

입상여과에서 액반플럭의 부착

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Alum Floc Attachment in Granular Media Filtration

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Abstract : Granular media filtration is used almost universally as the last particle removal process in conventional water treatment plants. Therefore, superb particle removal efficiency is needed during this process to ensure a high quality of drinking water. However, every particle can not be removed during granular media filtration. Besides the pattern of particle attachment is different depending on physicochemical aspects of particles and suspension. Filtration experiments were performed in a laboratory-scale filter using spherical glass beads with a diameter of 0.55 mm as collectors. A single type of particle suspension (Min-U-Sil 5) and alum coagulation was used to destabilize particles. The operating conditions were similar to those of standard media filtration practice: a filtration velocity of 5 m/h. More favorable particles, *i.e.*, particles with smaller surface charge, were well attached to the collectors especially during the early stage of filtration when zeta potential of particles and collectors are both negative. This selective attachment of the lower charged particles caused the zeta potential distribution (ZPD) of the effluent to move to a more negative range. On the other hand, the ZPDs of the effluent moved from more positive to less positive when the surface charge of particles was positive and this result was thought to be caused by ion transfer between particles and collectors.

keywords : Filtration, Particle attachment, Destabilization, Zeta potential distribution

1. 서론

A wide variety of particles including microorganisms, other organic materials, and inorganics are present in water as a result of either natural events or human activities. As higher quality drinking water is demanded, the need to remove those particles in drinking water treatment processes is increased.

Filtered water with a turbidity of 0.1 NTU is considered safe for drinking purposes (Hatukai et al., 1997). Even at this low turbidity, the water can contain hundreds of particles per milliliter. McTigue et al. (1998) reported that raw water particle counts (greater than 2 μ m) ranged from 176 to over 1 million particles/mL as a result of a survey of 100 water treatment plants (WTPs) in the U.S. The median filtered particle count (greater than 2 μ m) was found to be 14 particles/mL, and ranged from less than 1 particle to approximately 8,000 particles/mL. With proper pretreatment, *e.g.*, destabilization of particles, most of the particles can be efficiently removed. However, some

of the particles pass through the filters, or detach after being captured. The patterns of particle attachment vary with the particle size, solution chemistry, stage of filtration, and operating conditions including particle destabilization methods.

Destabilization in water treatment can be defined as the process in which the particles in a stable suspension are modified to increase their tendency to attach to other particles. One of the most popular destabilization methods applied in conventional WTPs is using an inorganic coagulant, such as aluminum sulfate (alum) or ferric sulfate, that rapidly hydrolyzes to form insoluble precipitates and/or soluble polymers.

When alum ($\text{Al}_2(\text{SO}_4)_3$) is added to water, hydrolysis reactions occur to form positive, negative, or neutral aqueous dissolved aluminum complexes. The speciation of aluminum depends on pH, the total concentration of aluminum, and the time elapsed after adding alum to the water. Depending on the reaction time, monomeric species, such as $\text{Al}(\text{OH})^{+2}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3$, and $\text{Al}(\text{OH})_4^-$; polymerized species such as $\text{Al}_8(\text{OH})_{20}^{+4}$ or $\text{Al}_{13}(\text{OH})_{34}^{+5}$; and the insoluble $\text{Al}(\text{OH})_3(\text{s})$, are formed before particle destabilization is started. The soluble hydrolysis products

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as well as the aluminum ion modify the surface charge of the particles, which in turn, produce the effect of charge neutralization (Letterman et al., 1999; Edzwald et al., 1997).

In drinking water treatment, coagulation caused by inorganic coagulants occurs predominantly by two mechanisms: charge neutralization and sweep coagulation. Charge neutralization is caused by the adsorption of charged hydrolyzed species onto the colloids. Adsorption of hydrolysis species affects the electrostatic properties of suspended particles, which, in turn, influences their tendency to attach. Sweep coagulation occurs between particles and the precipitating hydroxide, and generally occurs at higher concentrations of the metal addition than is required for charge neutralization (Amirtharajah and Tambo, 1991).

