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REVIEW Effects of Suspension Dispersity and Concentration on Flocculation Efficiency in Static and Dynamic Flocculators

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ARTICLE INFO	ABSTRACT
Article history:	Flocculation presents one of the most effective methods for enhancing separation of both an-
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Published: 31 December 2018	tive of this research is to study how the suspension dispersity and concentration effect the effi-
	ciency of its flocculation in a static tubular flocculator and in a dynamic Couette flocculator. In
Keywords:	these studies aqueous suspensions of ultra-fine calcium carbonate (<7 µm) and fine silica (<90
Flocculation	µm) were used as objects. It was established that treatment of ultra-fine calcium carbonate
Suspension	suspension in a static flocculator produced in the range 400-450 s ⁻¹ a pronounced primary max-
Flocculator	imum in the dependence "flocculation efficiency/shear rate". The increase of the suspension
Calcium carbonate	concentration to 70 g/l and above resulted in a small secondary maximum of the flocculation
Silicon dioxide	efficiency in the region of around 950 s ⁻¹ . This can be attributed to a higher dissolution rate of
	a flocculant and a to corresponding increase of particles adhesion forces in flocs, which coun-
	teract viscous forces destroying them. In silicon dioxide suspension treatment, the primary and
	secondary peaks occur at both small and high suspension concentrations, but in a latter case,
	they are by far more pronounced and comparable in magnitude.

1. Introduction

F locculation is one of the most effective methods for enhancing separation of both anthropogenic and natural suspensions by sedimentation, filtration and flotation techniques. Every year the industry uses millions of tons of flocculants, which in essence are water-soluble polymers, for such applications as potable water treatment, municipal wastewater purification, in water recycling systems in the mining, coal beneficiation and metallurgical sectors ^[1], as well as in various water treatment plants of machine building and food processing businesses, etc. However, as water resources deplete, in high-capacity industries, such as coal concentrators and mining businesses overall, the degree of water phase separation in water-sludge schemes for water recycling has recently become of particular importance.

The major role of flocculants is to bind separate suspension particles with polymer molecules into coarse and strong aggregates to facilitate their further separation from the aqueous phase. Compared to conventional commonly used inorganic coagulants, flocculants allow for significant reduction in volume and water cut of solid separation wastes; increase waste fluid loss in thickeners and filters, and simplify waste utilization. Since the molecular weight of some flocculants reaches several tens of millions Dalton, this complicates their application in suspensions of concentrations above 10 g/l. Normally, high molecular weight

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flocculants are introduced into a suspension in the form of an aqueous solution with concentration up to 0.1 w.%. Further steps like dissolution of the flocculant in the suspension aqueous phase, polymer molecules uniform distribution in the suspension volume, and their adsorption on the surface of particles require significant time, and may take hours. This process can be accelerated down to several seconds through suspension mixing in static or dynamic mixers (flocculators). The principle parameter of the flocculator, which determines the flocculation kinetics and quality, is the average shear rate (velocity gradient) of the medium, created inside the flocculator. The advantage of dynamic flocculators is that in them the medium shear rate can be controlled in a wide range, irrespective of the suspension flow rate and the treatment time, and is achieved by controlling the speed of moving elements (rotors) inside the flocculator. By contrast, static flocculators do not contain movable internal elements, and the shear rate is created by way of suspension interaction with fixed elements, which form obstructions to the flow and correspondingly local velocity non-uniformity. Since the degree of these non-uniformities is directly dependent on the velocity of the flow incoming on obstructing elements, the averaged shear rate depends on the suspension flow rate, and this feature complicates controlling optimal treatment conditions, especially when the suspension flow rate widely varies. Despite these downsides, static flocculators have become quite popular due to low cost and ease of production compared to their dynamic counterparts.

In the case of relatively dilute suspensions, where the solids concentration is below 10 g/l, the optimal suspension-mixing regime is characterized by shear rates in the range from 1500 to 3000 s⁻¹. Theoretical and experimental studies led to the development of a new method of flocculation treatment, later termed as "ultraflocculation" [2-4]. Unlike dilute suspensions, for concentrated suspensions with the solids content above 10 g/l, the optimal shear rate does not exceed 1500 s⁻¹ [5,6]. Hydrodynamic fields with such shear rate degrees can well be generated in static flocculators, which are relatively easy to manufacture. The best alternative for concentrated suspensions flocculation is a tubular type flocculator with no obstructing inner elements, which may cause its siltation and then disruptions in the optimum operating mode. In a tubular type flocculator, shear rates are induced by the friction of the flow on the flocculator wall and the resulting vortexes and turbulence. The objective of this study is to access the degree of suspension dispersion and concentration effects on the flocculation efficiency in dynamic and static flocculators. It is well established that the flocculation process involves several successive stages, and specifically mixing suspension with flocculant solution (water-soluble polymers); flocculant molecules dissemination in the suspension volume and their adsorption on the surface of flocculated

