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# Effect of shear rate on aggregate size and structure in the process of aggregation and at steady state

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ABSTRACT

The paper deals with the dependence of aggregate properties on the shear rate ($G$) in the aggregation process and at steady state. Natural raw water and ferric sulphate were aggregated in a Taylor–Couette reactor. The methods of image and fractal analysis were used to determine the aggregate size and structure. It was observed that at the early phase of aggregation, the aggregate growth rate is higher for lower shear rates. At $G \leq 150\ s^{-1}$, the time aggregation curve contains the local maximum before reaching the steady state. Moreover, the different extent of break-up and restructuring was proved for different values of shear rate. At $G \geq 200\ s^{-1}$, the aggregation curve misses the local extreme completely. It was found that with increasing shear rate ($G = 21.2–347.9\ s^{-1}$), the aggregates are smaller ($d = 1504–56\ \mu m$), more compact ($D_2 = 1.54–1.91$) and more regular ($D_{pf} = 1.37–1.10$). A relationship for the description of dependence of fractal dimension on the shear rate was also suggested.



## 1. Introduction

The processes of destabilization and aggregation are traditionally used to remove colloidal particles in water treatment. The purpose is to prepare aggregates of such properties (size, structure, shape, density, etc.) that are suitable for reaching the maximum effectiveness of following separation steps, such as sedimentation, filtration or flotation.

The formation of suspension includes the processes of *aggregation*, *break-up* and in some cases *restructuring* [1–5]. These processes can (but do not have to) proceed simultaneously and they depend on the balance between the hydrodynamic force $F$ and the cohesive force $J$. The hydrodynamic force arises from a flow of fluid around a particle and is thus determined by the magnitude of the shear rate $G$, cross-sectional area of a particle $A$ and dynamic viscosity of fluid $\mu$. The cohesive force is given by the sum of all attractive forces acting between interacting particles (e.g. van der Waals, electrostatic or hydrophobic forces). It depends particularly on the particle (and/or reagent) composition and concentration and determines the strength of formed aggregates [1,4,6–8]. If the cohesive force prevails ($J > F$), aggregation occurs. If the hydrodynamic force prevails ($F > J$), aggregates are not formed at all or a break-up of already existing aggregates takes place. When these forces are approximately in equilibrium, the restructuring occurs.

When chemical conditions (type and concentration of particles and reagents, pH and overall water composition) are kept constant, the cohesive force between two primary particles does not change during the aggregation process. However, the hydrodynamics are influenced by the shear rate in the mixed volume which is not spatially (and temporally) constant at all and which depends on the geometry of the mixing tank and stirrer shape and speed (and temperature as well). This fact allows the already formed aggregates to be broken again when exposed to the regions with higher shear rates [8–13]. Nevertheless, the global/mean/average shear rate is still used for the characterization of hydrodynamics for practical reasons.

There are different perspectives on studying aggregate properties. First, it is the development of properties in time as the suspension is being formed (aggregation kinetics) and another, it is the description of aggregate properties at a steady state when they stabilize at some constant values. Both can be studied theoretically and/or experimentally.

The aggregation kinetics is theoretically studied with the use of population balance modelling based on the classical equation developed by Smoluchowski [14] which expresses the change of the number concentration of aggregates in time. This model assumes that only binary collisions between particles occur, the collision efficiency is 100%, colliding particles are spherical and of equal size, and neither aggregate break-up nor restructuring is considered. This expression has been modified by adding terms representing the aggregate break-up [15] and structure changes [3]. Population balances were then used by many other authors [3,5,13,16–19]. Experimental results that have been reported so far generally show two different trends of the development of aggregate size in time. In the first case, the aggregate size increases with time quite rapidly in the early stage of aggregation, and the growth slows down gradually until the steady state is reached [2,5,20–24]. In the other case, the aggregates grow to a maximum and then their size decreases again before a steady state is reached [3,9,11,12,18,25,26]. The reason for the appearance of such a peak in a size-time profile has not yet been satisfactorily

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explained, although there are some suggestions that it might be the result of restructuring (break-up and re-aggregation) [11].

It has been reported up to now that the aggregate size at steady state decreases with increasing shear rate and a power function is often used for a description of this dependence [6,7,10,27–34]. The aggregate structure is described by means of different fractal dimensions which, in most cases, are calculated from the image analysis data [25,32,34–36] or light scattering data [2,5,8,11,23,24,37,38]. It follows from the published results that with increasing shear rate, aggregates become denser, more compact and less porous.

The paper deals with the dependence of the aggregate properties on the shear rate during the aggregation process and at a steady state. The aim of the paper is 1) to supplement existing knowledge of time evolution of aggregation process, especially with respect to processes of break-up and restructuring and 2) to suggest a new approach to the dependence of aggregate properties on the shear rate at a steady state. The relationship of aggregate properties and the shear rate was studied experimentally with the use of natural raw water and a hydrolyzing destabilization reagent, assuming action of other cohesive forces than just van der Waals and electrostatic. The aggregation was performed in a Taylor–Couette reactor, the flow conditions of which are well explored [5,24,35,39–45].

## 2. Materials and methods

### 2.1. Raw water and reaction conditions

The experiment used raw water from the Svihov reservoir (potable water source), Czech Republic. The tests were carried out during the winter period (January) when raw water quality was stable with the parameters given in Table 1. Ferric sulphate hydrate $Fe_2(SO_4)_3 \cdot 9H_2O$ (Analytika, Ltd., Czech Republic) served as coagulant. Its dose (3.98 mg $l^{-1}$ of Fe) was optimized by standard jar tests. Thus, the formed aggregates consisted of the particles of impurities present in raw water as well as the particles of ferric hydroxide (coagulant). All laboratory tests were carried out at a temperature of 20 °C.