During this research, the charge neutralization mechanism was adopted to investigate the relationship between surface charge of particles and particle removal patterns. This mechanism involves reducing the net surface charge of the particles in the suspension; in turn, the thickness of the diffuse layer surrounding the particles is reduced; and finally the energy that is required for making contact between particles is minimized.

The primary focus of this research was to investigate particle attachment during the clean bed removal stage for destabilized particles. During the research, the zeta potential distribution (ZPD) of particles, pH, solids concentration, ionic strength, and other significant parameters were measured or controlled to investigate why some particles penetrate granular media filters while others attach to the filter media.

2. MATERIALS AND METHODS

A schematic diagram of the experimental filtration system utilized in this research is presented in Fig. 1. A clear acrylic laboratory-scale filter column was used. This column has an inner diameter of 3.8 cm and a maximum media depth of 14.2 cm. During this research, the filter media depth was fixed at 10 cm. More detailed explanation on filter system can be found elsewhere (Kim, 2004).

Min-U-Sil 5 (U.S. Silica Company, WV) was used for the particle material during this research, and it was dispersed in Millipore water in order to make the particle suspension. Solid glass spheres (Potters Industries, Inc., NJ) in a size range of 0.5 to 0.6 mm were chosen for filter media. The filter media were cleaned to obtain uniform surface chemistry conditions as documented by Tobiason and O'Melia (1988). Particle and collector surface chemistry can be modified with many techniques, while alum destabilization were used to alter surface chemistry

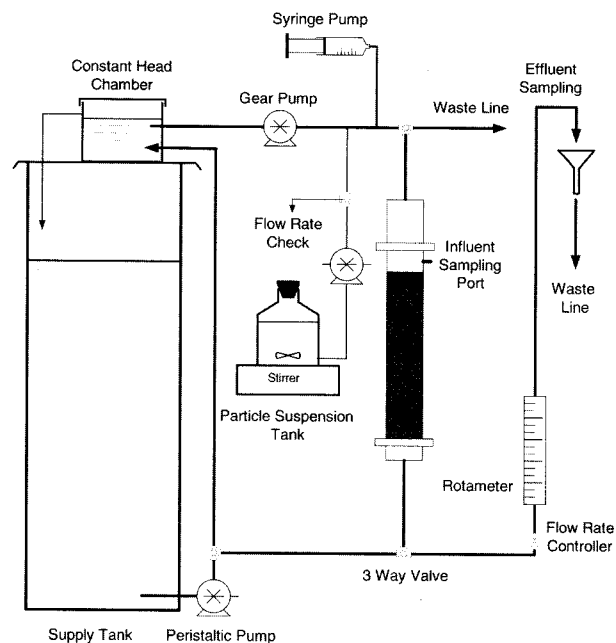


Fig. 1. Schematic of experimental filtration system (not to scale).

conditions during this research. Zeta potential of particles were measured by Zetaphometer IV (CAD, France) and solids concentration of particles were measured using a Perkin-Elmer UV/VIS spectrophotometer (Model: lambda 3).

Amirtharajah and Mills (1982) noted that charge neutralization mechanisms are dominant in the pH range between 5.0 and 5.5 when alum is used as a coagulant. Therefore, pH 5.2 was chosen during this research. Furthermore, to supply the proper buffer capacity and alkalinity, Min-U-Sil 5 particles were dispersed in $2 \times 10^{-3} \text{M}$ NaHCO_3 throughout the alum destabilization experiments, including jar-tests.

3. RESULTS AND DISCUSSION

To find a relationship between zeta potential and alum dose, a typical jar-test was adopted: 1 minute of rapid mixing (150 rpm), 20 minutes of slow mixing (50 rpm), and 20 minutes of settling. The mean zeta potential of Min-U-Sil 5 as a function of alum doses at pH 5.2 is shown in Fig. 2(A).