particles and, finally, aggregation of suspension particle into flocs. The efficiency of all these processes significantly depends on the characteristics of the hydrodynamic field inside the flocculator and also of the size and the concentration of flocculated particles. Obviously, the uniform distribution of molecules of the polymer having the mass of several million Daltons in a concentrated suspension presents a serious challenge, in particular, in the case when the particles size is comparable or slightly above the size of a polymer molecule. The best suitable way to increase the rate of the uniform distribution of flocculant molecules comprises the application of the hydrodynamic fields with high shear rates. However, the higher shear rates are, the lower is the probability of coarse flocs formation; and this may negatively affect their further separation from the dispersion medium. Hence, there must be some optimal conditions of the suspension hydrodynamic treatment depending on the suspension concentration and particles size. The data on the effects of the shear rates on the flocculation efficiency will provide the fundamental insights on the effectiveness of mixing the polymer solution with a suspension.

We have to note that mixing polymer solutions with suspensions is important not only for suspension phases separation, but also for other practical applications, for example, for the production of construction and composite materials, and for pharmaceutical and food industries. In our research, we have used as suspension models aqueous suspensions of ultra-fine calcium carbonate and fine silicon dioxide. The former one characterized by very fine particles size (<7 μ m), is commonly used for construction materials production, and the latter, rather coarse one (<90 μ m), is the major component of the flotation ore beneficiation tailings of non-ferrous and rare metals.

2. Theory

We have already mentioned that the major role of flocculation lies is binding separate suspended fine solid particles into coarse and strong aggregates (flocs). The theory of orthokinetic coagulation has demonstrated that the average size of the flocs formed at the early stages of the flocculation process in the first approximation can be estimated by the improved Smoluchowski formula ^[7]

$$D_A(t) = d_p exp\left(\frac{4\varphi G\alpha}{3\pi(1-p)}t\right) \tag{1}$$

where d_p is the initial size of flocculated suspended particles, $D_A(t)$ is the current average flocs size, p is their porosity, t is suspension treatment time, φ is the volume concentration of suspension dispersed phase, G is the averaged shear rate, α is the effectiveness of the elementary act of flocculation, or the probability of particles and/or aggregates binding at collision dependent on the flocculant properties and its concentration. Formula (1) shows that the size of flocs increases faster, with the increase in the suspension volume concentration and with the increase in shear rates. As with the flocs growth, the viscous stresses acting on them increase, at some moment these effects trigger the process of flocs disintegration. As a result, after some time from the flocculation start, some equilibrium flocs size distribution is reached in the suspension, and the maximum flocs size will be determined by the ratio between the particles binding forces and the viscous forces of the dispersion medium acting on flocs. Therefore, based on simple physical assumptions, it was shown in ^[7] that the maximum size of floccula could be estimated by the formula

$$D_{max} = \frac{6U(1-p)^{2/3}}{\pi^2 \eta G d_p^2}$$
(2)

where: η - is the dynamic viscosity of the medium, U is coupling binding energy of particles in a floc. From formula (2) follows that for given shear rate G the maximum size of floccules is greater, for smaller porosity p and the size of initial particles d_p . Thus, as it follows from formula (1), in the process of the concentrated suspensions treatment, the time for flocs to reach the maximum size is shorter for higher suspension volume concentrations φ . As for the optimal value of the shear rate G, then, formula (2) shows that, it would be smaller, for the larger required size of flocs D_{max} . The findings on finely dispersed quartz flocculation ^[8] show that if for a given treatment time the shear rate is significantly below its optimal value, flocs get very large, but they are highly porous, and, besides the solution would contain a lot of remaining initial unflocculated particles. If the shear rate significantly exceeds the optimum value, flocs will get very dense, but remain fine. Since the aim of flocculation is to enhance the process of the aqueous phase separation from the suspension and to ensure the solid phase dewatering by means of sedimentation, filtration and flotation, it is very important that flocs should have optimal dimensions, porosity and strength. These requirements are achieved through the correct selection of a specific flocculant dosage, and the suspension treatment hydrodynamic regime.

