JOURNAL OF COLLOID SCIENCE 19, 360–372 (1964)

A MATHEMATICAL MODEL OF COAGULATION[1]

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Received July 15, 1963: revised December 27, 1963

Abstract

A simplified mathematical model of floc growth in a stirred suspension is developed with the aid of the Smoluchowski equation for orthokinetic coagulation. Particles are assumed to be spherical and to conjoin into spheres of proportionate volume upon contact. Particle growth is restricted to different maximum sizes or multiple volumes, larger particles breaking up into smaller ones which are returned to the system. A smooth growth pattern asymptotically approaching a steady-state mean size results when a model parameter of gross contact opportunity is less than 0.04 in magnitude; as it approaches 0.10, the growth pattern becomes oscillatory. Oscillatory growth was observed also experimentally when a controlled shear gradient was imposed on a suspension of iron flocs.

Introduction

One of the most effective unit operations of water purification is the coagulation of colloidal and otherwise finely divided particles in advance of sedimentation and filtration. By incorporatng dispersed substances into chemical matrices or attaching them to each other or to flocculent precipitates, the resulting agglomerates become larger and heavier and, consequently, more settleable, and more filtrable. In essence, therefore, coagulation is preparation of unwanted suspensoids for phase separation. Because coagulation takes time, the rate of coagulation is one of the determing factors in water-purification design. The rate, it is known, is a function of many factors that affect coagulation in diverse ways. Those to be considered here may be lumped together under the rubric of contact opportunity, namely, the chance for particles to approach close enough for short-range, interfacial forces to come into play. Obviously this opportunity, which complements chemical destabilization, is time dependent as well as motion dependent. Accordingly, we have turned to resolution of Smoluchowski's formulations of colloid removal by coagulation, introducing to this purpose numerical solutions that have become computationally feasible through high-speed digital computers.

[1] Presented at the Symposium on Coagulation and Coagulant Aids, American Chemical Society General Meeting, Los Angeles, California, April 1–3, 1963.

According to Smoluchowski, colloids are coagulated in two primary ways: by perikinesis (1) or particle diffusion, and by orthokinesis (2) or fluid motion. Both of these he formulated as infinite sets of differential equations, each of which contains infinite series. Of the two, the equation for orthokinetic flocculation provides what we are after, namely, a rational and useful measure of the effect of fluid motion (natural or induced) on the rate of coagulation or degree of contact opportunity.

We shall write it as follows:

$$J_{ij} = (4/3)n_i n_j R_{ij}^3 (du/dz). \qquad [1]$$

Here J_{ij} is the number of contacts in unit time and fluid volume between n_i particles of size i and n_j particles of size j; du/dz is the local velocity gradient to which the particles were exposed within the fluid; and R_{ij} is the radius of the sphere of influence encompassing the two particles, or the greatest distance between particle centers at the time of their effective conjunction.

In order to test the validity of computational manipulation, let us turn also to Smoluchowski's perikinetic formulation

$$I_{ij} = 4\pi D_{ij} R_{ij} n_i n_j , \qquad [2]$$

where i, j, n, and R carry the same connotations as in Eq. [1], but D_{ij} is the mutual diffusion coefficient of an i and a j particle, and I_{ij} is their number of conjunctions by diffusion.

Neither equation is strictly and fully descriptive of the coagulation process. Yet both of them can be useful in water-purification design by identifying the manageable controls. Camp (3), for example, has referred to Smoluchowski's concepts in ordering the design and operation of mixing and coagulation basins and appurtenant stirring devices in water-treatment plants. Specifically, he identified empirically optimal or near optimal velocity gradients and detention times for stirring equipment and flocculation tanks. A wider and more general application of the equations in the practical management of coagulation has lacked a suitable analytic solution of the orthokinetic equation. Since it cannot be the purpose of this paper to provide one, we substitute a study of the utility of a mathematical model of floc growth based upon Smoluchowski's orthokinetic equation.

