

Electrolytic Aggregation Treatment without Coagulant Dosage for Retentate

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"This paper has not been submitted elsewhere in identical or similar form, nor will it be during the first three months after its submission to short communication in *Separation & Purification Technology*."

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Abstract

An electrolytic treatment promoting aggregation compatible with the production of a dense aggregate was developed and studied in a batch test to thicken the retentate without coagulant dosage. A kaolin suspension with turbidity of about 200 NTU with a large fraction of fine particulates was used as the retentate. The aggregation of the electrochemically treated suspension increased with increasing mixing intensity in the range of 40 to 160 rpm for 5 min. The electrolytic treatment could also decrease the residual turbidity at the retention of about 150 h to one-fourth that of the untreated suspension, and moreover did not significantly change the sludge concentration, in contrast to the decreased sludge concentration of the acidified suspension maintained in the pH range of 4.5-5.0. A positive shift of the surface charge of particulates observed in the treated suspension suggests that the particle destabilization occurred in a pH range of 5.5-7.0, because of the hydrolysis of Al ions released electrochemically from kaolin clay.

Keywords: Electrolytic treatment; Fine particulates; Retentate; Residual turbidity; Surface charge

19 **Introduction**

20 In water purification processes, coagulation has been widely used in order to
21 settle turbid substances quickly in raw water. However, it produces watery voluminous
22 sludge that gives rise to the issue of decreasing efficiency during the following sludge
23 treatment [1]. Current electrocoagulation utilizing metal ions dissolved from the anode
24 as the coagulant has not significantly decreased the sludge volume. In addition, it might
25 induce a decrease in the anode efficiency accompanied by an increase in the number of
26 anode replacement times [2,3]. On the other hand, the membrane filtration process with
27 a high solid-liquid separation ability has been increasingly used as a method without
28 coagulant in recent years [4]. This process yields a highly concentrated suspension as
29 the retentate, because the filtered particles must be removed from the membrane by
30 regular washing. However, the thickening process requires a long retention time because
31 the retentate has a large fraction of fine particulates without the addition of coagulant.
32 Therefore, a more improved process is desired [5].

33 In this study, an aggregation treatment based on an electrolytic process for the
34 retentate was developed instead of adding a coagulant. In this innovative idea, there is
35 no need to use sacrificial anodes. This method postulated that 1) direct anodic oxidation
36 of the retentate by an insoluble electrode induces charge neutralization of the negatively
37 charged particles owing to protonation and reduces repulsive forces between the
38 particles, and 2) subsequent mixing promotes interparticle binding, resulting in an
39 increase in the aggregation. Turbidity removal from concentrated suspensions by an
40 electrolytic process alone has not previously been reported. In a batch test, using kaolin
41 suspension with a large fraction of fine particulates to simulate the raw retentate, the
42 effects of the electrolytic treatment on the aggregation characteristics, such as turbidity
43 removal, and aggregating ability that is related to the mixing strength, were evaluated

compared to that of the untreated suspension and the acidified suspension in the pH range of 4.5-5.0.

2. Experimental

2.1. Experimental setup and procedures

A cylindrical platinized titanium anode (12 cm diameter \times 12 cm height) and a cylindrical steel cathode (14 cm diameter \times 17 cm height) were installed in a 3 liter cylindrical cell at a distance of 1 cm (Fig. 1). The cathode surface was covered with filter paper (ADVANTEC, No. 5C) to retard the diffusion of the catholyte and avoid the direct contact with kaolin particles, and tiny holes were made at the top of the covered filter paper for effluent hydrogen gas. The anode and cathode were connected to a galvanostatic rectifier (PMC35-2A, KIKUSUI). Each electrolysis was conducted at an anode current density of 4-6 mA/cm².