It should be highlighted that the suspension treatment in a flocculator is necessary not only for increasing the collision frequency of particles and aggregates, but, first and foremost, for ensuring the uniform dissemination of flocculant molecules in the suspension volume and for achieving the optimum degree of their adsorption on the surface of flocculated particles. Obviously, compared to a dilute suspension, in concentrated suspensions mixing of the initially fairly viscous flocculant solution with the suspension aqueous phase proceeds harder and, as it has been shown in ^[5] involves the decreased flocculation efficiency and increased flocculant consumption and longer treatment time., As it was shown in ^[2], this challenge can be resolved by the sufficient increase of the medium shear rate. Clearly, with the increased suspensions dispersity the problem of mixing the flocculant and dispersing its molecules in the water phase becomes even more prominent. As the shear rate impacts not only the collision frequency of suspended particles, but also affects the efficiency of flocculant molecules dissemination in the suspension volume, these considerations suggest that there must be some optimal shear rate value, which within acceptable time period would allow for both good mixing of a flocculant with suspension and for a high efficiency of the particles flocculation. When the shear rate values are far below the optimal one, not enough number of flocculant molecules will manage to reach the particles surface within a set time, and hence, small flocs are produced, and many particles will not be flocculated. However, when the shear rate exceeds its optimal value, the flocculant molecules will dissolve rapidly in the suspension aqueous phase and adsorb on the surface of particles, but thus formed aggregates are small [8].

3. Experiment

In the experiments, we used aqueous suspensions of calcium carbonate and silicon dioxide as model samples. The size of 95% calcium carbonate particles was below 7 µm; and 91% silicon dioxide particles were smaller than 90 µm and 61% smaller than 60 µm. Flocculation was performed in a horizontal tubular flocculator, modelled by a PVC tube of 5 mm in diameter. The length of the tube was adjusted to ensure the suspension treatment time of 6 seconds. In experiments of calcium carbonate flocculation, the high-molecular anionic flocculant AN-956-SH produced by SNF FLOERGER Company (France) was applied. In silicon dioxide flocculation tests a high molecular weight anionic flocculant Magnafloc 338 produced by BASF company (Germany) was used. In the measurement runs (see Figure 1), a metering peristaltic pump 3 pumped the suspension from the container 1 through a tubular flocculator 6 of a specified length. A damper 4 was placed between the metering pump 3 and the flocculator 6 for smoothing the flow pulsations. Before a suspension entered the flocculator 6, a metering peristaltic pump 5 injected into a suspension a dosage of a flocculant solution. From the flocculator output, a peristaltic sampler 8 discharged part of the suspension flow to the flocculation efficiency analyzer 7 placed in the UltraflockTester device produced by TURBOFLOTSERVICE company (Ukraine), which was described in detail in ^[5]. The principle for measuring the flocculation efficiency was first proposed in ^[9] and is based on measurements of the mean-root-square fluctuation of intensity of a light beam passing suspension, which goes through a transparent channel, and in first approximation, it is proportional to the mean flocs size. The concentration of the flocculant solution and its flow rate were adjusted to ensure the conditions that for a given

suspension flow rate the flocculant dosage per unit mass of solid was in the range of 5-50 g/t. Before assessing the averaged shear rate in a tubular flocculator for a given suspension flowrate, the calibration function of the pressure drop in the flocculator Δ_P on the suspension water flowrate Q was established. The obtained data were used to calculate the dependence of the averaged shear rate Gon the suspension flowrate Q, presented in Table 1 for clean water. The calculations of shear rate for suspension were performed by formula

$$G = \sqrt{\frac{\varepsilon_v}{\eta}} = \sqrt{\frac{\Delta PQ}{\eta W}}$$
(3)

where ε_v is energy dissipation per unit volume of medium, η is the suspension dynamic viscosity; *W* is internal volume of a tubular flocculator. The suspension dynamic viscosity was calculated by Einstein formula

$$\eta = \eta_0 \left(1 + 2, 5\varphi \right) \tag{4}$$

where η_0 is the clean water viscosity.



Figure 1. Lay out of a laboratory set-up for measuring the flocculation efficiency of a suspension treated in a tubular flocculator

 Table 1. Mean shear rate versus water flowrate in a tube with 5 mm diameter.