We proceed first to the perikinetic equation, for which there is an apparently reasonable solution. Written in differential form, it states that at time t the time rate of change in the number n_k of particles of size k in a unit volume of sol during coagulation is:

$$\frac{dn_k}{dt} = 2\pi \left[\sum_{\substack{i=1 \\ j=k-i}}^{k-1} D_{ij}\, R_{ij}\, n_i\, n_j - 2n_k \sum_{i=1}^{\infty} D_{ik}\, R_{ik}\, n_i \right], \qquad [3]$$

where D_{ik} and R_{ik} are simple variates of D_{ij} and R_{ij}. In similar fashion the orthokinetic equation states that:

$$\frac{dn_k}{dt} = \frac{2}{3}\frac{du}{dz}\left[\sum_{\substack{i=1\\j=k-i}}^{k-1} n_i\, n_j(R_i + R_j)^3 - 2n_k \sum_{i=1}^{\infty} n_i(R_i + R_k)^3\right], \qquad [4]$$

where R_i, R_j, and R_k are the effective radii of particles of size i, j, and k, respectively. Utilizing Smoluchowski's assumption that $D_{ij}R_{ij} = (D_i + D_j)(R_i + R_j)$, where D_i and D_j are the individual diffusion coefficients of particles of size i and j, respectively, one can write (4)

$$D_{ij}R_{ij} = D_1R_1[4 + (\sqrt{R_i/R_j} - \sqrt{R_j/R_i})^2]. \qquad [5]$$

Moreover, when R_i and R_j are of about the same size, $D_{ij}R_{ij}$ closely equals $4\, D_1R_1$, and one arrives by this simplification at the following analytical solution for Eq. [3]:

$$n_k/N_0 = (t/T)^{k-1}/(1 + t/T)^{k+1}, \qquad [6]$$

where t is the time allowed for coagulation and $T = 1/(8\pi D_1R_1N_0)$ is the half-time of coagulation, namely, the time required to halve the starting number N_0 of particles per unit volume. At time t the total number N_t of particles per unit volume is

$$N_t/N_0 = 1/(1 + t/T). \qquad [7]$$

Computational Methods and Tests

To develop the growth pattern of coagulation described by Eq. [4], its equivalent finite difference equation was programmed for numerical solution by an iterative procedure[2] based upon the following simplifying assumption: all particles are spherical and conjoin into spheres of equivalent total volume. This assumption was introduced even though it applies more closely to the coalescence of emulsions than to the coagulation of sols. For it does in fact represent the simplest possible merging of particles and creation of the smallest possible radius of interaction of the resultant mass.[3]

Maximum stable sizes of coagulum (MAXVOL) were read into the computer, the largest one being 100. Although this would have had to be

[2] Flow charts and FORTRAN listings are contained in the junior author's doctoral thesis entitled "Some Aspects of Orthokinetic Flocculation." See reference 7.

[3] In a more specific study of coagule form resulting from aggregation, published since our results were first presented, Vold (5) has assumed that spheres conjoin randomly without coalescence. The radius of interaction of the resultant mass appeared to vary as the 0.43 power of its volume. It would be a simple matter, therefore, to apply this exponent in our computational procedures in place of the 0.33 power characteristic of coalescence.

done, in any case, because available computer memory space is finite, the action rested also on consideration of coagulum breakup by hydraulic shear supported by experimental observation of chemical floc growth. In our computations, finally, growth towards a limiting steady-state particle size was observed and no significant shift in growth pattern manifested itself when the maximum size limit was raised progressively. What is not yet resolved is whether conjunction stops, or oversize particles break up into two or more particles equal or unequal in size. Accordingly, both possibilities were accepted into the program.

Conjunction stoppage could be simulated by returning oversize aggregates to their immediately preceding and hence stabel size (BRAKUP 1); hydraulic breakup by splitting unstable conjunctures into approximately equisized particles (BRAKUP P), where P is an integer equal to or greater than 2. In computer operations with BRAKUP 1, therefore, the rate of aggregation was dropped to zero when a particle of the maximum size was involved; in BRAKUP P, aggregation involving a particle of maximum size proceeded at an undiminished rate. The magnitude of P was a specific input variable.

