

*2004 ECI Conference on Separations Technology VI: New
Perspectives on Very Large-Scale Operations*

Kingfisher Resort, Fraser Island, Queensland, Australia

Editors: Chris Fell, University of New South Wales, Australia

George E. Keller II, MATRIC, USA

Year 2006

Paper 8

Coagu-Flocculation Mechanism of Flocculant
and its Physical Model

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http://services.bepress.com/eci/separations_technology-vi/8

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Abstract

On the basis of summarizing and analyzing the theory of coagu-flocculation and its practical application, this paper proposes a physical model for coagu-flocculation. The model defines the process of coagu-flocculation as three steps: mixing, coagulation and flocculation, though there is no strict distinction in the practical processes themselves. Through experiment, two facts are verified: (1) with organic flocculants mixing and flocculation occur substantially in the same step, and need strong mixing intensity; while with inorganic flocculants much weaker mixing intensity is needed; (2) so as to ensure big floccules are formed, weaker mixing for a certain period of time is required.

COAGU-FLOCCULATION MECHANISM OF FLOCCULANT AND ITS PHYSICAL MODEL

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ABSTRACT

On the basis of summarizing and analyzing the theory of coagu-flocculation and its practical application, this paper proposes a physical model for coagu-flocculation. The model defines the process of coagu-flocculation as three steps: mixing, coagulation and flocculation, though there is no strict distinction in the practical processes themselves. Through experiment, two facts are verified: (1) with organic flocculants mixing and flocculation occur substantially in the same step, and need strong mixing intensity; while with inorganic flocculants much weaker mixing intensity is needed; (2) so as to ensure big floccules are formed, weaker mixing for a certain period of time is required.

1. INTRODUCTION

Coagu-flocculation is a unit purification process and has the formation of floccules as its core. Two aspects determine its overall effectiveness. One involves the chemical function of coagulant, while the other involves the fluid dynamics of the facility. Not only highly efficient and economical coagulant usage are important for coagu-flocculation, but also good hydraulic conditions within the equipment are necessary to form denser coagulation particles, which will be helpful in the efficient operation of subsequent sedimentation and filtration. Because of the influence of many interactions, coagu-flocculation is a real headache for process operators. Previous studies have focused on a specific variable and have not given consideration to other variables . So far, there is no comprehensive study about the inter-relation between different variables. The efficiency of coagu-flocculation depends on: PH value, temperature, density and so on, but mainly depends on two factors ^[1]: an electric neutralization effect after hydrolysis of the coagulant and emerging compression of the electrical double layer; and □adsorbent bridging forming a macromolecular complex. All of these are determined by the characteristics of coagulant; the collision rate of particles and how it is ensured that the particles collide reasonably and efficiently. Particle contact and collision in water occur in five ways^[2]: □ Brownian Motion of particles; □ settling velocity difference of particles; □ laminar shear; □ turbulent shear; □ turbulent inertial collision. The last three are contributed to by the hydraulic conditions within the fluid.

The collision velocity of particles caused by Brownian motion is proportional to the temperature of water and the square of the concentration of particles, and this has nothing to do with the size of particles. In fact, only small particles undergo Brownian

*This project belongs to the Fund Subsidy Project of National Natural Science (Sanction Number: 50574111)

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Motion. With increase in particle size, Brownian Motion becomes weaker gradually and nearly disappears when diameter is more than $1\mu\text{m}$ [3]. For a common coagu-flocculation process, the diameter of particles usually increases from a micron level to a millimeter level, so the collision caused by Brownian Motion can be ignored. With respect to the collision caused by the differences of settling velocity, there are significant effects in the settler, but in the reactor, due to the strong turbulence present, the effect of differences in settling velocity is very small. Especially in the initial step of coagu-flocculation, the particle size is small, and settling velocity is low, so settling velocity differences between particles are even smaller. So the collision caused by differences of settling velocity usually can be ignored. Based on the above analysis, we can confirm that turbulent effects within the reactor are dominant in the acceleration of coagu-flocculation of particles.