The isoelectric point (IEP) of Min-U-Sil 5 was observed at an alum dose of approximately 0.6 mg/L, when the influent solids concentration was 20 mg/L. On the other hand, the solids concentration remaining (C/C_0) versus alum doses in the jar-tests is shown in Fig. 2(B). As expected the solids concentration removal was better near the IEP. It can be thought that the attraction force was dominant at this point, leading to the best floc formation at the IEP.

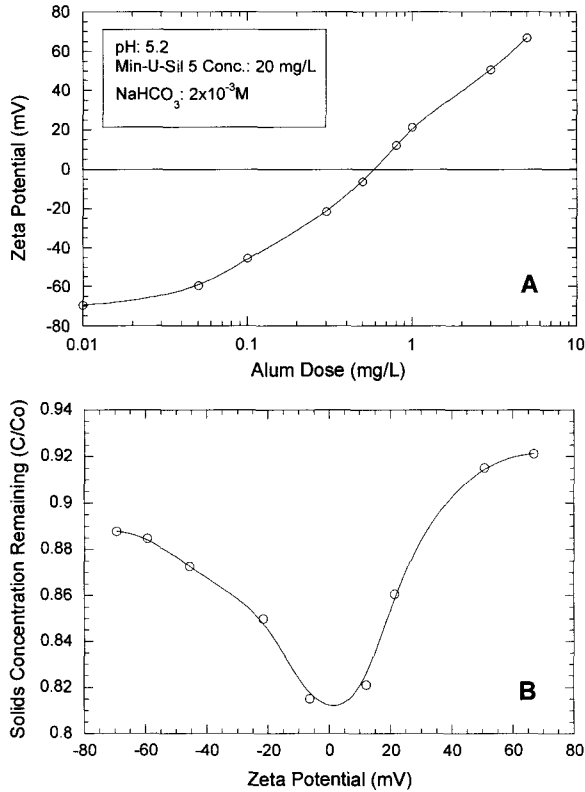


Fig. 2. Effect of alum dose on surface charge (A) and effect of surface charge on coagulation (B).

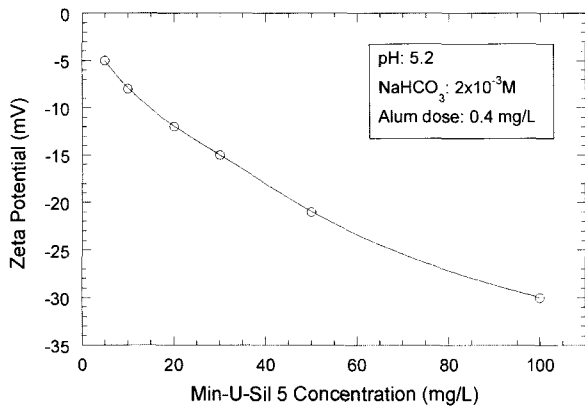


Fig. 3. Mean zeta potential of Min-U-Sil 5 as a function of solids concentration.

During the alum destabilization, one concern is whether the mean zeta potential of particles is a function of particle concentration. When the charge neutralization mechanism is adopted, the amount of needed positive

charge, *i.e.*, the amount of coagulant, can be assumed to be proportional to the total surface area of particles in the suspension (Letterman et al., 1999). This idea is confirmed in the results shown in Fig. 3.

One assumption made throughout this research is that the surface charge of the glass beads and Min-U-Sil 5 was the same, or at least similar. However, during the alum destabilization experiments, this assumption may be void because the surface areas of both materials were not the same, as presented in Table 1. During the coagulant destabilization, the magnitude of destabilization of particle surface charges was a function of the surface area of particles.