Other program inputs were the initial particle size distributions, either mono- or polydisperse; and the magnitude of a constant (XKK), a simulant of the velocity gradient du/dz together with numerical constants of the equation and scale factors. Although a breaking up of coagula into other than two equisized particles seems unlikely, this possibility could not be denied with certainty. Accordingly, it was retained in the program. Indeed, Bartok and Mason (6) have shown that there are conditions under which large droplets assume sigmoidal shapes from which many smaller droplets are shed.

Whether programming modifications could affect computer results significantly was tested by incorporating the procedures applied to orthokinetic calculations also in a parallel computer program for the perikinetic equation (Eq. [3]) and comparing the calculated results obtained with available analytical evaluations. Moreover, the two relationships for $D_{ij}R_{ij}$, namely, that of Eq. [5] and that of Smoluchowski's simplification $D_{ij}R_{ij} \doteqdot 4D_1R_1$, were introduced into separate computer runs. By choice, the initial population of particles was monodisperse, the velocity-gradient, particle-number product C was 0.02, the limiting particle size (MAXVOL) was 40, and the breakup routine (BRAKUP) was 1. The computer results are plotted in Fig. 1 along with Smoluchowski's analytical solution. Half times of coagulation were approximated by graphical interpolation between computer values. As shown in Fig. 1, comparisons are eased by plotting the reciprocal of the proportion of particles remaining (N/N_0) against the relative coagulation time t/T. For Run 24, $D_{ij}R_{ij}$ issues from Eq. [5]; for Run 26, from Smoluchowski's simplification for particles of

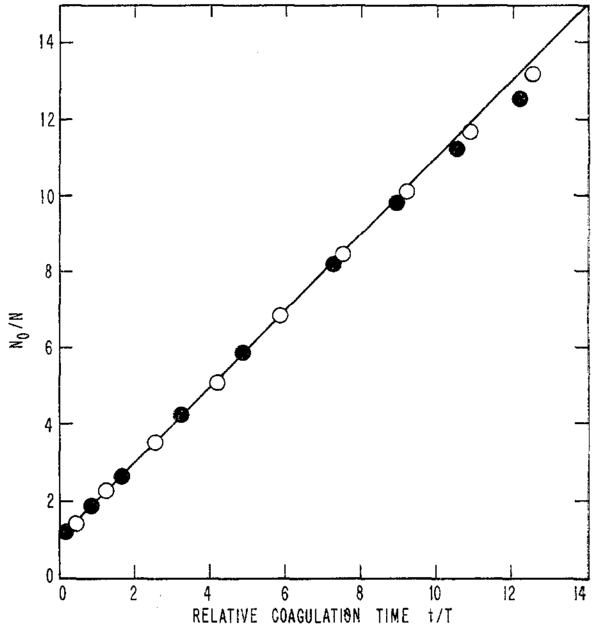

FIG. 1. Linearizing plot for second-order decrease in total number of particles in perikinetic coagulation. ○ Run 24, ● Run 26, analytic solution by Smoluchowski shown as solid line.

not too different size: $D_{ij}R_{ij} = 4D_1R_1$. Agreement between analytical and computational results and agreement between approximate and fully simplified values are seen to be good, especially during early coagulation. Up to $t/T = 10$, divergence is less than 3%; beyond that, it is somewhat more.

ORTHOKINETIC RESULTS

Only enough results are included in this paper to suggest a wider usefulness of the mathematical model of orthokinetic coagulation for evaluating the presumptive effects of: size-limited growth; initial concentration of particles; velocity gradient; relative time of exposure; and combination of gradient and initial concentration as contact opportunity.