2. MATHEMATICAL EXPRESSION FOR COLLISION BETWEEN PARTICLES IN COAGU-FLOCCULATION

2.1 Vortex shear Coagu-flocculation

The motion within an eddy in turbulent flow can be expressed as follows: [4]

$$u = \frac{k}{R^m} \quad (1)$$

where u is the tangential velocity at the point of interest, k is a constant; m an index, generally, between 0.5 and 0.9; and R is the distance between the point and the centre of the eddy (eddy radius).

The velocity gradient (plastic deformation) at radius R is:

$$s_R = \frac{\partial u}{\partial R} - \frac{u}{R} = -(m+1) \frac{k}{R^{m+1}} = -(m+1) \frac{u}{R} \quad (2)$$

Heisenberg has pointed out [5] that the turbulence also can be treated as an average flow with short term superimposed perturbations. This is identical to the idea of Cross that turbulent motion is a combination of complex compound laminar motion [6]. Using the Coagu-flocculation formula of Camp, the collision frequency N_{ij} between i and j particles, which is caused by the velocity gradient of the eddy in unit time and unit volume, can be expressed as:

$$N_{ij} = \frac{4}{3} n_i n_j (r_i + r_j)^3 \times |s_R| = \frac{4}{3} (m+1) n_i n_j (r_i + r_j)^3 \frac{u}{R} \quad (3)$$

where n_i is the concentration of particle i , n_j the concentration of particle j , r_i the radius of particle i and r_j the radius of particle j . The remaining symbols are as above.

2.1 Coagu-flocculation within vortex produced by rotation

In a vortex velocity field, coagu-flocculation particles move with the flow. If the vortex radius is R , particle radius is r , and density of the spherical particles is ρ_s , the collision frequency N'_{ij} between particle i and particle j , in unit volume and time caused by the radial velocity difference can be described as :

$$N'_{ij} = \pi n_i n_j (V_{0i} - V_{0j})(r_i + r_j)^2 \frac{u}{\sqrt{gR}} \quad (r_i > r_j) \quad (4)$$

where V_{0i} is the free settling velocity of particle i ; V_{0j} the free settling velocity of particle j ; The remaining symbols are as above.

The collision frequency brought about by a radial inertial centrifugal force not only increases as particle radius increases, but also depends on particle radius. Collision will never occur between particles with the same radius even at high velocity. So inertial centrifugal coagu-flocculation is remarkable for forcing small particles to stick to each other and the resultant particle radius to increase. We can reasonably conclude that in turbulent flow, vortex shear force and inertial centrifugal force are the major dynamic factors accelerating the collision of particles, with vortex shear force being the dominant effect.

So far no coagu-flocculation dynamic model can perfectly describe the real situation in the field of water treatment. This is because: (1) the Smoluchowski formula describes the collision frequency of particles under laminar flow conditions, but does not conform to the conditions in coagu-flocculation where turbulence is dominant [7]. (2) The Camp and Stein formula brings an energy factor into calculating velocity gradient, which is appropriate in water-treatment technology. But it is obvious that the calculated result is far different from the velocity gradient in a coagu-flocculation tank. According to the Camp and Stein calculation, the larger the velocity gradient, the better the coagu-flocculation effect that can be obtained. But in the grid coagu-flocculation reaction facility typically used, at the given distance behind the grid the turbulence can be approximately regarded as average turbulence whose characteristics are the same in every direction. Thus the time average velocity gradient is zero, but its impact is far superior to that in other coagu-flocculation facilities. An engineering example fully illustrating the limitation of the Camp and Stein formula is provided in [8]. (3) the Levich formula is derived for another technological field and has limited application in a turbulence viscous field [9, 10].

3. REAGENT DISPERSION AND COLLISION IN THE COAGU-FLOCCULATION MECHANISM

The coagu-flocculation mechanism for reagent dispersion and interaction of reagent with particles includes: double electric layer compression, electric neutralization, and adsorption bridging. After adding electrolyte, the counter-ion formed by the electrolyte in solution causes the double electric layer to be compressed, zeta potential of colloid (ζ) to be reduced (hydrate membrane on the colloid particle surface disappears or becomes weaker). Adding coagulant with the opposite electric charge to the colloid can neutralize an electriferous colloid in water with the absolute value of zeta potential descending, while adding excessive coagulant will make the colloids electriferous and of opposite charge, as illustrated in Figure 1.

