wastewater bypass situations. Influent iron concentration = 600 mg/L.

these runs, made over a range of influent flow rates, were disappointing. Evidently the introduction of the bypassed waste in the feed plane did not provide sufficient mixing to produce the desired effects. A second experiment was therefore performed in which the bypassed waste was introduced with the precipitated waste at the top of the reactor cone. These runs also bypassed 10% of the waste.

Blanket rise velocities measured in the bypass experiments appear in Fig. 21, together with the predictions of the model for a clarifier and a reactor-clarifier treating the same wastewater (600 mg Fe/L). The bypass entering at the top of the reactor cone produced a significant decrease in blanket rise velocity as compared to bypass entering at the bottom of the cone and to operation as a simple clarifier. The blanket rise velocities produced by the second bypass experiment at the lower flow rates appear to be even lower than those produced under similar low flow conditions by the reactor-clarifier. If this difference turns out to be statistically significant on more detailed study, it is probably due to the fact that low flow rates in our reactor-clarifier produce increased rapid-mix retention times, allowing less dissolved iron to leave the rapid mixer and subsequently to be available for agglomeration of floc particles. Thus, at low flow rates the bypass may provide more iron for bridging of floc particles in quiescent regions of the clarifier than would be available in normal reactor-clarifier operation.

One can assess the impact of a wastewater bypass on clarifier capacity by extrapolating the measured blanket rise velocity data to determine the influent flow rate at zero blanket rise velocity. This gives the maximum flow rate of the given wastewater which can be treated by the clarifier while maintaining stable operation. Extrapolation of the upflow clarifier data gives a maximum treatable flow of 28 mL/s. The reactor-clarifier data extrapolate to give 37 mL/s, a 32% increase in capacity.

Extrapolation of the data for the run with a 10% bypass entering the top of the reactor cone yields a maximum treatable flow of about 50 mL/s, an increase of 79% over the capacity of the simple upflow clarifier.

The use of a wastewater bypass had relatively little effect on effluent quality. Effluent dissolved iron was less than 0.14 mg/L for all but one run, as seen in Fig. 22. The effluents from the bypass experiments were higher in suspended solids than the effluents produced from either upflow clarifier or reactor-clarifier runs, as we see in Fig. 23. We note that additional work is needed on this point. These data were obtained under conditions of hydraulic overload, which is not the normal mode of clarifier operation. Second, little effort was made to insure complete mixing. Use of an in-line blender or similar device to provide thorough mixing of the bypassed effluent with the main stream under conditions of very short rapid-mix retention time may

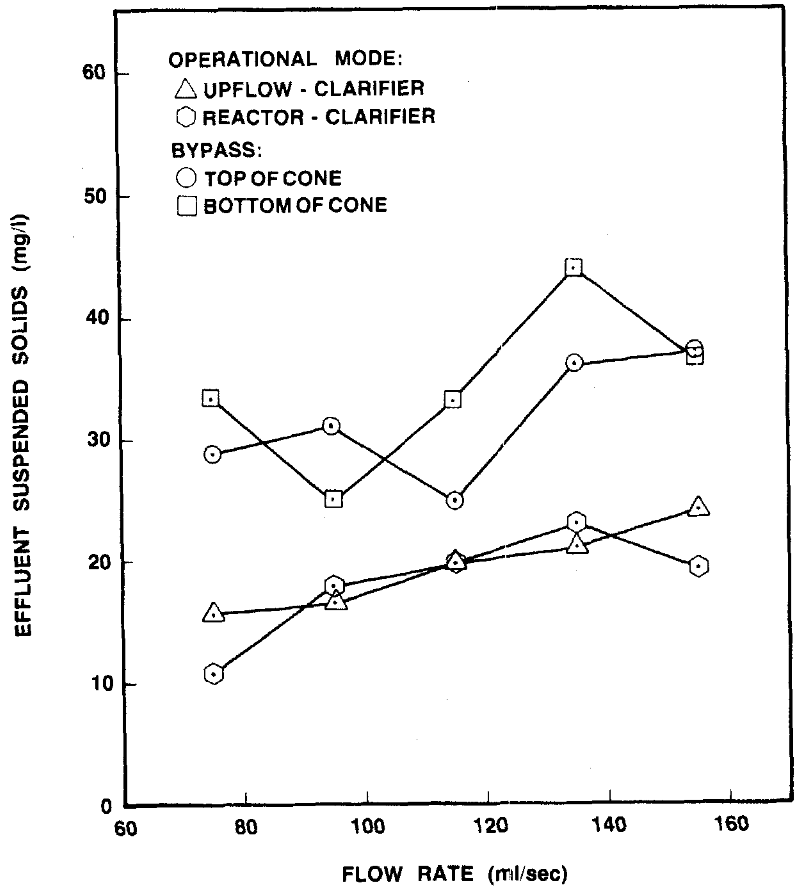

FIG. 23. Effluent suspended solids as a function of flow rate for two clarifier operational modes and two wastewater bypass situations. Influent iron concentration = 600 mg/L.

provide substantial improvement. We hope to explore both of these points shortly.

DISCUSSION AND CONCLUSIONS

The model developed above can be explained qualitatively in the following way. First, the *G* values in the rapid mixer are so large that any floc aggregates in the rapid mixer are disrupted essentially instantaneously, even for *G* values at the lower end of the range used. Second, the failure of well-beaten flocs to re-agglomerate indicates that agglomeration and disruption of these flocs are not readily reversible; if floc agglomeration were by van der Waals forces or weak coulombic attractions, the flocs should be able to re-agglomerate after exhaustive rapid mix. The fact that they can't indicates that the agglomeration forces are of a different type. Third, agglomeration appears to occur most readily within less than a minute after the reagents are mixed.

These facts suggest that the agglomeration of ferric hydroxide flocs is brought about by the continued precipitation of filaments, meshes, etc. of $Fe(OH)_3$ from the still supersaturated solution after it has moved from the rapid mixer into a portion of the clarifier in which the *G* values are small enough that the aggregates, bound together by these filaments of $Fe(OH)_3$, are not torn to pieces.

This in turn suggests that reactor-clarifier performance would be very markedly improved by employing an extremely violent rapid mix of as short duration as possible consistent with adequate mixing of the reagents. The resulting solution should then be moved immediately from this region into a region in which the *G* values are low enough so that as the floc particles are linked together by the continued deposition of floc, they are not torn apart. The introduction of the precipitant (in this case NaOH) immediately upstream from an in-line blender at the influent entry to the reactor-clarifier should improve performance. So should the placement of baffles in the vicinity of the influent entrance to localize the entry turbulence in the main body of the clarifier.

There is also the possibility of improving the performance of upflow clarifiers by bypassing a small fraction of the influent around the precipitator and introducing it, with mixing, at the entrance to the clarifier. Our preliminary pilot scale studies on this look rather promising.

We note that the rate of reaction to form precipitate can be expected to vary from one metal hydroxide to another, and that work is needed on other elements than iron. It is unlikely that the values of the rate parameters K_1 and K_2 for aluminum or chromic hydroxides, for instance, are quite similar to those for ferric hydroxide. A comparison of Figs. 7 and 10 indicates the possibility of doubling or trebling the settling velocity of a floc, with a comparable increase in clarifier capacity. This makes the modest effort necessary to get the data for other metals definitely worth while.

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