The results incorporated in Fig. 2, for example, are an indication of how conjunction stoppage (BRAKUP 1) and breakup into 2, 3, and 4 equisized particles affect the relative number (N/N_0) and mean volume of particles when velocity gradient and initial concentration of particles are the same ($C = 0.01$), along with the maximum particle size (MAXVOL = 20). Generally, similar curves exhibit rapid initial increases in particle mean sizes and appropriate decreases in relative particle numbers. Steady-state

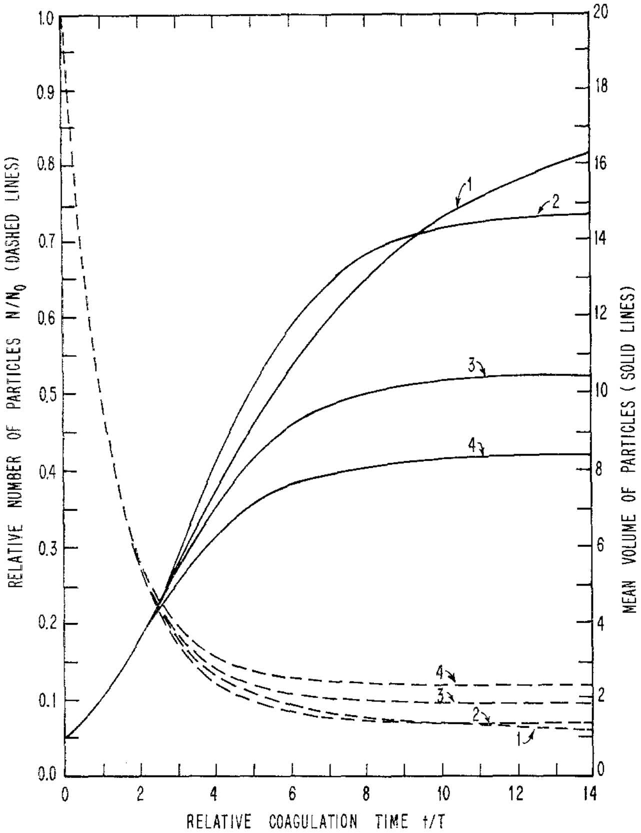

FIG. 2. Effect of conjunction and breakup on floc growth and total number of particles in orthokinetic coagulation. $C = 0.01$, MAXVOL $= 20$, $T = 17.7$; 1, BRAKUP 1 (Run 21); 2, BRAKUP 2 (Run 29); 3, BRAKUP 3 (Run 13); 4, BRAKUP 4 (Run 30).

conditions are soon reached, although less quickly when oversized conjunctions are returned to their immediately preceding stable size than when split into equisized parts. Understandably, multiple breakup makes for smaller mean particle volumes and larger relative numbers of particles.

The results plotted in Fig. 3 are internally more complex though outwardly quite comparable. The velocity-gradient, initial-number parameter C occurs twice each as 0.01 and 0.02, and once as 0.04; MAXVOL appears once as 8, three times as 20, and once as 40; half time of coagulation T is as small as 4.0 once, becomes 8.7 twice, and once each as large as 17.7 and 18.7, but the breakup routine is the same (BRAKUP 3). A change in maximum stable particle volume (MAXVOL) from 8 to 40 units (fivefold) is seen to shift the steady-state mean particle volume from about 4 to 20 units (also fivefold). At the same time the steady-state relative number of particles drops from 0.23 to 0.05 unit (also fivefold). The general nature of the curves, however, is much the same. Because the velocity gradient parameter (XKK) and the initial concentration of particles (N_0) were found to behave as their product $C = N_0(XKK)$, the component variables are not shown by themselves.

As seen in Fig. 3, the small difference in range of C from 0.01 to 0.04 did not bring out significant differences in the curve traces. However, when C was pushed up to 0.08 or more and the size-limiting mechanism was shifted to BRAKUP 10, particle growth began to oscillate as in Fig. 4. Here, initial growth rates and steady-state mean volumes do not differ

