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Hydraulically irreversible membrane fouling during coagulation–microfiltration and its control by using high-basicity polyaluminum chloride

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ABSTRACT

The extent of hydraulically irreversible membrane fouling in a coagulation–filtration system depends on several factors, including properties of the coagulant. Effects of polyaluminum chloride (PACl) coagulant properties, specifically basicity and sulfation, were investigated by conducting long-term direct filtration experiments. Elemental analysis determined Al and Si to be the major foulants, though the Si/Al ratios of the foulants differed from that of coagulated floc particles. While floc particle size depended on the concentrations of sulfate ions and polymeric species in the PACls, floc-size changes did not affect transmembrane pressure (TMP) buildup and thus did not affect irreversible fouling. Differences in PACl basicity, which affected the distribution of aluminum species, resulted in changes to the degree of irreversible fouling.

Pretreatment with high-basicity (71%) PACl was superior to pretreatment with normal-basicity (51%) PACl in reducing irreversible fouling and attenuating TMP buildup during filtration. Higher basicities resulted in less Al breakthrough and a decrease in the Si/Al ratio of the foulants. However, TMP buildup was the same for PACls with basicities of 71% and 90%, therefore, TMP buildup is not simply related to Al breakthrough and deposition. Increasing the basicity of PACls would be an effective way to reduce the amount of foulant deposited on the membrane by decreasing the amount of aluminum that passes through the membrane.

Keywords: Ceramic; Foulant; Silicate; Coagulant; Basicity

1. Introduction

Coagulation, adsorption, and oxidation are widely used as pretreatment processes for microfiltration (MF) in water purification to alleviate membrane fouling and enhance the removals of micropollutants and disinfection byproduct precursors [1]. In MF with ceramic membranes, coagulation–flocculation with polyaluminum chloride (PACl) is a successful pretreatment for removing soluble substances and reducing the decrease in membrane permeability during long-time operation [2]. This process is commonly used in full-scale water treatment. Coagulation pretreatment destabilizes and agglomerates the colloidal and particulate foulants, increasing their size and thereby mitigating pore constriction and blockage and the formation of a porous cake layer. Additionally, increased particle size reduces the specific cake resistance, according to the Carman–Kozeny relationship, and thus increases permeability. However, membrane fouling is not completely avoided since aquatic colloids are not removed, which cause fouling by narrowing or blocking membrane pores, and substances retained on the membrane that form a gel or cake layer still contribute resistance.

The permeability of the cake layer formed from floc particles during coagulation has been extensively studied for dependence on floc size, strength, and fractal structure [3-5]. Coagulated flocs with a high fractal dimension have low compressibility, leading to low membrane permeability [6]. Other studies, however, found high compressibility in flocs related to a higher specific resistance of the cake layer [7, 8]. Coagulated flocs with a high fractal dimension formed by PACl have a more compact structure than flocs formed by alum [9]. Therefore, the MF membrane permeability deteriorates more severely during PACl coagulation than during alum coagulation due to the higher specific resistance of the cake layer. Liu, Chen, Yu, Shen and Gregory [10], in contrast, report that floc particles of a high fractal dimension as well as a large size formed by two-stage coagulant dosing mitigated TMP development more than those formed by a single dose. The strength (resistance toward shear stress) of floc particles formed by coagulation also plays an important role in the permeability of the cake layer [11-13]. The increase in transmembrane pressure (TMP) in an ultrafiltration (UF) system is lower with floc breakage, which lowers the fractal dimension of flocs, than without breakage [14]. Xu and Gao [3], however, reported that an increased shear for floc breakage considerably decreased the floc size and increased the floc compactness, thus increasing resistance and lowering the permeability of the cake layer. Therefore, an increase in floc strength could enhance the permeability of the cake layer [4]. Overall, findings on the relationship of floc characteristics to membrane performance are not consistent, though it is clear the structure of the cake layer plays an important role in membrane permeability.

In a ceramic membrane MF system, the permeability of the cake layer may not be a crucial issue, because an integrated, intensive, hydraulic backwash process would eject most of the cake layer. After coagulation, the affinity of the membrane for destabilized contaminants and their aggregates is lower than without coagulation, which leads to a more effective backwash. Hence, with an integrated, hydraulic backwash, the degree of fouling from cake layer formation would be minimized. Hydraulically irreversible fouling is the main concern in full-scale membrane filtration facilities because it determines energy consumption for long-term membrane filtration and affects the sustainable operation of the facility. Irreversible fouling is caused by contaminants that do not react with or adsorb to hydrolytic species formed by the coagulant and thus are not destabilized [15]. Many studies have been conducted to better understand the behavior of membrane foulants and elucidate fouling mechanisms, but these studies have seldom identified practical solutions to the membrane-fouling problem.