Table 1. Physical characteristics of particle and glass beads

Characteristics	Min-U-Sil 5	Glass bead
Median particle size (μ m)	1.7	550
Specific gravity (g/cm ³)	2.65	2.50
Concentration (mg/L)	20	1,525,000 ²⁾
Particle number (number/mL)	907,000 ¹⁾	7,000
Surface area (cm ² /mL)	1.4	67.0

1) larger than 0.9 μ m when particle concentration is 20 mg/L

2) at the filter column (porosity is 0.39)

Table 1 shows that the surface area of the glass beads was at least 50 times that of the particle suspension. This difference could make dissimilar surface charge characteristics of particles and collectors during the coagulant destabilization. As the surface area of the glass beads was much larger than that of the particles, it was necessary to provide alum for the filter media prior to the introduction of particles. The alum flow was started an hour before the particle suspension in the filtration experiments. In this way, it was thought that the glass media would be at (or near) equilibrium with the alum and therefore be destabilized throughout the filtration period. Unfortunately, measurement of the ZPD of the media was not possible.

Based on the jar-test and preliminary tests, three different chemical conditions were chosen to represent three different surface charge conditions of particles: negative, positive (charge reversal), and near neutral. A summary of zeta potential measurements at the three different alum doses is shown in Table 2, while the corresponding influent ZPDs are presented in Fig. 4.

Table 2. Summary of Zeta Potential Measurements at Three Different Alum Doses (rapid mixing)

Alum dose (mg/L)	Mean zeta potential (mV)	Number of particles measured	Standard deviation (mV)	Coefficient of variation (%)
0.06	-38.9	108	12.1	31.1
0.2	7.9	166	12.2	154.4
0.8	54.3	96	9.9	18.2

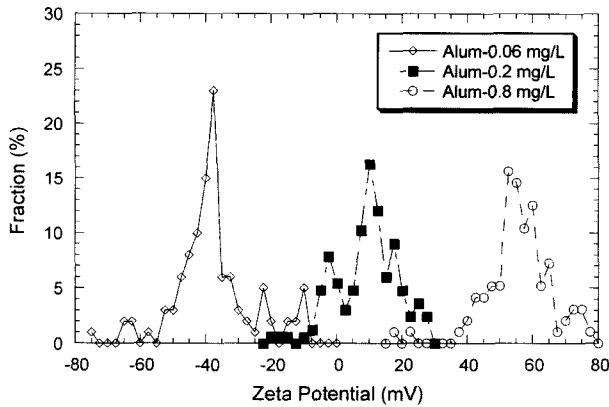


Fig. 4. ZPDs of influent at three different alum doses (pH-5.2).

3.1. Below-optimum dose (0.06 mg/L alum dose)

The ZPDs of particles at an alum dose of 0.06 mg/L during the initial stage of filtration are shown in Fig. 5(A). The ZPD of the effluent after 2 minutes clearly shifted to more negative values. During the initial stage of filtration, less negative particles were well attached to the collectors, while more negative particles were not. The same trend was noticed in the sample of effluent at 10 minutes, and its trend is more obvious than that of the 2 minute sample. From this graph, it can be thought that, at the initial stage of the filtration, less stable particles were well attached to the filter media. Therefore, during this time, water chemistry appears to be one of the most important parameters for particle removal.

On the other hand, Fig. 5(B) shows the ZPDs of alum dose of 0.06 mg/L during the later stage of filtration. During this stage, ZPDs of the effluents moved from a more negative region to a less negative region, but remained less than the ZPD of the influent throughout the filtration experiment. This trend was also noted in the pH control experiments (Kim, 2004). This trend is assumed to be caused by two reasons. The first reason is the ripening effect. As the surface area of collectors increased with particle accumulation, particles whose attachment was not favorable during the initial stage of filtration can attach to the collector. The second reason is the possibility of detachment of attached particles. Flocs that were once attached to the filter media can be assumed to have less negative surface charge than particles that never become attached; thus, detachment of flocs can move ZPD from a more negative to less negative region.