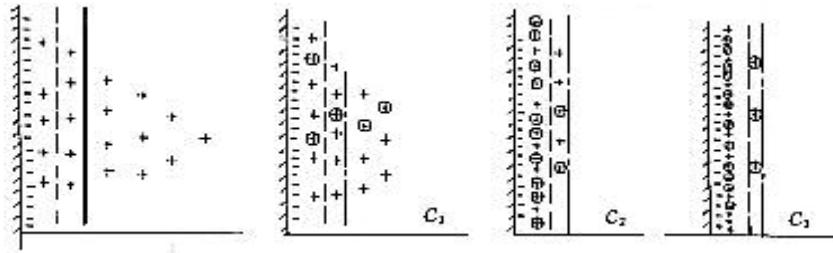


Figure 1: Variation of ζ electric potential on the colliding particles surface

While the process of reagent dispersion and its interaction with particles is rather complex the most important factors are the hydraulic conditions, reagent characteristics, PH value and colloid characteristics .

4. PHYSICAL MODEL OF REAGENT DISPERSION AND ITS INTERACTION WITH PARTICLES IN COAGU-FLOCCULATION

The process of coagu-flocculation can be divided into three stages^[11]: ① reagent dispersion and interaction with particles (defined as mixing effect); ② coagulation, and ; ③ flocculation, as shown in Figures 2 and Figure 3.

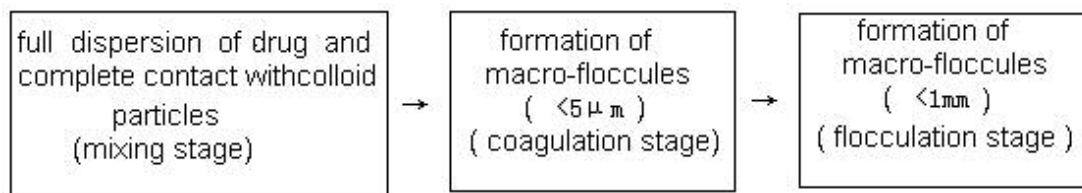


Figure 2: Coagu-flocculation process

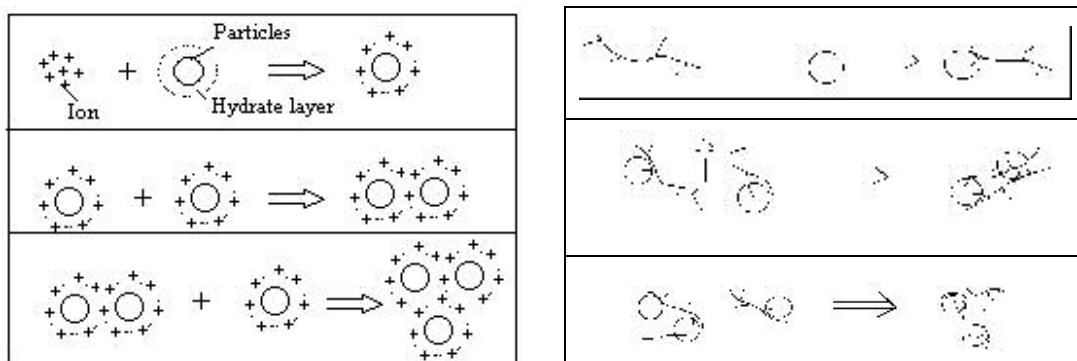


Figure 3: Physical models of Coagu-flocculation process

Coagu-flocculation includes the processes of coagulation and flocculation. In the process of coagulation, the added coagulant reacts relatively quickly with colloid particles in water to cause neutralization of the surface charge and double layer compression. The particles then coagulate to form primary micro-floccules. During the flocculation process, micro-floccules continue increasing in size to form settling floccules with large size and density. The interval between coagulation and

flocculation is effectively instantaneous.