2.2. Preparation of test suspensions and Al ion concentration

After settling a suspension of kaolin (Wako Chemicals) dispersed in tap water (total iron concentration of less than 0.1 mg/L, pH 7.5, alkalinity of 40 mg/L) to a concentration of 0.5 g/L, the supernatant with an aggregated mass (AGM, see later) of less than 80 mg/L, taken from the reported data [5] was suction-filtered through a 0.2 μ m membrane filter (ADVANTEC, MFS), and the residue on the filter was used as kaolin sludge. An original kaolin suspension (OKS) was prepared by dispersing the kaolin sludge to a turbidity of about 200 NTU [6], and an acidified kaolin suspension (AKS) was prepared by adjusting the pH of OKS using HCl in the range of 4.5-5.0, which was retained for at least 1h for a comparative test. The turbidity was determined using a turbidimeter (2100N, Hach Corp.). An OKS of 1.2 L in the cell was electrolyzed

until the solution-pH measured with a glass electrode (TOA-DKK) reached less than 4. Thereafter, both electrodes were simultaneously removed from the cell to collect the catholyte, and the cathode was placed in another vessel. Finally, the anolyte was withdrawn through the outlet of the cell and stored for at least 20 h, by which pH was adjusted to 5.5-7.0 with the collected catholyte of pH 12 and retained for at least 1 h to produce an electrolytically treated kaolin suspension (EKS) for the comparative test.

The increase of the Al ion concentration in the anolyte was measured by atomic-adsorption spectroscopy (AA-6300, Shimadzu). The anolyte and catholyte were collected separately to avoid a sudden change in the solution pH in the cell after the electrolysis stopped.

2.3. Assessment of aggregation ability: AGM

AGM is defined as the mass index assessing the degree of aggregation by taking into account the following: a) the early dispersion of the kaolin sludge is required to represent the same particle distribution as that in the supernatant before filtration, b) the turbidity of kaolin suspension is proportional to its mass concentration in the range of less than 300NTU [2], c) the amount of sludge produced in a water purification process used to be calculated on the basis of a difference between the turbidity of raw water and purified water in the engineering field [7].

The difference between the turbidity of a 30 ml sample (T_0) taken from the test suspension after gentle mixing, and the turbidity of the filtrate (T_{10}) of the sample passed through a 10 μm filter is defined as the AGM ($= T_0 - T_{10}$). The AGM is expressed as the mass concentration (mg/L) in a suspension with turbidity of 200 NTU in this study.

2.4. *Residual turbidity and sludge concentration*

In the aggregation test, each 300 ml sample of test suspension taken from OKS and EKS was mixed at 40, 90 and 160 rpm for 5 min using a jar tester (VT-4P, Sugiyamagen). The mixer was placed as close as possible to the bottom to prevent the aggregates from settling. Test suspensions of 3.0 L of each mode mixed at 160 rpm were each placed in the cell (Fig. 1), after which the measurement of the AGM in the mixed suspension was carried out, the suspensions were then allowed to sufficiently settle for 72h. Thereafter, the supernatant was moved to another cell by siphoning, followed by the withdrawal of the sludge into a graduated cylinder. The sludge concentration was determined in accordance with the method [8] after 48 h of retention. The residual turbidity during 145 h of retention was measured at certain intervals for a 30 ml sample removed from about 50 mm below the water level using a pipette. These experiments were carried out at room temperature.

2.5. *Surface charge*

Each 120 ml sample of the two modes of suspension adjusted to a turbidity of about 30 NTU and to the range of pH 7.5 to 8.0 by adding tap water and the catholyte was mixed at 40 rpm for 20 min followed by retention for 30 min. The stabilized pH was then measured, followed by the determination of the surface charge for duplicate 50 ml samples taken from the gently mixed suspension by titration using Toluidine Blue as an indicator [9].

3. Results and Discussions

3.1 pH change in original suspensions during the electrolysis and concentration of released Al ions

After the 20 min electrolysis elapsed, the pH of the anolyte and the catholyte divided by the covering filter paper clearly changed to less than 4 and 12, respectively. At the anode, the contact and diffusion of the kaolin particles were promoted more than at the cathode because of the effect of the covering filter paper. Under the above electrolysis conditions, the power consumption per liter of the retenate was average 38 kJ. The increase in the concentration of Al^{3+} ions in the anolyte with a turbidity of 230-245 NTU was 15.9-17 ppb.