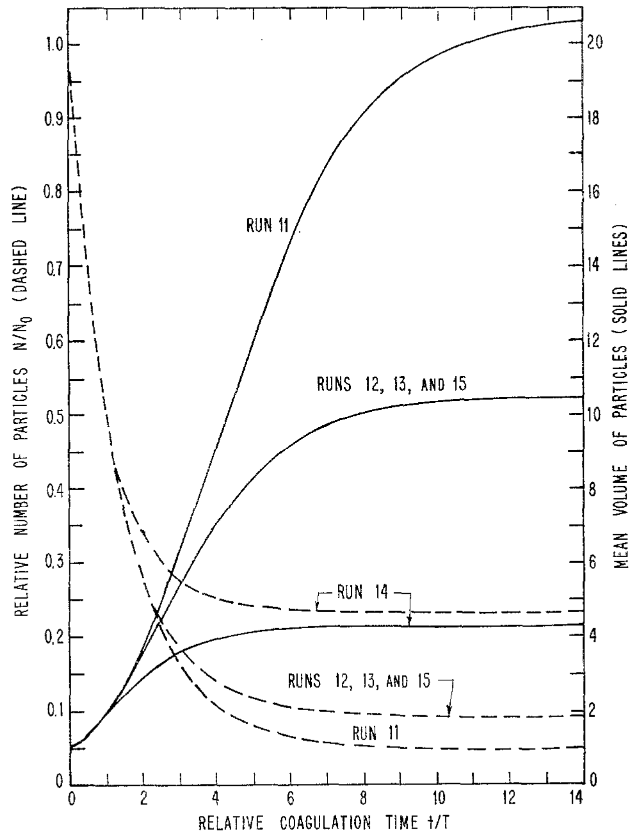

FIG. 3. Effect of other input variables on floc growth and total number of particles in orthokinetic coagulation. All runs used BRAKUP 3. Run 11, $C = 0.02$, MAXVOL = 40, $T = 8.7$; Run 12, $C = 0.04$, MAXVOL = 20, $T = 4.0$; Run 13, $C = 0.01$, MAXVOL = 20, $T = 17.7$; Run 14, $C = 0.01$, MAXVOL = 8, $T = 18.6$; Run 15, $C = 0.02$, MAXVOL = 20, $T = 8.7$.

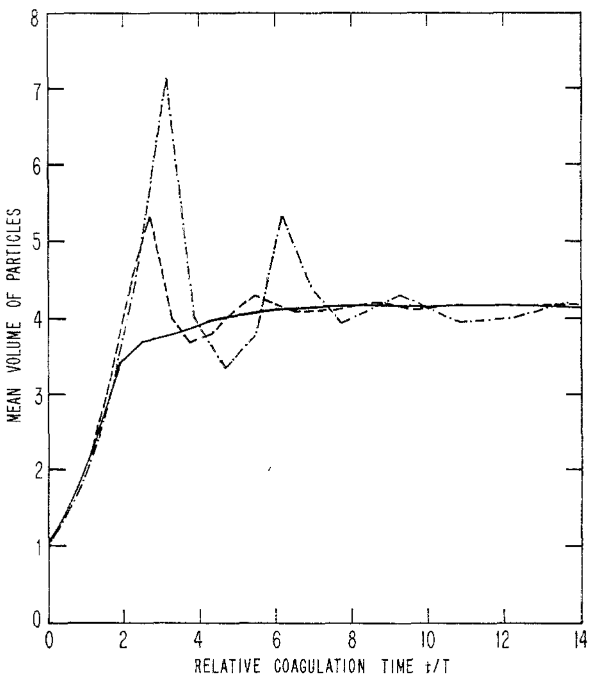

FIG. 4. Effect of input variables on floc growth in orthokinetic coagulation. MAXVOL = 20, BRAKUP = 10; Run 45, C = 0.04, T = 4.09 ——; Run 46, C = 0.08, T = 1.84, -----; Run 47, C = 0.10, T = 1.42 —·—·—.

much at the beginning. Soon, however, peaking becomes pronounced and the more so, the greater the value of C. When C is as low as 0.04, particle growth is steady and the size-limiting effect of BRAKUP asserts itself before the supply of small particles is exhausted. Indeed, small particles are reborn continuously. As C approaches 0.1, it appears that particles grow so rapidly in size and the supply of original particles is drawn upon so heavily before BRAKUP can take effect that virtually no small particles remain in reserve at peaking times. Rebuilding these reserves produces the trough in the growth curve, and subsequent cyclical swings are understandably repeated in decreasing amplitude.