The size distribution of micro-floccules in a high energy intensity coagu-flocculation process depends on a balance between adsorption bridging and the effect of turbulent shear^[12]. Turbulent shear mainly depends on vortex size and intensity. The smaller the vortex size and the larger vortex intensity, then the stronger the effect of shearing of micro-floccules. In the process of coagu-flocculation, classification of micro-floccules and the capacity of the flocculation vessel needs to be adjusted to meet process requirements. It is found, for example that with the addition of alum, the energy input can be reduced correspondingly, and control of the hydrodynamics in the process can readily be achieved. Therefore, the authors believe that only when the colloid particles completely contact with the well dispersed reagent, it is possible to form micro-floccules, and further completely or highly efficiently (if time is short) form big floccules. That is to say, with well developed mixing, coagulation with high quality and flocculation with high efficiency are possible. For instance, if a colloid particle does not contact effectively with the reagent, the opportunity for the colloid particle to coagulate (flocculate) is rather small. The more small particles, the worse the effect on coagu-flocculation and settling. Therefore, (1) reagent dispersion and its reaction with particles is a most important factor; (2) the hydraulic conditions in the subsequent coagulation are also of vital consideration.

5. EXPERIMENTAL STUDY OF COAGU-FLOCCULATION

Experimental installation and operating conditions.

The experimental installation is shown in Figure 4. The size of the impellor blade is fixed in all experiments, with the intensity of stirring changed by varying the rotational velocity (as determined by the voltage applied to the stirrer motor).

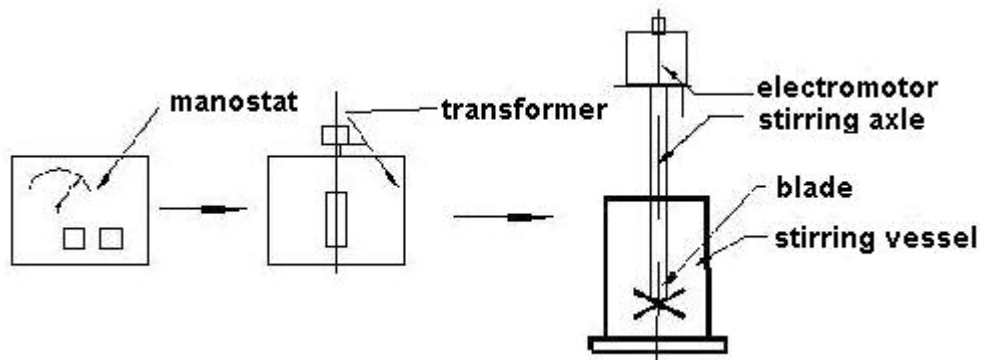


Figure4. Experimental installation for coagu-flocculation

5.1 Determination of the best turbulent conditions in the mixing stage

Tables 1 and 2 show that in the early stage of the coagu-flocculation process, neither stirring time nor stirring intensity affects coagu-flocculation excessively.

Table 1: The influence of stirring intensity and time on mixing effect (inorganic reagent)

No.	Stir intensity and Time /min			Original Turbidity (NTU)	Purified Turbidity (NTU)	Remarks
	50V	70V	50V			
1	1		3	185	70	1. Suspension clay 2. PH=6.5 Reagent dosage:10mg/l 3. Sedimentation duration: 1 min 4 Reagent $AlCl_3$
2	3		3	185	69	
3	5		3	185	71	
4		3	3	185	85	
5		5	3	185	98	

Table 2: The influence of stirring intensity and time on mixing effect (organic flocculant)

No.	Stir intensity and Time /min			Original Turbidity (NTU)	Purified Turbidity (NTU)	Remarks
	50V	70V	50V			
1	1	2	3	185	70	1. Suspension clay 1. PH=6.5 Reagent dosage: 0.1mg/l 3.Sedimentation duration: 1 min 4 Reagent PAM
2	3	2	3	185	69	
3	5	2	3	185	71	
4	5	3	3	185	55	
5	5	5	3	185	58	

5.2 Determination of the best turbulence conditions in the coagulation stage

Table 3 shows that from the view of theory stronger stirring makes the collision rate between particles increase, but is not conducive to the formation of micro-floccules.