3.2 Aggregated mass, Residual turbidity and sludge concentration

Changes in the AGM for the three modes of suspension mixed at 40, 90 and 160 rpm are shown in Fig. 2. The pH of the EKS remained constant during mixing. The AGM of the OKS decreased with increasing mixing intensity, while the AGM of the AKS increased with wider variations and that of the EKS steadily increased with increasing mixing intensity.

Changes in the average residual turbidity as a function of retention time for the three modes of suspension with the same initial AGM of 70.7 mg/L are shown in Fig. 3. The residual turbidity-time curves can be clearly divided into two groups corresponding to the treated and untreated suspensions, particularly in the retention time range after 24 h. The rate of decrease of the residual turbidity for each suspension showed the trend that the suspension with a larger AGM has a higher rate. Although the average AGM of the AKS was larger than that of the EKS (AKS: 116 mg/L, EKS: 92 mg/L), a large rate difference between the two modes cannot be seen. However, the final residual turbidity of each EKS remained above 10 NTU, whereas that of each EKS and AKS decreased to below 10 NTU at 72 h. Comparison of the final values revealed that those of the EKS decreased to about one-fourth those of the OKS. Next, the mean sludge concentrations

versus the AGM for the two modes of suspension were almost the same, but that of the AKS decreased as shown in Fig. 4. The surface charge of the OKS indicated negative values, while that of the EKS indicated positive ones in the pH range of tap water and that of the OKS at pH 5 indicated positive value owing to protonation less than that of the EKS, as shown in Table 1.

Generally, the particle association of platelike clay particles, such as kaolinite, has three different modes: edge to edge (E-E), edge to face (E-F) and face to face (F-F) [10]. The E-F association predominates in the low pH range less than 5.5 as a result of attractive electrostatic interactions between negatively charged surfaces and positively charged edges at low pH. At pH values above 6 when ionic strengths are high, the most probable association is the F-F mode, in which particles can link up in the E-E and E-F modes to produce continuous networks within the suspension [11,12].

The steadily increasing trend of the AGM for EKS as the mixing intensity (40 to 160 rpm) increases is thought to be due to the evolution of the F-F mode reinforced with the networks leading to shear-induced aggregation compatible with the production of strong, dense fragments at low alum concentrations [13, 14]. In contrast, the unstable aggregation trend of the AKS seems to be induced by the E-F mode with random particle orientation producing fragile aggregates that are more susceptible to fragmentation caused by fluid shear than those in the case of the EKS[12].

The significant difference in the rate of decrease of the residual turbidity between the two modes suggests that the fine particles passed through a 10 μm filter in the EKS formed larger aggregates with the mean size less than 10 μm that are not captured by the 10 μm filter, but have increased density that leads to a faster settling rate. That is, the electrolytic treatment is expected to have a significant effect on the aggregation of fine particles.

The sediment with mostly the E-F mode has a voluminous, card-house structure, while that with the F-F mode has a card pack structure as a result of the van der Waals attractive force, showing a dense, closely packed arrangement of particles and a relatively lower water content [12]. The sludge concentration of the EKS showed a value very close to that of the OKS, which indicates that this treatment could proceed without contamination by dissolved metal ions, i.e., without coagulant dosage. The increased concentration of Al ions in the anolyte seems to have been caused by the dissolution of Al adsorbed on the kaolin clay owing to the anodic reaction accompanied by acidification and oxidation [15]. The dissolved Al ions would produce various hydrolysis species when the solution pH is in the range of 5.5 to 7.0 which may cause charge reversals of the negative charge of the surface on which they adsorb. Because of the extremely low Al ion concentration in the EKS, the charge reversal is considered to be induced by adsorption-destabilization [16].