Suspension flowrate, l/min	0.2	0.4	0.6	0.8	1.0	1.2
Maine shear rate, s ⁻¹	250	600	1000	1450	2000	1650

In a dynamic flocculator, the flocculation efficiency was also measured with the UltraflockTester instrument, incorporating Couette flocculator, and schematically shown in Figure 2. In order to avoid the accumulation of the aggregated suspended particles in the flocculator, the flocculator rotor was manufactured in two parts, namely, an upper cylindrical and lower conical elements and the suspension was fed from the top down. It should be noted that the gap between the surfaces of the rotor and the chamber was only 1.5 mm, which is about 3 times smaller than the diameter of the above-mentioned tubular flocculator. In the measurement runs, the metering peristaltic pumps 4 and 5 were feeding the suspension and the flocculant solution in specified ratios into the dynamic flocculator 6 and then into the flocculation efficiency analyzer 7. The suspension treatment time in the flocculator was 6 seconds, and the shear rate varied in the range from 250 to 1750 s⁻¹.



Figure 2. Lay out of a laboratory set-up for measuring the flocculation efficiency of a suspension treated in dynamic Couette flocculator.

4. Results and Discussion

Table 2 shows the date relating calcium carbonate suspension flocculation efficiency with flocculant dosage and the suspension concentrations received with the help of UltraflockTester, when the flocculation was performed in a dynamic Couette flocculator at shear rate of 1000 s^{-1} (see Figure 2). The findings have shown that the dependence of flocculation efficiency on the flocculant dose is substantially affected by the suspension concentration, the higher is the suspension concentration, the larger the flocculation efficiency.

Figure 3 presents the curves of the calcium carbonate suspension flocculation efficiency versus shear rates for treatment regimes in static and dynamic flocculators. The findings show that for any suspension concentration values and flocculant dosages, in a tubular flocculator in the range of shear rates 400-450 s⁻¹ pronounced maximum in flocculation efficiency is observed. However, in a dynamic flocculator for flocculation efficiency we observe monotonic growth with increasing shear rates, and in the area of low shear rates (around 250 s⁻¹) and in the range over 700 s⁻¹ its value is significantly higher than the flocculation efficiency in the static flocculator. The latter can be attributed to the design of a dynamic flocculator, which comprises a cylindrical part at an inlet and a conical part at an outlet. In a dynamic flocculator the shear rate is smaller for lower the circumferential velocities of a rotor surface. Therefore,

Flocculant dosage, g/t	Suspension concentration, g/l			
	30	50	100	
	Flocculation efficiency, Relative units			
5	7	7	7	
10	10	8	8	
15	17	11	10	
20	33	20	15	
25	50	35	21,5	
30	65	49	29	
35	79	63	39	
40	87	74	49	
45	92	84	61	
50	95	91	74	

Table 2. Calcium carbonate suspension flocculation efficiency versus flocculant (AN-956-SH) dosage in the dynamic Couette flocculator at a shear rate of 1000 s⁻¹.

as the suspension moves top down, first, it experiences the effect of high shear rates in a cylindrical portion of the flocculator, and then going to exit, it is influenced by linearly decreasing shear rates in the conical part of the unit. Thus, high shear rates in the cylindrical part of the flocculator induce effective distribution of the flocculant molecules in the volume of the suspension and the formation of relatively fine flocs; and in the conical part of the flocculator, they merge into coarser aggregates, which promotes higher flocculation efficiency.

The data presented in Figure 3, show that in a static flocculator in the range of high shear rates suspension concentrations impact the dependence of calcium carbonate flocculation efficiency on the shear rate. For example, for a suspension concentration of 30 g/l (Figure 3a), the minimum flocculation efficiency occurs at shear rates of 1200-1300 s⁻¹ but in the range of 1400-1750 s⁻¹ it significantly rises. At suspension concentration of 50 g/l (Figure





Figure 3. Dependence of the flocculation efficiency of calcium carbonate suspension on the shear rate in the tubular flocculator (solid line) and in the dynamic Couette flocculator (dashed line) at various flocculant (AN-956-SH) dosages. Suspension concentration, g/l: 30 (a), 50 (b), 70 (c), 100 (d).

3b), at a shear rates above 500 s⁻¹ flocculation efficiency monotonically decreases. At suspension concentrations in the range of 70-100 g/l (Figure 3c, d), a small maximum in flocculation efficiency is observed in the shear rate range 900-1000 s⁻¹. The latter phenomena can be explained by the fact that the flocculation effectiveness is sensitive not only to a flocculant dosage, but it is also affected by flocculant molecules dissemination in the suspension volume during the hydrodynamic treatment. The presence of the primary and secondary maxima of the flocculation efficiency for concentrated suspensions is due to the interaction between particles adhesion force in a floc and the viscous forces acting to break flocs. The first one of these forces depends on the effectiveness of flocculant molecules mixing with the suspension and adsorption on particles surface. In concentrated suspensions and specifically, in ultrafine one, the distribution of flocculant molecules is hindered and much depends on the shear rate. At low shear rates, the flocculant poorly disperses in the suspension volume, but viscous stresses that break flocs are also not very strong, which defines the appearance of a primary maximum on the curve flocculation efficiency / shear rate in 400-450 s⁻¹ range. As shear rates grow, the flocculant dissolution enhances, but viscous forces increase much faster and this leads to a minimum in the 550-600 s⁻¹ range. Further increase of the shear rate, spurs better dissolution of a flocculant, which results in the appearance of a secondary maximum in the range of about 950 s⁻¹. In the case of very fine calcium carbonate particles, this maximum is not significant, as in this suspension, the distribution of flocculant molecules is very slow even at high shear rates.