The multiple effects that comprise Fig. 4 are identified more closely in Tables II and III for Runs 45 and 47. Table I, containing the results of Run 21, precedes them in order to highlight the gradual transitions in size distribution that typify smooth growth. The marginally stable pattern of Run 45 is detailed in Table II. A selection of results from Run 47, finally, illustrates the high degree of fluctuation in numbers of particles of specified size when the growth pattern becomes notably oscillatory.

Reduction of the number of particles in the course of coagulation did not

TABLE I

Particle Size Distribution Changes during Coagulation. Run 21, C = 0.01, BRAKUP 1, T = 17.7, N_0 = 1000

Paticle volume V_i	Relative coagulation time t/T						
	1.13	2.85	4.52	5.65	7.92	11.30	16.95
1	256.61	72.50	31.93	20.71	10.01	4.01	1.05
2	87.63	26.80	11.93	7.85	3.95	1.73	0.54
3	43.25	15.19	7.02	4.73	2.51	1.20	0.45
4	24.63	10.21	4.92	3.40	1.89	0.97	0.41
5	15.23	7.63	3.89	2.76	1.62	0.90	0.44
6	9.82	6.03	3.24	2.36	1.45	0.86	0.46
7	6.57	5.03	2.88	2.17	1.40	0.89	0.53
8	4.48	4.30	2.62	2.03	1.37	0.91	0.59
9	3.12	3.81	2.50	1.99	1.42	1.00	0.71
10	2.18	3.43	2.40	1.97	1.46	1.08	0.81
11	1.55	3.15	2.35	1.97	1.51	1.15	0.86
12	1.11	2.94	2.35	2.03	1.61	1.27	1.00
13	0.80	2.82	2.44	2.17	1.80	1.49	1.25
14	0.58	2.74	2.55	2.34	2.01	1.74	1.51
15	0.43	2.74	2.77	2.62	2.36	2.13	1.95
16	0.31	2.78	3.06	2.99	2.81	2.62	2.48
17	0.24	2.97	3.57	3.61	3.55	3.45	3.40
18	0.18	3.31	4.41	4.62	4.75	4.79	4.85
19	0.15	4.16	6.30	6.93	7.52	7.92	8.25
20	0.13	7.76	15.26	18.42	22.26	25.05	26.86
Mean volume	2.18	5.25	8.45	10.24	12.94	15.35	17.12

yield successfully to first- or second-order kinetic description. However, multiplication of the parameter of contact opportunity $C = (XKK)N_0$ by its associated half time of coagulation T reduced a 25-fold variation in C between 0.004 and 0.10 to a less than 1.4-fold variation of CT in a range of 0.19 to 0.14. Had the drop in relative numbers been of second order, the product CT would have been a constant.

Although chemical floc-growth studies provided the incentive for our computer program, only brief reference is made here to comparable experimental results. To produce chemical coagula, ferric sulfate solution was added to bicarbonate solution to produce initial concentrations of 1.6×10^{-4} molar $Fe_2(SO_4)_3$ and 1.0×10^{-2} molar $NaHCO_3$, the final pH value being 6.8. After rapid stirring, the mixture was transferred to wide-annulus Couette cylinders that produced a wanted shear gradient at a specific rate of rotation. Particle growth was recorded in a series of photographs from which mean areas were determined by scaling the longest

TABLE II

Particle Size Distribution Changes during Coagulation. Run 45, C = 0.04, BRAKUP 10, T = 4.09, N_0 = 4000