3.2. Above-optimum dose (0.8 mg/L alum dose)

A second experiment with alum was conducted at an alum dose of 0.8 mg/L. At this dose, almost every particle had a positive surface charge because the alum feed

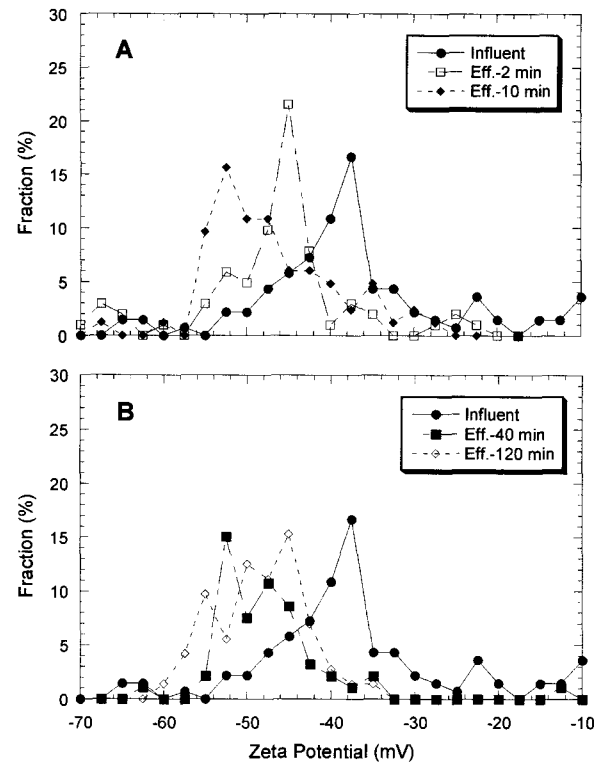


Fig. 5. ZPDs of Min-U-Sil 5 at alum dose of 0.06 mg/L during the initial stage (A) and later stage (B).

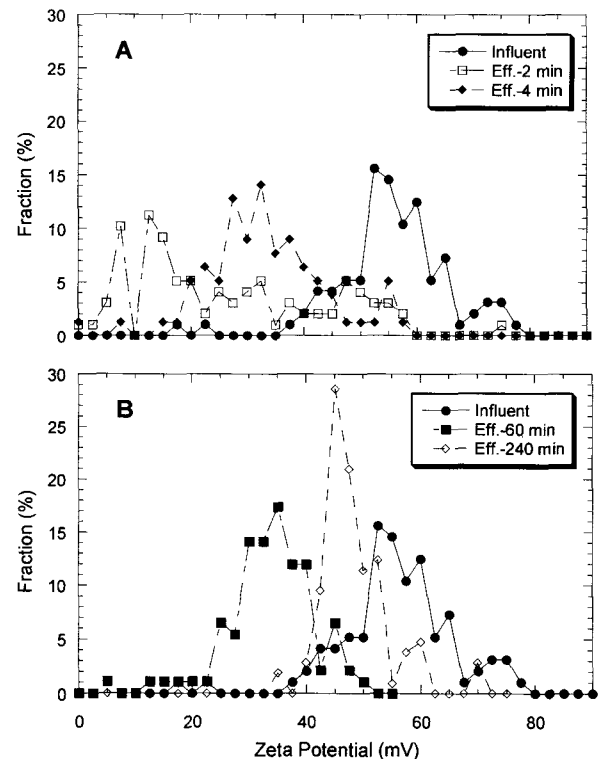


Fig. 6. ZPDs of Min-U-Sil 5 at alum dose of 0.8 mg/L during the initial stage (A) and later Stage (B).

exceeded the optimum dose.

The ZPDs of effluent during the initial stage of filtration at alum dose of 0.8 mg/L are shown in Fig. 6(A). The

majority of zeta potentials of the influent particles ranged from 30 mV to 80 mV, whereas the Eff.-2 min sample ranged from 0 mV to 60 mV, and the Eff.-4 min ranged from 10 mV to 60 mV. On the other hand, Fig. 6(B) represents the ZPDs of effluent during the later stage of filtration. The ZPDs of the effluent moved from more to less positive in the early part of the filter run and then gradually shifted back closer to the ZPD of the influent (*i.e.*, from less to more positive) in the later stage. Two things can be inferred from these graphs.

