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# Fractal structure of floc formed by composite powder flocculant

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## INTRODUCTION

Flocculation is a widely used process for solid/liquid separation in water/wastewater treatment. Recently the clarification method using composite flocculants in dry powdered form has been developing in the flocculation process for small amount of suspensions. To evaluate effects of flocculants on colloidal suspension, floc structure is one of the most important factors. Fractal dimension of a floc, the measure of how complex the floc structure is, determines hydrodynamic properties of the floc such as permeability and settling velocity.

In this study, fractal dimension of flocs was investigated to gain further knowledge on the structure of flocs of polymethyl methacrylate (PMMA) particles formed by composite powder flocculants. The model composite flocculants consist of inorganic flocculant, anionic polymeric flocculant and calcium carbonate as a flocculation aid. To find the fractal dimension of the flocs, the settling velocity and the radius of the sphere circumscribed on the floc were obtained using image analysis technique. The theory derived by Gmachowski [1] which considers the relationship between the fractal dimension and the permeability of flocs was used to analyze the results of experiments in this paper.

## EXPERIMENTAL

### Materials

0.4  $\mu\text{m}$  PMMA (MP-1000, Soken Chemical & Eng. Co.) particles were used as a colloidal material. Aluminum sulfate hydrate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{-}18\text{H}_2\text{O}$ , Wako Pure Chemical Ind., Ltd.) was used as an inorganic flocculant. Anionic acrylamide-acryl acid copolymer (AP335B, Mitsubishi Chemical Corporation) was used as a polymeric flocculant. Calcium carbonate (Nacalai tesque, Inc.) was used as a flocculation aid which helps good dispersion of polymeric flocculant as well as acceleration of flocculation of PMMA particles [2]. These three components were mixed, all in powder form, with a spatula for more than one minute to use as a composite powder flocculant.

### Procedure

Flocs were formed as follows. 20 mL of 1.00 g/L PMMA suspension was introduced into a 25 mL test tube. A composite powder flocculant was added to the suspension, and mixed by inverting and swirling the tube ten times in twenty seconds. After mixing, the contents of the tube were moved carefully to a laboratory dish. The dosage of three components of composite powder flocculant is shown in **Table 1**.

For the measurement of the settling velocity of a floc and the radius of the sphere circumscribed on the floc, each floc was gently taken up from the dish with a spoon or a small syringe and introduced into the settling tube (76×28×112 mm), filled with the same concentration of alum solution as the supernatant of the tube. Settling flocs were observed through a video camera for recording. Settling velocity of each floc and the radius of the sphere circumscribed on the floc were obtained by analyzing the video.

Table 1 Dosage of components of flocculant

Run No.	Dosage [g/L]		
	Inorganic flocculant	Polymeric flocculant	Flocculation aid
1	2.5	2.5	10
2	0.10	0.025	10

### Analysis

Assuming that flocs are impermeable fractal spheres of monodisperse primary particles, the mass-radius relation, the connection between number of primary particles flocculated and the size of the floc, is often written as [3]:

$$i = k_f \left( \frac{R_g}{a} \right)^D \quad (1)$$

where  $i$  is the number of primary particles forming the floc,  $R_g$  is the radius of gyration of the floc,  $a$  is the radius of the primary particles, and  $k_f$  is the prefactor. Using Eq. (1), the settling velocity of a floc is written by the following equation.

$$u = \frac{2k_f (\rho_s - \rho_w) a^{3-D} g}{9\mu} R_g^{D-1} \quad (2)$$

Here  $u$  is the settling velocity of a floc,  $\mu$  is the viscosity of water,  $\rho_w$  is the density of water,  $\rho_s$  is the density of the primary particles,  $g$  is the acceleration due to gravity. From Eq. (1), the prefactor  $k_f$  for fractal flocs will become constant with increasing size. Its dependence on the packing fraction of flocs and the shape of flocs and primary particles was studied by many researchers. However, since its definition is unclear, it is difficult to calculate  $k_f$  and the prefactor of Eq. (2) correctly. Since the packing fraction of the floc depends on the fractal dimension,  $k_f$  will be a function of the fractal dimension of the floc. Considering the relationship between  $k_f$  and the fractal dimension, Gmachowski proposed the mass-radius relation for fractal flocs of polydisperse particles as