### 2.2. Taylor–Couette reactor and mixing conditions

The Taylor–Couette reactor was used as a mixing device. It consisted of a pair of concentric cylinders, with an inner rotating cylinder. The inner cylinder had a radius of $R_1 = 76$ mm and the outer had a radius of $R_2 = 85.5$ mm, which results in a gap width of $d = R_2 - R_1 = 9.5$ mm and radius ratio of $\eta = R_1/R_2 = 76/85.5 = 0.889$. The height of the cylinders was $H = 350$ mm resulting in the aspect ratio of $\Gamma = H/d = 350/9.5 = 36.8$.

Both cylinders were made of plexiglass (Umaplex, Perspex); the inner one was painted white, and served as a contrast background for the aggregates having an orange-brownish color. The outer cylinder was transparent and allowed the photographic imaging of the aggregation process. The inner cylinder was driven by a variable speed drive with a torque-meter. The hydrodynamic conditions in the Taylor–Couette reactor were characterised by the global shear rate $\overline{G}$ calculated according to the relationship as follows:

$$\overline{G} = \sqrt{\frac{P_i}{V\mu}} = \sqrt{\frac{\omega\ M}{V\mu}} = \sqrt{\frac{2\pi f M}{V\mu}}, \quad (1)$$

where $P_i$ represents the power dissipated in the aggregation space, $V$ is the volume of the aggregation space, $\mu$ is the dynamic viscosity of the fluid, $\omega$ is the angular velocity of inner cylinder rotation, $M$ is the torque and $f$ is the rotation frequency.

The flow regime in the gap between two cylinders is characterized by the Reynolds number

$$Re = \frac{\omega R_1 d}{\nu}, \quad (2)$$

where $\omega$ is the inner cylinder angular velocity, $R_1$ is the radius of the inner cylinder, $d = R_2 - R_1$ is the annular gap width, and $\nu$ is the kinematic viscosity.

For a fixed outer cylinder and Newtonian fluid, it is well known that as the angular velocity of the inner cylinder increases from rest, the flow undergoes a series of transitions: laminar Couette flow → laminar Taylor vortex flow → wavy vortex flow → modulated wavy vortex flow (→ weakly turbulent vortex flow) → turbulent vortex flow → turbulent flow [42]. These flow regimes can be characterised by the means of Reynolds number ratio $R = Re/Re_c$, where $Re_c$ is the critical Reynolds number depending upon the specific geometry (i.e., the radius and aspect ratio) of the Taylor–Couette reactor used [44,45].

Table 2 shows the values of the global (mean) shear rate used in the experiment and corresponding angular velocities, Reynolds numbers and Reynolds number ratios. The value of $Re_c$ for $\eta = 0.889$, $Re_c = 130.65$, was determined according to DiPrima et al. [41].

It follows from Table 2 and the literature that the flow regime in the Taylor–Couette reactor during the experiments varied from wavy vortex flow to turbulent vortex flow, transition at $R \sim 35$, and further, to fully developed turbulence, $R > 100$ [24,40,43–45].

### 2.3. Image analysis

The size of aggregates formed during the aggregation process in the Taylor–Couette reactor was determined by two-dimensional image analysis. This image processing technique has been developed to measure the aggregate size distribution in an aggregating suspension at any moment [32,34,46]. It is based on three steps:

1) Illuminating a slice of flow in the aggregation reactor with a laser light sheet (width = 1.2 ± 0.1 mm) generated by a laser diode (λ = 675 nm, power capacity 20 mW).
2) Recording images of the aggregate using a digital camera Pentax K20D (Asahi Co., Japan) with a Sigma AF 105/2.8 EX MACRO lens magnification 1:1 (Sigma Co., Japan).

**Table 1**
The quality of raw water.

| Parameter | Value |
|---|---|
| $T$ [°C] | 3.6 |
| pH [-] | 7.2 |
| Alkalinity [mmol $l^{-1}$] | 1.09 |
| Turbidity [NTU] | 2.9 |
| DOC [mg $l^{-1}$] | 3.8 |
| Fe [mg $l^{-1}$] | 0.05 |
| TSS [mg $l^{-1}$] | 22.6 |

DOC — Dissolved Organic Carbon.
TSS — Total Suspended Solids.

**Table 2**
The values of global shear rate used in the experiment and corresponding angular velocities, Reynolds numbers and Reynolds number ratios.

| $G$ [$s^{-1}$] | $\omega$ [rad $s^{-1}$] | $Re$ [−] | $R$ [−] |
|---|---|---|---|
| 21.2 | 2.50 | 1779 | 13.6 |
| 38.7 | 4.57 | 3247 | 24.9 |
| 58.9 | 6.95 | 4941 | 37.8 |
| 79.8 | 9.42 | 6695 | 51.2 |
| 102.3 | 12.08 | 8582 | 65.7 |
| 149.1 | 17.60 | 12509 | 95.7 |
| 202.2 | 23.87 | 16963 | 129.8 |
| 252.8 | 29.84 | 21208 | 162.3 |
| 300.5 | 35.48 | 25210 | 193.0 |
| 347.9 | 41.07 | 29187 | 223.4 |