First, ZPDs of the effluent at the initial stage of filtration moved from a more stable to a less stable region, and soon afterwards they moved from a less stable to a more stable area. This finding is quite different from the results that were previously noticed during the alum dose of 0.06 mg/L experiments. More stable particles were well removed during the initial stage of filtration, and the ZPDs of the effluent moved from a less stable to a more stable area during the later stage of filtration at alum dose of 0.8 mg/L.

Second, effluent ZPDs did not overlap that of influent, which means that the ZPDs of the effluent were changed for some reason. Several assumptions can be made to explain this phenomenon. One likely possibility is that the surface charge of the glass beads was not similar to that of Min-U-Sil 5. Under alum destabilization, the surface charge of particles is a function of particle concentration, *i.e.*, surface area, as shown in Fig. 3. Therefore, the surface charge of particles can be different from that of the glass beads at the same alum dose, because their surface areas were different.

At above-optimum alum dose, though there was equilibrium between the supply water and glass beads during the pre-filtration step, equilibrium would not exist as soon as Min-U-Sil 5 particles were fed through the filtration system, because the chemistry of the solution can be changed with the feeding of particle suspensions. To create a surface charge equilibrium, positive charges, *i.e.*, coagulant, of particle surface can be desorbed, and after that desorbed coagulant can be adsorbed to the surface of the glass beads during the filtration. This, in turn, causes movement of the mean zeta potential of particles from more positive to less positive. With the accumulation of particles on collectors, equilibrium can be gradually reached between particles and collectors. Therefore, the rate of molecular exchange leading to ion transfer may decrease during the later stage of filtration, which in turn causes the movement of the mean zeta potential of particles from less positive to more positive.

Other possible explanations for the discrepancy between

surface charge ranges of influent and effluent ZPDs were considered, such as not establishing equilibrium before the filtration. To check this possibility two different equilibrium durations (*i.e.*, time periods of adding alum before adding suspension at time zero) were adopted and compared: 1 hour and 3 hours. However, there was no significant difference between them, which means that equilibrium duration was not a problem during this experiment.

3.3. Optimum dose (0.2 mg/L alum dose)

Another experiment was conducted near the neutral surface charge of particles. The ZPD at alum dose of 0.2 mg/L was broad, and the ZPDs at the initial stage of filtration were somewhat different from previous results.

The ZPDs of the influent and effluent at time 4 and 6 minutes after filtration began are shown in Fig. 7(A). The influent ZPD reveals that the majority of particles were between 30 and -15 mV, which means the influent ZPD ranged from negative to positive, including zero surface charges. On the other hand, the ZPDs of the effluent shifted slightly to the left toward the more negative area. One of the possible reasons for discrepancy of ZPDs ranges between the influent and effluent is charge adsorption/desorption in the filter column, as explained in the discussion of alum dose of 0.8 mg/L.