$$i = \left(\frac{r}{R}\right)^D \frac{R^D}{\langle a^D \rangle} \quad (3)$$

with the prefactor which is the  $D$ th power of the normalized hydrodynamic radius

$$\frac{r}{R} = \sqrt{1.56 - \left(1.728 - \frac{D}{2}\right)^2} - 0.228 \quad (4)$$

where  $r$  is the hydrodynamic radius of the floc,  $R$  is the radius of sphere circumscribed on the floc,  $D$  is fractal dimension, and  $\langle a^D \rangle$  is the  $D$ th moment of the primary particle radius distribution. Using Eq. (3), the settling velocity of a floc can be derived as

$$u = \frac{2}{9\mu} (\rho_s - \rho_w) g \left(\frac{r}{R}\right)^{D-1} \frac{R^{D-1}}{a_{\text{eff}}^{D-3}} \quad (5)$$

where  $a_{\text{eff}}$  is the effective primary particles radius defined by the following equation.

$$a_{\text{eff}} = \left(\frac{\langle a^D \rangle}{\langle a^3 \rangle}\right)^{1/(D-3)} \quad (6)$$

Compared to Eq. (2), Eq. (5) is a simple formula with the only fitting parameter  $D$ . To analyze the experimental results with Eq. (5), size distribution of primary particles i.e. PMMA and  $\text{CaCO}_3$  particles was measured using a laser diffraction particle size analyzer (SALD-3100, Shimadzu Corp.). Fractal dimension of flocs was determined so that the settling velocity calculated using Eq. (5) corresponds to the results of floc settling experiment.

## RESULTS AND DISCUSSION

The settling velocity of a floc,  $u$ , was plotted against the radius of the sphere circumscribed on the floc,  $R$ , in **Figs. 1** and **2** for Run No. 1 and 2, respectively. The composite flocculant which contains a larger amount of inorganic and polymeric flocculant formed stronger flocs whose fractal dimension is smaller (the

results of floc strength experiments are not shown). From Eq. (3), the number of primary particles formed a floc of radius  $R$  can be calculated using the fractal dimension. If Eqs. (3)-(6) are applicable to this system, the measured total mass of some flocs will be proportional to the total number of primary particles forming the flocs which is calculated from Eq. (3). Further study is needed along this line.

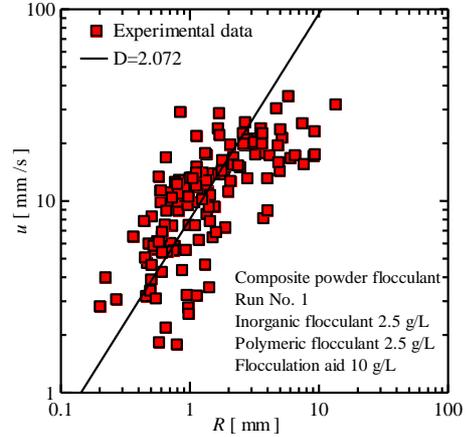


Fig. 1 The relation between  $u$  and  $R$  of flocs formed with the composite powder flocculant (Run No. 1).

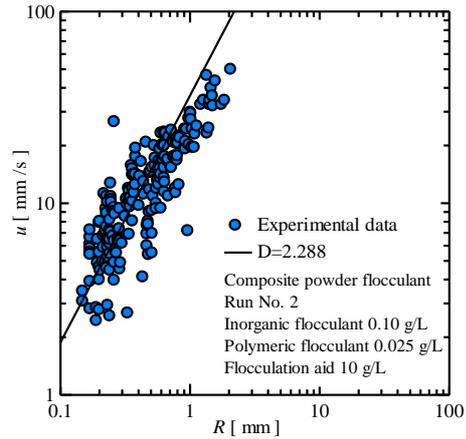


Fig. 2 The relation between  $u$  and  $R$  of flocs formed with the composite powder flocculant (Run No. 2).

## CONCLUSION

We analyzed the results of floc settling experiments using the theory considering the dependence of the prefactor of fractal mass-radius relation on the fractal dimension. Fitting with the theoretical line, we were able to determine the fractal dimensions of flocs formed with composite powder flocculants.

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