

(1) Coagulation Behaviors and Coagulant Dosage Control of Kaolin and Bentonite Suspensions

カオリンとベントナイトの凝集特性および凝集剤注入量のコントロール

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Abstract ; The coagulation behaviors of two widely used model clay particles, kaolin and bentonite were investigated by using ferric chloride as coagulant in this paper. Through experiment, the effects of their suspension concentrations, alkalinity and charge properties on the coagulation behaviors were discussed. The results presented in this paper demonstrated that bentonite possesses very large negative surface charge comparing with kaolin particles. This determined its coagulation behavior shows great difference with that of kaolin. Initial colloid charge and alkalinity of raw water are regarded to be the most important factors influencing coagulant dosage. Eventually, using these two parameters, a formula was proposed for coagulant dosage control for the first time. Optimal dosage estimated by the formula showed a high correlation with jar-test data.

Keywords ; kaolin, bentonite, coagulation, colloid charge, pH, alkalinity

1. Introduction

The study of coagulation is of fundamental interest in the field of water treatment. Also Fe(III) salts are receiving extensive attention as an alternative coagulants to aluminium for (1)Health concerns about residue aluminum in treated water (2) Possible cost savings comparing with other alternative coagulants, and (3) More efficient removal of turbidity and color causing organic materials, bigger floc generating than aluminum salts, etc. (Johannes Haarhoff, 1988, Lim-Seok Kang, 1995). This research focus on the use of Fe(III) salt as the coagulant and the turbidity removal of two widely existing clay particles, kaolin and bentonite.

The determination of an optimal and economical coagulant dosage is a crucial problem in water treatment plant: improper dosage will lead to poor removal of the raw water turbidity and leave bad condition to the following treatment process such as precipitation, filtration, sludge disposal, etc.¹⁾. At the every moment of sudden change of raw water quality caused by rainfall or typhoon, it is not enough to rely on empirical formula now used by the most water treatment plants.

The objectives of this study are to quantify the different coagulation behaviors of kaolin and bentonite suspensions and to provide fundamental data for dosage control of Fe coagulant.

2. Materials and Methods

2.1 Material

A given amount of kaolin and bentonite (Kukita. Co. Japan) in powder form was dissolved in distilled water for preparing a test suspension with the desired turbidity. Ferric chloride coagulant was

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prepared by analytical reagent-grade $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako.Co. Japan). Na_2CO_3 (Wako.Co. Japan) was used as alkalinity source for keeping a buffer capacity in coagulation processing. N/10 of NaOH and N/50 HCl were used for pH adjustment. Methyl glycol chitosan (MGC) (Wako. Co. Japan) and potassium polyvinyl sulfate (PVSK) (Wako. Co. Japan) were applied as standard positive and negative colloids. Toluidine blue (TB) (Wako. Co. Japan) was used as a color indicator.

2.2 Jar-Test

A standard jar test stirrer having six paddles was used for the coagulation-flocculation tests. The tests were performed by adding the ferric chloride reagent to the turbid samples, followed by mixing at 60rpm for 5 minutes, and thereafter slower mixing at 30rpm for 25 minutes. The aggregates were allowed to settle for 30 minutes before turbidity and pH measurement of supernatant. 500ml beakers were used in all the jar test experiments.

2.3 Colloid Titration

Almost all particles, smaller than several μm have an electric charge on their surface and the magnitude of the charge is generally expressed as zeta potential. Zeta potential, however, must be calculated from the migration velocity of the suspension particles in an electric field under a microscope. As an simple alternative method, colloid titration techniques can quantify the electrical charge (S.Kawamura, 1996) and the charge is expressed as meq/L or meq/g. Colloid titration was performed by adding 1~10ml MGC, then titrated by PVSK solution. Reaction endpoint was determined by using a multi-spectrum meter in full wavelength. Colloid titration was regarded as a reliable method for the determination of the isoelectric point instead of the electrophoresis mobility measurement (Sang-kyu Kam and John Gregory, 1999, Steven K. Dentel and James M. Gossett. 1988, Kawamura S, 1996).

In this study, HM-14P pH meter was used for pH measurement. Turbidity measurement was done by Water Analyzer 2000. SHIMADZU Multispec-1500 spectrophotometer was used for all the absorbance measurements.