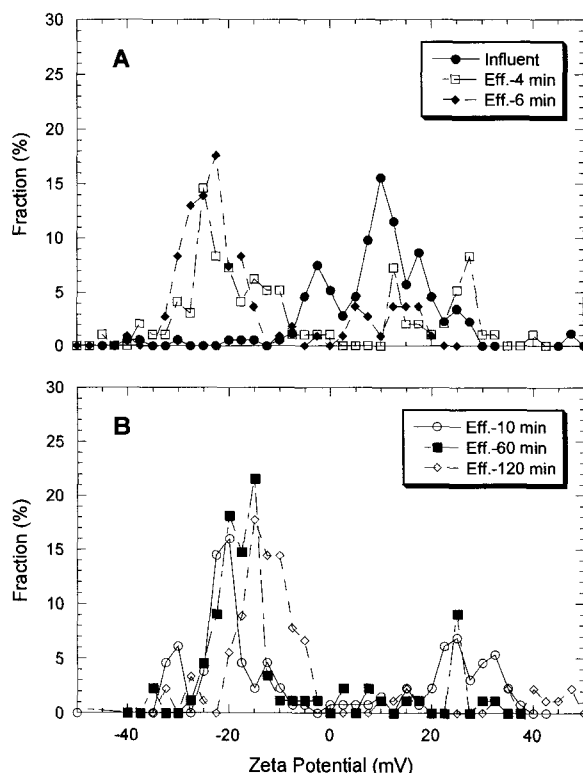


Fig. 7. ZPDs of Min-U-Sil 5 at alum dose of 0.2 mg/L during the initial stage (A) and later stage (B).

Unlike the experiment at an alum dose of 0.8 mg/L, a small peak was also noticed in the positive region of the ZPD for alum dose of 0.2 mg/L. The reason why this happened is not clear, but there was a possibility that some of impurities of the particles, glass beads, and coagulant might make this small peak in the positive area.

The ZPDs of the effluent after the initial stage of filtration are shown in Fig. 7(B). Both the negative and positive regions of this graph are worth considering. First, in the negative region, the general trend of the ZPDs is a movement from more to less negative (*i.e.*, to the right). A possible reason for this is that the mean surface charge of collectors was negative, though they had a broad ZPD. If this assumption is true, then less negative particles were well removed during the initial stage of filtration, but this removal will decrease with time. In the positive region, on the other hand, it is hard to find any trend, but with time the magnitude of positive particles was decreasing, which means that positive particles were well removed with time.

4. CONCLUSIONS

The major observations based on these filtration experiments are stated below.

1. During the initial stage of filtration, the mean zeta potential of the effluent was more negative than that of the influent, when the zeta potential of influent particles and collectors were both negative. It can be assumed that, during this stage, less stable (more destabilized) particles are better attached to collectors than more stable particles.
2. After the initial stage of filtration, the absolute value of the mean zeta potential of the effluent decreased slightly or remained constant with time for 4 hours of filtration when the zeta potentials of the influent particles and collectors were both negative; nevertheless, it still remained higher than that of the influent. Two reasons can be assumed to explain this trend: ripening effects and detachment of flocs.
3. When equilibrium is not present in terms of the surface charge among particles, collectors, and supply water, then there is a possibility for ion transfer to occur among them during the filtration. This phenomenon is more severe at the beginning of filtration, and its magnitude decreases with the accumulation of particles on the surfaces of collectors.

국문요약

입상여과는 표준식 정수처리 공정에서 입자물질 제거의 최종공정으로 대부분 사용되고 있다. 따라서 양질의 수돗물을 만들기 위해서는 입상여과에서 높은 수준의 입자물질 제거가 요구되고 있다. 그러나 여과공정에서 모든 입자물질을 제거할 수 없으며, 또한 입자물질의 부착특성은 입자와 용액의 물리화학적 특성에 따라 달라진다. 실험실규모의 여과칼럼과 입경 0.55 mm의 유리구슬을 여재로 한 여과실험이 수행되었다. Min-U-Sil 5가 입자물질로 사용되었으며 입자물질을 불안정화하기 위하여 액반을 사용하였다. 운전조건은 표준입상여과와 동일하였으며 여과속도는 5m/h였다. 입자와 여재가 모두 음의 표면전하를 갖을 경우 작은 표면전하를 갖는 입자가 여과초기에 여재에 잘 부착되었다. 작은 표면전하를 갖는 입자의 선택적 부착은 유출수의 제타전위분포를 더 음인 방향으로 이동시켰다. 한편 입자의 표면전하가 양의 큰 값에서 작은 값으로 변화했는데 이는 입자와 여재사이의 이온전이에 기인하는 것으로 생각된다.

주제어 : 여과, 입자물질부착, 불안정화, 제타전위분포

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