5. CONCLUSIONS

Kaolin suspensions simulating raw retentate were electrolyzed until the solution pH decreased to less than 4, using a newly designed cell followed by pH adjustment. The aggregation trend of the treated suspension was investigated in relation to the mixing intensity and the surface charge shift. Aggregation of the electrolytically treated kaolin suspension (EKS) was steadily promoted while aggregation of the acidified kaolin suspension (AKS) was unsteadily promoted by increasing the mixing intensity, and the residual turbidities of the EKS and AKS were significantly decreased compared to that of the original kaolin suspension (OKS). Averaged high sludge concentrations for the OKS and EKS were shown to be nearly equal, however that of the AKS decreased. This fact suggests that this electrolytic treatment is effective also for

decreasing the sludge volume because no coagulant is added. Different trends between the AKS and EKS in terms of aggregation, turbidity removal and sludge concentration are attributable to the different particle associations.

Al^{3+} ions released from kaolin by the electrolysis are presumed to form insoluble hydroxide species upon pH adjustment, which would have a significant effect on the destabilization of fine particulates.

References

- [1] J.H. Bruns, P.H. Nielsen, and K.Keiding, On the stability of activated sludge flocs with implications to dewatering. *Water Res.* 26 (1992) 1597-1604.
- [2] T.Uchibori, Electrocoagulation of kaolin suspensions using *Al* and *Fe*. Master Thesis Saitama University (1999) (in Japanese).
- [3] G.Chen, X.Chen, and P.L.Yue, Electrocoagulation and electrofloatation of restaurant wastewater. *J. Envir. Engng.* 126 (9) (2000) 858-863.
- [4] Japan Water Res. Center, www.jwrc-net.or.jp
- [5] J.Y.Huang, S.Takizawa, K.Fujita, Retentate thickening by submerged hollow-fiber MF thickener in membrane water purification process. *Envir. Engng. Research* 36 (1999) 277-286 (in Japanese).
- [6] K.Fujita, S.Takizawa, and J. Lee, Retentate thickening by hollow-fiber MF thickner. *J.JWWA* 755 (19) (1997) 29-36 (in Japanese).
- [7] S.Naito, and K.Fujita, *Water Supply Engineering Handbook*, third ed., Gakukensha, Tokyo 1993 pp.168-191 (in Japanese).
- [8] *Test Method for Water Supply*, second ed. JWWA Tokyo 1993 pp.90-91 (in Japanese).
- [9] S.Kawamura, G.P.Hanna Jr, and K.S.Shumate, Application of colloid titration

219 technique to flocculation control. J.AWWA Aug (1967) 1003-1013.

220 [10] H.Van Olphen, Introduction to clay colloid chemistry, Wiley, New York, (1977)

221 93-95.

222 [11] I. E. Melton, R. Rand, Particle interactions in aqueous kaolinite suspensions. J. Coll

223 & Interface Sci.60(2) (1977a) 308-320.

224 [12] V. Ravisangar, K.E. Dennett, T. W. Sturm, A. Amirtharajah, Effect of sediment pH

225 on resuspension of kaolinite sediments, J. Envir. Engng. 127 (6) (2001) 531-538.

226 [13] P.T.Spicer, and S.E.Pratsnis, Shear-induced flocculation: The evolution of floc

227 structure and the shape of the size distribution at steady state. Water. Res. 30 (5)

228 (1996) 1049-56.

229 [14] V.Oles, Shear-induced aggregation and breakup of polystyrene latex particles. J.

230 Coll. & Interface Sci., 154 (2) (1992) 351-358.

231 [15] I.E. Melton, and R. Rand, Particle interactions in aqueous kaolinite suspensions. J.

232 Coll. & Interface Sci., 60(2) (1977b) 321-330.

233 [16] A.Amirtharajah, and K.M.Mills, Rapid-mix design for mechanisms of alum

234 coagulation. J.AWWA 74(4) (1982) 210-216.