3. Results

3.1 Physical properties of kaolin and bentonite suspensions

The compositions of bentonite and kaolin clay particles used in this study are listed in Table 1 (based on weight percentage).

Table 1 The compositions of kaolin and bentonite clay particles

	SiO_2 %	Al_2O_3 %	CaO%	K_2O %	Fe_2O_3 %	MgO %	Na_2O %	pH	Mesh	Specific gravity	Swell
Bentonite	77.3	13.5	1.0	0.30		2.0	2.90	9.4~10.0	300	0.34~0.4	18
Kaolin	72.1	19.57	0.8		0.39	0.54		6.8	300	0.37	

Bentonite is widely known for its expansion. Its crystal structure is constituted by two sheets of tetartoids inlaying with an octahedron. Kaolin crystal is constructed simply by one tetartoids sheet and one octahedron sheet with a plain structure^{5),6)}. When solved in water, their surface charge increased with the increase of suspension concentration shown in Fig.1 for a comparison of two clay particles. Kaolin shows a subtle negative surface charge and bentonite is greatly negative charged.

3.2 Effect of alkalinity on coagulation behaviors of two clay suspensions

In this experiment, 50mg/L kaolin and bentonite suspensions in distilled water were prepared, and Na_2CO_3 concentration of this solution was set to be 30mg/L, 50mg/L and 100mg/L respectively. Ferric

chloride was added in the dosage range from 0 to 0.9mmol/L.. Experimental results are shown in Fig.2 and Fig.3 for kaolin and bentonite suspensions, respectively. It can be concluded from these figures that the increase of raw water alkalinity changed the effective Fe dosage range greatly for both clays at a similar way. As the increasing of alkalinity, coagulation Fe dosage range moved to higher dosage side and meantime the range was broadened greatly. The charge variation accompanying with the coagulation process is shown in the same figures. It indicates that at the condition of suspension concentration 50mg/L, coagulation occurred nearly around charge zero for both kaolin and bentonite suspensions even though at high alkalinity conditions. Therefore besides its buffer function, the increasing of alkalinity stimulated much more hydrolysis production, which promotes the coagulation reaction.

3.3 The effects of suspension concentrations on coagulant dosage range

For comparison of the effects of clay particles concentration on their coagulation behavior, jar test was performed by making suspensions of different clay concentrations followed by the additions of 30mg/L Na_2CO_3 and ferric chloride. Suspension concentrations as a function of Fe dosage and turbidity removal ratio are shown in Fig.4 and Fig.5. Bubble symbols denote the experiment results under which the turbidity removal ratio was from 50% to 95% (small bubbles) and more than 95% (large bubbles) ignoring the experimental results with a removal ratio lower than 50%.

In contrast to kaolin suspension of concentration from 20mg/L to 300mg/L, the effect of suspension concentration on Fe dosage range was obviously observed in the case of bentonite suspensions at concentration from 3mg/L~50mg/L. Coagulation critical dosage increased from 0.04 to 0.07mmol/L as bentonite suspension concentration increased from 3mg/L to 50mg/L. For kaolin suspensions, little change of Fe dosage range was observed even though at a high concentration of 300mg/L. It was also observed certainly that different coagulation dosage range caused a different coagulation pH range.