Table 3: The influence of stirring intensity and time on coagulation effect (inorganic reagent)

No.	Stir intensity and Time /min			Original Turbidity (NTU)	Corrected Turbidity (NTU)	Remarks
	50V	100V	40V			
1	1	1	3	190	90	1. Suspension clay 2. PH=6.5 Reagent dosage: 10mg/l 3. Sedimentation duration: 1 min 4 Reagent $AlCl_3$
2	1	2	3	190	118	
3	1	3	3	190	135	
4	1	4	3	190	170	
5	1	5	3	190	175	

Table 4 shows that stronger stirring is more helpful to coagulation, making more micro particles coagulate and forming big floccules.

Table 4: The influence of stirring intensity and time on coagulation (organic flocculant)

No.	Stir intensity and Time /min			Original Turbidity NTU	Purified Turbidity NTU	Remarks
	50V	100V	50V			
1	1	1	3	190	80	1. Suspension clay 2. PH=6.5 Reagent dosage: 0.1mg/l 3. Sedimentation duration: 1 min 4 Reagent PAM
2	1	2	3	190	78	
3	1	3	3	190	35	
4	1	4	3	190	25	
5	1	5	3	190	31	

5.3 The determination of the best turbulent value in the flocculation stage

Table 5 shows that forming bigger floccules needs a certain time in the flocculation stage.

Table5: The influence of stirring intensity and time on coagulation (inorganic flocculant)

No.	Stir intensity and Time /min			Original Turbidity (NTU)	Purified Turbidity (NTU)	Remarks
	50V	100V	40V			
1	1	1	1	188	86	1. Suspension clay 2. PH=6.5 Reagent dosage: 10mg/l 3. Sedimentation duration: 1 min 4 Reagent AlCl ₃
2	1	2	2	188	79	
3	1	3	3	188	75	
4	1	4	4	188	25	
5	1	5	5	188	23	

Table 6 shows that flocculation stage needs a certain time to form bigger floccules, but if the stirring time is too long, it destroys forming floccules.

Table 6: The influence of stirring intensity and time on flocculation (organic flocculant)

No.	Stir intensity and Time /min			Original Turbidity NTU	Purified Turbidity NTU	Remarks
	50V	100V	50V			
1	1	3	1	188	46	1. Suspension clay 2. PH=6.5 Reagent dosage: 0.1mg/l 3. Sedimentation duration: 1 min 4 Reagent PAM
2	1	3	2	188	39	
3	1	3	3	188	35	
4	1	3	4	188	25	
5	1	3	5	188	30	

5.4 Analysis for experiment results

Generally the coagu-flocculation process is defined as stages of mixing, coagulation and flocculation. Though there is no strict distinction in the practical process of coagu-flocculation, experiments have proved that (1) the mixing and coagulation using organic flocculant are substantially accomplished at the same time and need strong mixing intensity; while the mixing and coagulation of inorganic floccules also are accomplished almost at the same stage but need weaker stirring intensity; (2) in order to form bigger floccules, weaker stirring is needed.

6. CONCLUSIONS

1. This early study of the coagu-flocculation mechanism has mainly focused on the collision mechanism of particles and velocity gradient theory. It does not coincide with grid coagu-flocculation as sometimes used in practical applications.
2. Experiments have proved the correctness and guidance of the above definition and physical model of coagu-flocculation. Definition of coagu-flocculation process in the microscopic view and the proposition of a physical model will be helpful to a detailed study of the coagu-flocculation mechanism in the future.
3. Mixing and coagulation of organic flocculant are almost accomplished at the same time and need strong mixing intensity.
4. The mixing and coagulation of inorganic floccules are accomplished almost at the same time but need weaker mixing intensity.
5. In order to form bigger floccules, weaker stirring is needed for a certain time.

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KEY WORDS

Coagu-flocculation, mix, coagulation, flocculation, inorganic flocculant, organic flocculant, physical model, experimental installation