Table 3 shows the dependence of flocculation efficiency of a concentrated calcium carbonate suspension in a static flocculator on treatment time, wherefrom it follows that at shear rates of 400 s⁻¹ and at a flocculant dosage of 30 g/t the maximum efficiency is achieved within of 8-10 s treatment time.

Table 3. Dependence of calcium carbonate suspension (100 g/l) flocculation efficiency on treatment time in a static tubular flocculator at a flocculant dosage of 30 g/t and at shear rate of 400 s⁻¹

Treatment time, s		2	4	6	8	10
Flocculation efficiency, Relative units		4	15	35	51	54

Figure 4 shows the dependence between the flocculation efficiency of silicon dioxide suspension and shear rates for the treatment in static and dynamic flocculators. The findings presented in Figure 4a, b, demonstrate that for relatively low suspension concentrations (below100 g/l), at shear rates above 400 s⁻¹ the treatment in a static flocculator ensures comparable, or even slightly better, flocculation performance in terms of efficiency. When the suspension concentration climbs to 100 g/l, this threshold shifts closer to 500 s⁻¹ (see Figure 4c). In contrast to the ultrafine calcium carbonate suspension, in silicon dioxide flocculation the secondary maximum of the flocculation efficiency appears not only in concentrated (Figure 4d), but also in relatively dilute suspensions (Figure 4a,b,c). The most plausible explanation for this fact may be that dispersity of silicon dioxide used in this study is about by an order of magnitude smaller than that of calcium carbonate, which greatly facilitates mixing of flocculant molecules with the suspension aqueous phase.

Finally, it is appropriate to note that the fundamental differences in the flocculation efficiency versus shear rates ratios for static and dynamic flocculants may be attributed to the specifics of their geometries and special orientation. For example, the gap between the surfaces of the rotor and the wall of the dynamic flocculator was 1.5 mm, while the diameter of the static tubular flocculant was 5 mm. Obviously, the wall effects were not the same, since the walls of a dynamic flocculator are practically upright, and those of a static one - horizontal. Besides, it has already been noted that at the outlet of the dynamic flocculator could merge into coarse ones. Undoubtedly, these effects need further investigation.

The data presented in Figs. 3 and 4 suggest the important practical conclusions. When flocculating ultra disperse suspensions of calcium carbonate at low shear rates static flocculators allow achieving higher flocculation quality compared to dynamic flocculators. Therefore, for flocculating of ultradisperse suspensions, it is more expedient to use static flocculators, which are cheaper, easier in operation and require less power. However, when it comes to coarse suspensions of dioxide silicon type, at low shear rates (up to 400 s⁻¹) and, respectively, at low power demand, it is more effective to use a dynamic flocculator.

5. Conclusions

The findings of the research allow the following summary:

a. Dispersity and concentration of the suspension significantly affect the efficiency of flocculation in a static flocculator.

b. For an ultrafine calcium carbonate suspension, a pronounced maximum of the flocculation efficiency / shear rate is observed in the range $400-450 \text{ s}^{-1}$.

c. With the increase of calcium carbonate suspension concentration to values of 70 g/l and above, in the range of around 950 s-1 a secondary maximum of the flocculation efficiency appears. This can be attributed to a higher dissolution rate of the flocculant and a corresponding increase in the cohesion forces of particles in flocs that counteract the viscous forces that break flocs.

d. When suspension dispersity decreases, the static flocculator efficiency substantially increases over the entire range of shear rates above 600 s^{-1} ; the secondary



Figure 4. Dependence of silicon dioxide flocculation efficiency on the shear rate in a tubular flocculator (solid line) and in a dynamic Couette flocculator (dashed line) for various flocculant (Magnafloc 338) dosages. Suspension concentrations, g/l: 50 (a), 70 (b), 100 (c), 200 (d).

maximum of flocculation efficiency is observed not only in concentrated suspensions but also in relatively dilute suspensions as well.

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