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Table 1 Surface charge for two modes of suspension

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solution pH	Charge in meq/1X 10 ⁴ L	
	OKS	EKS
5	49	60
7.5	-1.3	17.5
8	-13.8	5

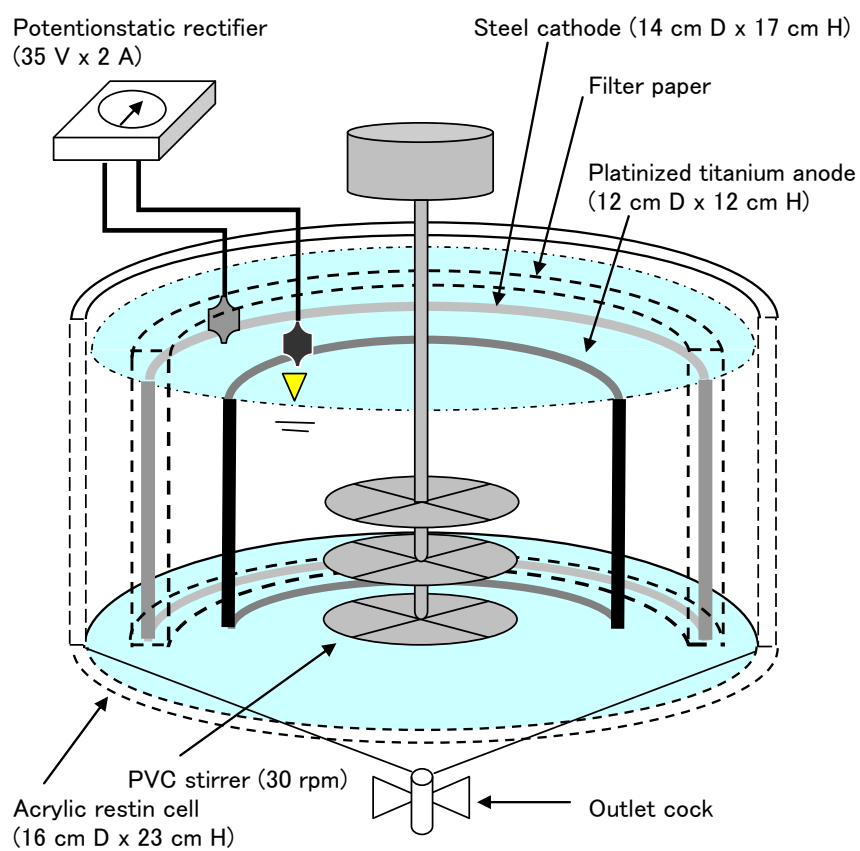


Fig. 1 Schematic diagram of the experimental setup for electrolytic treatment