3.4 Effect of suspension concentration on coagulation charge range

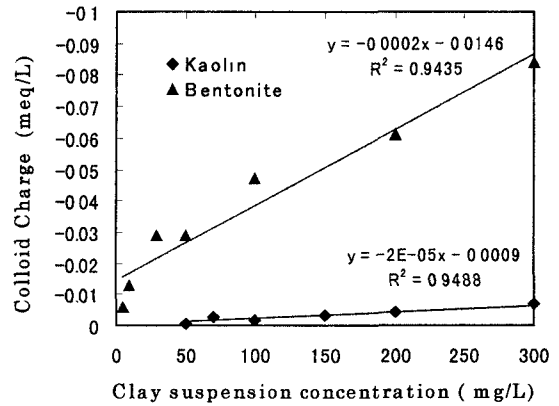


Fig. 1 The comparison of surface charge between bentonite and kaolin particles

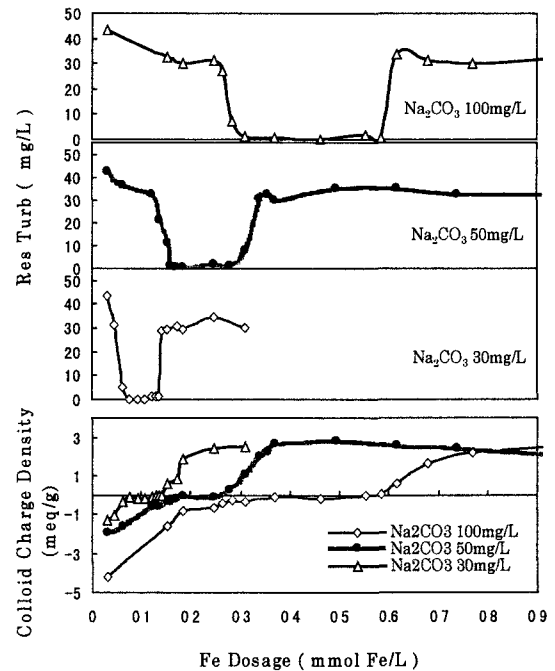


Fig.2 The effect of alkalinity on the coagulation of kaolin suspension

The interaction between clay suspensions and Fe^{3+} additives was investigated by means of jar-test and colloid titration method. The colloid charge measurement results presented as charge variation in coagulation processing of clay particles are shown in Fig.6 and Fig.7 for kaolin and bentonite suspensions. The figures show that good coagulation occurred at zero charged condition for kaolin suspensions at each investigated Na_2CO_3 concentration. On the other hand, coagulation could occur even at negatively charged condition in the case of bentonite. These figures show that negatively charged clay particles were neutralized by the addition of Fe coagulant. As the increasing of coagulant dosage, colloid charge density tend to zero and over dosage of the coagulant led the charge density reverse to positive charge with no destabilizing of colloid suspension.

From the experiment results, the charge neutralization upon adsorption between kaolin particles and Fe^{3+} seems to be the most important coagulation mechanism. It seems also that electric neutralization is not a sole mechanism governing the coagulation process of bentonite suspensions in which coagulation even occurred at negatively charged condition. Bridging enmeshment might be the second mechanism. We would study about the detailed mechanism of bridging enmeshment between the reaction of Fe^{3+} and clay particles continuously.

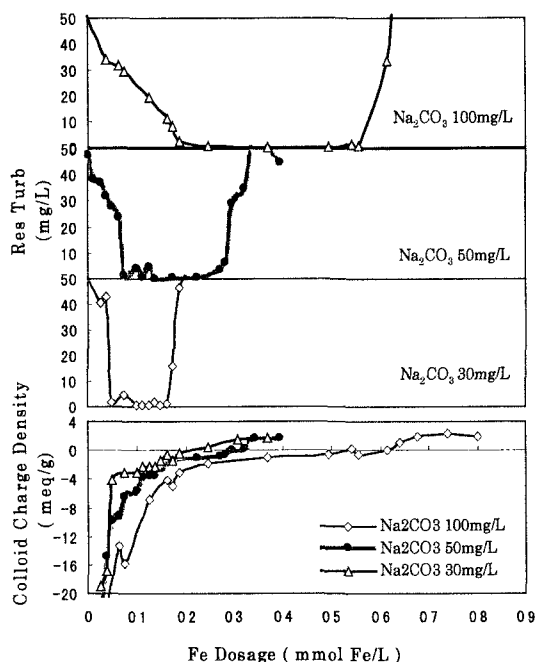


Fig.3 The effect of alkalinity on the coagulation of Bentonite suspension

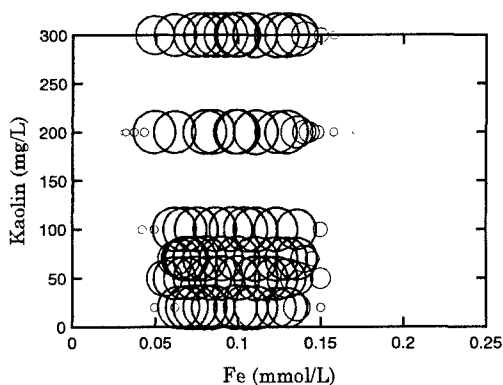


Fig.4 Suspension concentration's effect on coagulant dosage range for the turbidity removal of kaolin