Values of $n_i \times 10^3/N_0$ for stated V_i and t/T

Particle volume V_i	Relative coagulation time t/T						
	1.47	2.94	4.31	5.87	7.83	13.70	23.47
1	164.19	51.70	17.15	5.81	1.38	0.02	0.00
2	71.04	88.27	101.31	105.16	107.40	108.15	108.16
3	41.67	55.50	56.41	55.86	55.38	55.13	55.11
4	27.35	16.65	17.08	16.57	16.65	16.74	16.74
5	18.93	10.91	13.60	13.77	13.98	14.00	14.00
6	13.39	7.83	8.91	8.55	8.48	8.45	8.45
7	9.55	5.77	6.38	6.39	6.48	6.50	6.50
8	6.80	4.69	5.13	5.12	5.12	5.11	5.11
9	4.82	3.94	4.06	4.06	4.06	4.07	4.07
10	3.37	3.38	3.36	3.42	3.43	3.43	3.43
11	2.33	2.97	2.87	2.92	2.91	2.91	2.91
12	1.58	2.64	2.47	2.53	2.53	2.53	2.53
13	1.06	2.37	2.17	2.24	2.24	2.24	2.24
14	0.69	2.14	1.93	2.00	1.99	2.25	2.00
15	0.45	1.95	1.77	1.81	1.81	2.06	1.81
16	0.28	1.78	1.59	1.65	1.64	1.64	1.64
17	0.17	1.64	1.47	1.52	1.51	1.52	1.52
18	0.10	1.51	1.36	1.40	1.40	1.40	1.40
19	0.06	1.39	1.27	1.31	1.31	1.31	1.31
20	0.04	1.29	1.19	1.22	1.22	1.23	1.23
Mean volume	2.72	3.73	3.98	4.11	4.15	4.16	4.16

dimension of the floc image and the greatest width at right angles to this length. The resulting areas are plotted for three mean shear gradients in Fig. 5 against a nondimensional abscissa Gt, where G is the mean shear gradient in sec.$^{-1}$ and t is the time of flocculation in seconds. The product Gt, therefore, replaces[4] the normalized time-scale ratio t/T of the computational schemes. Fluctuations in floc area are seen to move towards steady-state values and oscillatory growth is most pronounced when the shear gradient is least (G = 3.2 sec.$^{-1}$). Its suppression by higher gradients of shear may be explained in part by the smaller size of compatible flocs. Failure of the rising limbs of the plotted values to be colinear at the start may be ascribed to inadequacies of time-scale approximations as well as information on early flocculation.

[4] If we accept the approximation of the second-order decrease in relative number of particles, the product Gt simulates the normalized time scale t/T for a constant value of N_0.

TABLE III

Particle Size Distribution Changes during Coagulation. Run 47, C = 0.10, BRAKUP 10, T = 1.42, N_0 = 1000

Values of $n_i \times 10^3/N_0$ for stated V_i and t/T

Particle volume V_i	Relative coagulation time t/T						
	1.55	3.10	4.64	6.19	7.74	13.94	31.0
1	76.09	22.97	9.04	2.84	1.08	0.02	0.00
2	68.19	12.10	140.13	65.91	112.72	106.20	104.84
3	92.61	9.31	83.47	22.87	72.16	57.93	52.77
4	127.42	7.14	23.11	15.47	17.00	14.90	16.29
5	0	7.78	17.53	13.65	13.00	10.96	14.24
6	0	7.06	8.53	9.11	7.45	6.68	8.45
7	0	6.60	1.82	9.66	3.92	5.72	6.45
8	0	6.76	1.63	8.50	2.75	4.49	4.98
9	0	9.74	1.36	7.95	2.40	3.78	4.04
10	0	9.07	1.21	7.39	2.08	3.17	3.43
11	0	9.10	1.28	5.77	1.85	2.82	2.95
12	0	9.08	1.33	4.32	1.64	2.75	2.62
13	0	9.00	1.25	3.30	1.60	2.64	2.36
14	0	7.26	1.11	2.22	1.69	2.44	2.05
15	0	5.07	0.93	1.51	1.75	2.28	1.79
16	0	2.04	0.74	1.07	1.83	2.02	1.62
17	0	0	0.73	1.00	1.97	1.72	1.59
18	0	0	1.14	1.45	2.18	1.57	1.53
19	0	0	1.47	1.82	2.24	1.71	1.53
20	0	0	1.53	1.21	1.59	1.45	1.47
Mean volume	2.74	7.14	3.34	5.35	3.95	4.25	4.26