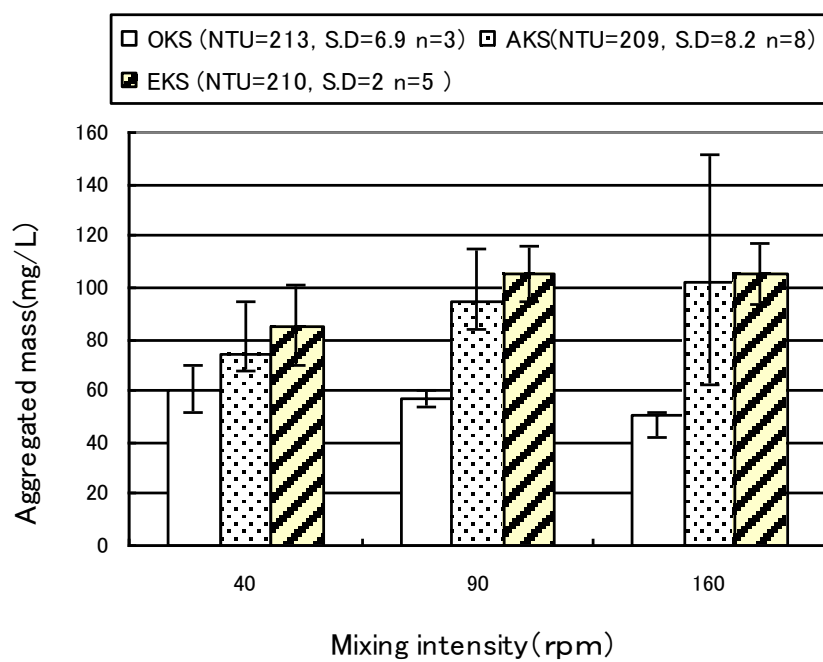


Fig. 2 Aggregated mass of OSK, AKS and EKS at each mixing intensity

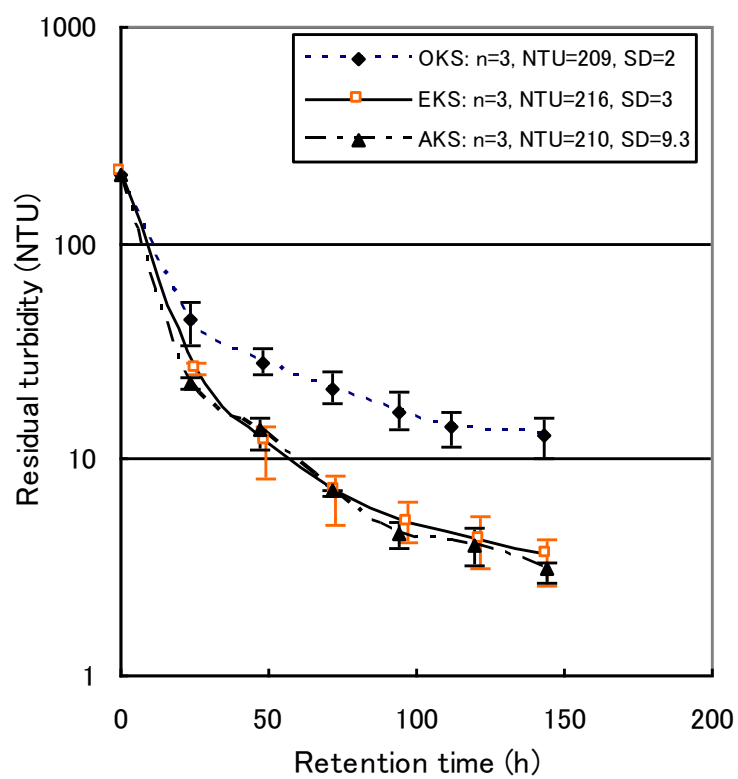


Fig. 3 Time variations of the residual turbidity for OKS, AKS and EKS mixed at 160 rpm for 5 min

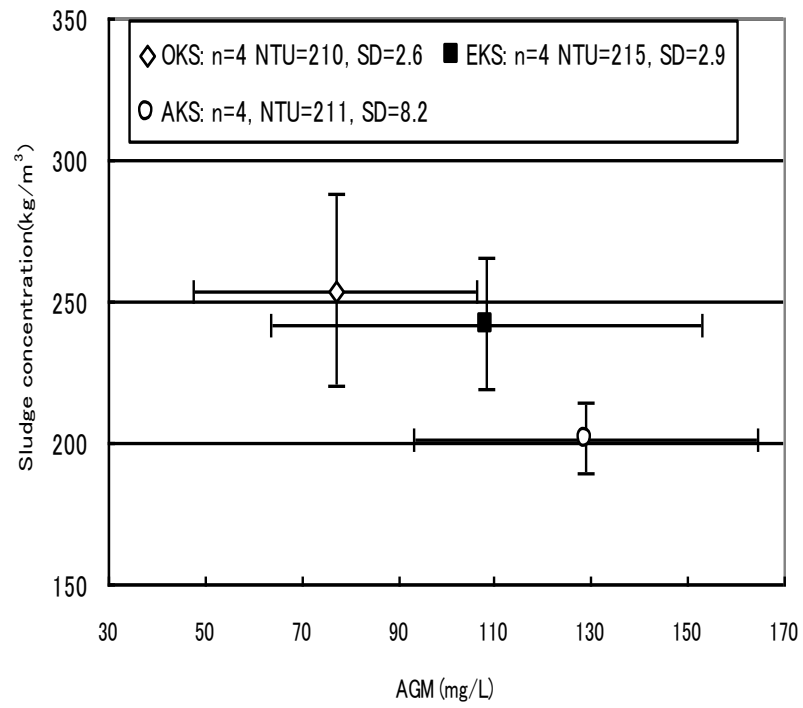


Fig. 4 Sludge concentration range versus aggregated mass range for OKS, AKS and EKS