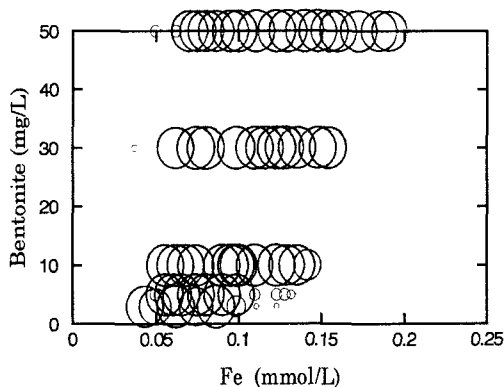


Fig.5 Suspension concentration's effect on coagulant dosage range for the turbidity removal of bentonite

4. Discussion

4.1 Difference in coagulation behaviors of kaolin and bentonite suspensions

The difference in coagulation behaviors of kaolin and bentonite suspensions were observed in (1)

different coagulant dosage range, (2) different coagulant charge range and (3) different coagulation pH range. These discrepancies can be explained by the characteristics of their surface properties such as the surface charge property and their great difference in cation exchange capacity (CEC). The detailed information about clay's cationic exchange capacity of kaolin and bentonite was published in reference¹⁾ (Fumio Nakamura, 1974).

Bentonite is mainly composed of montmorillonites with traces of silica, quartz and other clay materials. The particular structure of montmorillonites generates a very high surface area and charge, when dispersed in water⁵⁾. The layered structure of kaolin is quite different from that of bentonite. Kaolin is not swelling clay. On the other hand, the silica faces of kaolin are large flat areas characterized by Si-O-Si structures, and carry a relatively small negative charge as a result of isomorphous substitution of Al (III) for Si (IV)⁶⁾.

CEC is an important index to identify clay particles. The magnitude of CEC depends on the substituting cations. According to Fumio Nakamura¹⁾, it was in the order of 65 meq/100g and 3meq/100g measured by MB⁺ method for bentonite and kaolin respectively. The relationship between initial surface colloid charge and clay's CEC is shown in Fig.8. Both clay particles showed about the same linear relationship which indicates that colloid charge of clay suspensions can reflect their cation exchange capacity to a great extent.

The colloid charge as a function of pH in the absence of Fe is shown in Fig.9 for the comparison of kaolin and bentonite at the concentration of 50mg/L and 5mg/L, respectively. N/10 of NaOH and N/50 HCl were used for pH adjustment. The result shows that the particles were all negatively charged at all of the pH values examined. Their absolute value decreased as the decreasing of pH indicated that the surface charge of kaolin and bentonite clay particles was of pH dependence. Moreover, bentonite suspension showed possessing of much more high negative charge than kaolin despite at one-tenth lower concentration than that of kaolin.

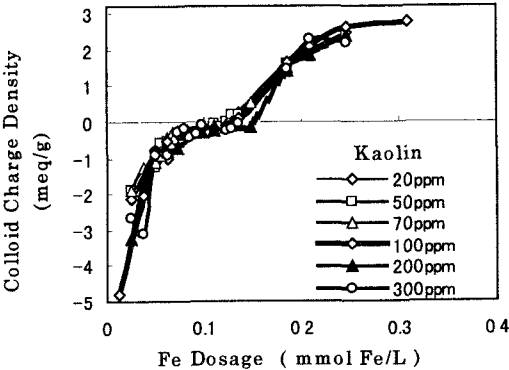


Fig.6 Variation of colloid charge versus Fe dosage in the coagulation processing of kaolin suspensions