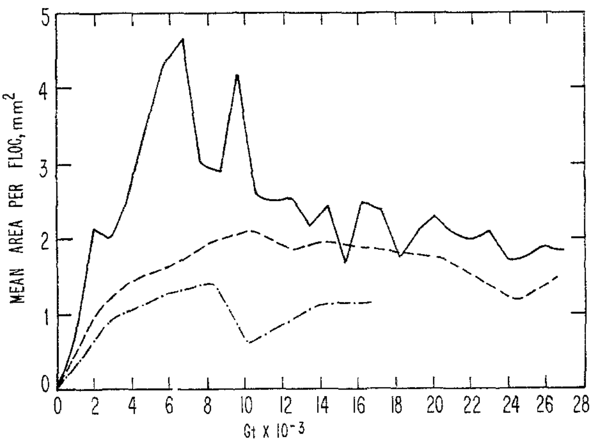

FIG. 5. Variation in mean floc size during flocculation. $Fe_2(SO_4)_3$ = 1.6×10^{-4} mole/liter, $NaHCO_3$ = 1×10^{-2} mole/liter, G = Mean Shear Gradient (sec.$^{-1}$), t = time of flocculation (sec.), pH = 6.8; —— G = 3.2; -----G = 6.8; —·—·—G = 9.3.

SUMMARY

Smoluchowski's equations for orthokinetic coagulation, that is, coagulation promoted by fluid motion, cannot be solved analytically. They can, however, be adapted to produce numerical solutions by reasonable use of high-speed digital computers. Adaptation includes imposition of both an upper, conceivably shear-controlled, limit on particle size and a breakup routine on oversized particles. The technique employed receives support from the fact that its application to Smoluchowski's formulation of perikinetic flocculation is in reasonable agreement with the analytical solutions available for the perikinetic equation. The proposed modification is but one of many alternatives. Its limitations remain to be explored more fully. Exactly why and how flocs break up in different circumstances remains to be determined experimentally. So does the upper size limit of conjunction, although existing evidence (7) suggests it may be inversely related to the magnitude of the mean velocity gradient.

The decrease in number of particles during coagulation cannot be fitted by a second-order kinetic expression. Yet the divergence may be small enough to justify the assumption of second-order kinetics in the design and operation of water-treatment plants. The product of mean shear gradient, G, initial concentration of particles N_0, and half-time of coagulation, T, then becomes nearly constant. Accordingly increases in G (a function of stirring) and N_0 (a function of coagulant dose) may result in a proportionate decrease in the half time of coagulation or a proportionate speed-up in rate of particle growth. Within limits, too, small values of N_0 may be offset by larger values of G.

Comparable chemical studies suggest that mean floc size decreases with increasing G values, thus limiting the usefulness of high mean shear gradients; for the aim of particle growth in water treatment is not only the rapid coagulation of colloids but also their conjuncture into particles of such size and weight that they are readily separated from the suspending water by sedimentation, filtration, or both.

If oscillatory floc growth is reproducible in practice, it should be possible to improve sedimentation by terminating fluid agitation at or just before a peak (preferably the highest in magnitude and shortest in time) is reached. At that instant, virtually no small particles are left in suspension and mean particle size is maximal. Settling rates, too, are presumably optimal and sedimentation basins can be reduced in size without lowering their efficiencies.

The conclusions here presented are drawn from batch-type operations. Continuous flow is expected to replenish small particles and diminish the likelihood of oscillatory growth—a matter that remains under study.

The work reported in this paper was supported in part by Public Health Service Research Grant WP-00024 from the Division of Water Supply and Pollution Control. The computations were performed, in part, at the computation centers of the Massachusetts Institute of Technology and Harvard University.

References

1. Smoluchowski, M., *Physik. Z.* **17,** 557 (1916).
2. Smoluchowski, M., *Z., Physik. Chem.* **92,** 129, 155 (1917).
3. Camp, T. R., *Trans. Am. Soc. Civil Engrs.* **120,** 1 (1955).
4. Müller, H., *Kolloid-Z.* **38,** 1 (1926).
5. Vold, M. J., *J. Colloid Sci.* **18,** 684 (1963).
6. Bartok, W., and Mason, S. G., *J. Colloid Sci.* **14,** 13 (1959).
7. Gemmell, R. S., Ph.D. Thesis, Harvard University Archives, Cambridge, 1963.