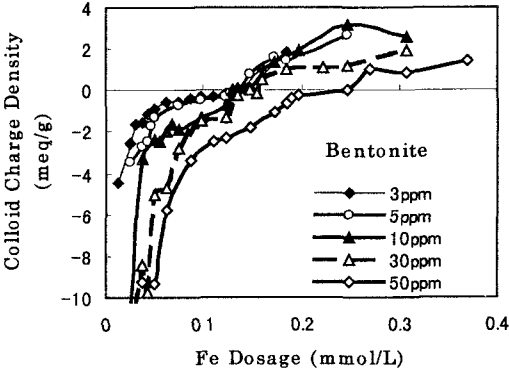


Fig.7 Variation of colloid charge versus Fe dosage in the coagulation processing of bentonite suspensions

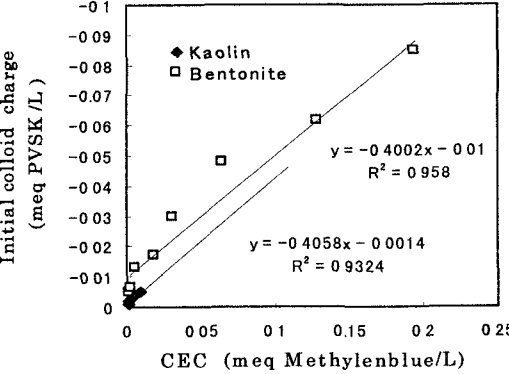


Fig 8 The relationship between cation exchange capacity and surface charge of clay particles

Many references reported that Fe^{3+} ions behave in a complex fashion in aqueous media ^{7)~9)}. Fe^{3+} ions undergo hydrolysis and polymerization reactions involving the formation of different Fe hydroxylated species over different pH ranges. These chemical products interact with the surface of clay particles and significantly change their electrical properties in aqueous media. Therefore, the dispersion-coagulation behaviors of clay suspensions exhibit a complex behavior in the presence of Fe^{3+} ions.

Experimental results imply that as the increase of particle concentration, aggregates of clay particles and Fe hydrolysis tended to be much more negatively charged, especially for bentonite particles which possess about twenty times negative charge comparing with that of kaolin. The addition of Fe^{3+} altered the surface charge properties of both clay suspensions by the function of neutralization and bridging enmeshment as shown in Fig.6 and Fig.7.

4.2 Coagulant dosage control

In view of the above discussion that the properties of clay particles and raw water alkalinity play the dominant roles in the coagulation dosage control, we tried to use initial colloid charge and alkalinity as dominant parameters to determine the optimal FC dosage.

Performing jar-test and colloid titration experiment using bentonite (3mg/L~300mg/L) and kaolin (20mg/L~300mg/L) as clay suspension source and Na_2CO_3 as alkalinity source (30mg/L~200mg/L), a series of data about critical coagulant dosage, raw water charge and raw water alkalinity were obtained.

Based on multiple regression analysis of the above data, a linear regression model was proposed showing at below:

$$D = -0.13466 \times \exp(C) + 0.00314 \times \text{Alk} + 0.148$$

Where, D; predicted coagulant dosage (mmol/L), C; raw water colloid charge (meq/L),

Alk; raw water alkalinity (mg/L as Na_2CO_3)

The predicted coagulant dosage calculated from above formula is showing in Fig.10. Abscissa presents the sample order of raw water and ordinate is Fe dosage (mmol/L) as Fe. Curves D_1 and D_2 denote the coagulation critical dosages getting from jar-test experiments. Calculated result denotes the estimated values by multiple regression analysis. The result on the relationship between critical coagulation Fe dosage D_1 , obtained from jar-test and the dosage calculated by the formula shows a very high correlation.

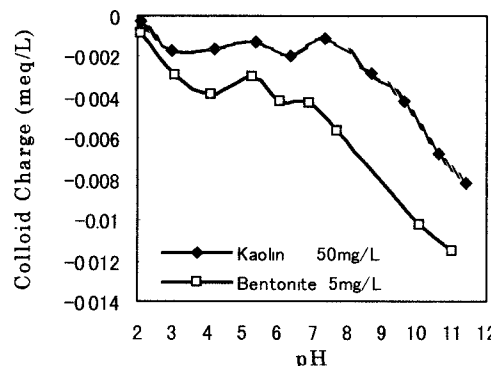


Fig. 9 Colloid charge as a function of pH at suspension concentration of kaolin 50mg/L and bentonite 5mg/L

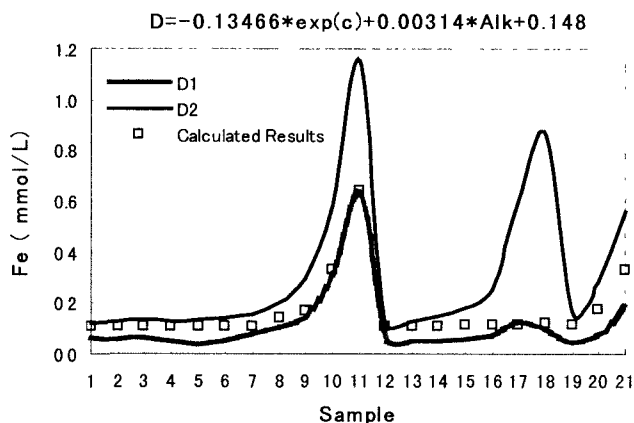


Fig.10 The result of multiply regression analysis for the dosage control

The analysis of kaolin and bentonite source water was just for giving an example, which is far away from identifying the real situation. A detailed investigation of the dosage control using raw water alkalinity and colloid charge as parameters in the presence of coexist ions and organic substances is the subject of our next work.

5. Conclusions

The objectives of this study were twofold. First one is to quantify the different coagulation behaviors of kaolin and bentonite suspensions. Second, to provide a formula for Fe coagulant dosage control in water treatment processing.

The results presented in this paper demonstrate that bentonite possesses very large negative surface charge comparing with kaolin particles. This caused its coagulation behavior to be greatly different with that of kaolin. The effects of alkalinity were to increase the optimum coagulant dosage, enlarge the effective coagulant dosage range and also enlarge the optimum pH range. Colloid charge of clay suspensions reflected their cation exchange capacity to a great extent. The surface charge of clay particles and raw water alkalinity were considered to play the dominant roles in the coagulation dosage control. Considering initial colloid charge and alkalinity as parameters, a multiple regression formula was proposed to estimate the optimal dosage of Fe coagulant. Comparison between the results obtained from jar-test and the dosage calculated by the proposed formula showed a high correlation. From these facts, it was estimated that colloid charge of clay particle is a good index for understanding coagulation behaviors of clay suspensions, and for the estimation of optimum dosage of coagulant. Moreover, it can be measured easily in a very short time.

References

1. Nakamura Fumio (1974) The Study about the Determination of Coagulant Dosage, I, II, III, J. Japan Water Works Association, No.480, pp.2-14, No.481, pp.26-33 and No.482, pp.2-15
2. Sang-kyu Kam, John Gregory (1999) Charge determination of synthetic cationic polyelectrolytes by colloid titration, Colloids and Surfaces A, 159, pp.165-179
3. S.Kawamura (1996) Optimization of basic water-treatment process-design and operation: coagulation and flocculation, J. Water SRT Aqua, Vol.45, No1, pp.34-47.
4. Steven K. Dentel and James M. Gossett. (1988) Mechanisms of Coagulation with Aluminum Salts, J. AWWA, 168:4:187-199
5. Tom Asselman and Gil Garnier (2000) Adsorption of model wood polymers and colloids on bentonites, Colloids and Surfaces A, Vol.168, pp.175-182
6. Stephen B. Johnsona, David R. Dixonb and Peter J. Scalesa (1999) The electrokinetic and shear yield stress properties of kaolinite in the presence of aluminum ions, Colloids and Surfaces A: Vol.146, pp.281-291
7. Hsiao-Wei Ching, Theodore S. Tanake and Menachem Elimelech. (1994) Dynamic of Coagulation of Kaolin Particles with Ferric Chloride, Water Research, Vol.28, pp.559-569.
8. J. Leentvaar, T. S. J. Ywema and R.E.Roersma (1979) Optimization of Coagulant Dose in Coagulation –flocculation of Sewage, Water Research, Vol.13, pp.229-236
9. Johannes Haarhoff and John L. Cleasby (1988) Comparing Aluminum and Iron Coagulants for In-line Filtration of Cold Water, J. AWWA, 168:4:80