A limited amount of research has concerned the extent to which different coagulant types might be exploited to most effectively reduce the extent of irreversible fouling. Tran, Gray, Naughton and Bolto [16] reported that polysilicato-iron coagulants were better at mitigating irreversible fouling than aluminum-based coagulants at a higher dose while aluminum-based coagulants worked better at a lower dose. Their study suggests that the effect on membrane fouling is a complex phenomenon where many factors including the residual DOC and the property of small-size flocs influence the fouling to various extents. Membrane fouling may also be caused by hydrolytic species of coagulants, though it has not been fully studied [1]. The key consideration is that coagulant characteristics required for membrane pretreatment are not necessarily the same as those for coagulation and settling. Conventional coagulation is designed to form large-size floc particles that settle out, whereas, for membrane pretreatment, coagulation should allow for direct filtration of floc that results in improved filtrate water quality and alleviates membrane fouling.

In this study, we investigated five PACl coagulants suitable for direct MF. The effect of PACl properties (basicity and sulfated/nonsulfated) on hydraulically irreversible membrane fouling (hereafter called irreversible fouling), which results in a long-term TMP rise, was studied, in particular, by focusing on the residual aluminum concentration in filtrates and aluminum deposits on membranes.

2. Materials and methods

2.1. Coagulants

Four PACls were obtained from the Taki Chemical Co. (Kakogawa, Japan): conventional normal-basicity (51%) sulfated PACl (designated as PACl-51s), high-basicity (71%) sulfated PACl (PACl-71s), high-basicity (71%) nonsulfated PACl (PACl-71), and very-high-basicity (90%) nonsulfated PACl (PACl-90). A second very-high-basicity (90%) nonsulfated PACl (PACl-90b) was prepared in the authors' laboratory by the base titration method using NaOH (0.3 M) and $AlCl_3$ (0.5 M) [17]. The distributions of aluminum species in the coagulants were determined by the ferron method [17]. These species were assumed to be monomeric, polymeric, and colloidal aluminum species on the basis of their reaction rates with ferron reagent (8-hydroxy-7-iodo-5-quinolinesulfonic acid; Wako Pure Chemical Industries, Osaka, Japan), denoted Ala, Alb, and Alc, respectively [18]. Ala denotes aluminum species that reacted with ferron instantaneously (within 30 s); Alb denotes species that reacted with ferron within 120 min; and Alc denotes species that did not react. Properties of the PACls are listed in Table 1S (supplementary data).

2.2. Pilot-scale MF system

Experiments were conducted with the coagulation-direct MF pilot plant at the Water Quality Center of the Sapporo Waterworks Bureau, Japan. The plant has two parallel lines (Lines A and B) with the same configuration, each consisting of coagulation mixing tanks, a feed pump, a membrane module, and a hydraulic backwash unit in series (Fig. 1). The two lines were operated in parallel under identical conditions except for coagulant type and dosage of caustic soda for pH control, which enabled direct comparison of the experiments. The coagulation process was performed in rapidly and slowly stirred mixing tanks with detention times of 7.3 and 12.5 min, respectively. Mixing intensities were 60 rpm (G = 68.5 s^{-1}) and 20 rpm (G = 13.3 s^{-1}), respectively, unless otherwise noted. Each line has a small membrane module containing a tubular, ceramic monolith membrane element (nominal pore size, 0.1 μm; 55 channels; diameter, 3 cm; length, 10 cm; effective filtration area, 0.043 m^2; Metawater Co., Tokyo, Japan). The element was specially designed for small-scale experiments; in comparison, the membrane element used for the full-scale filtration plant has a membrane surface area of 25 m^2, a diameter of 1800 mm, and a length of 1.5 m. Before each filtration run, the membrane element was chemically-cleaned and, after housing the module, the initial permeability was checked. The module was configured for dead-end filtration with constant flow to the membrane module (filtration rate, 0.125 m/h) by positive pressure. The membranes were hydraulically backwashed every hour from the filtrate

side with membrane permeate at a pressure of 500 kPa for 20 seconds, and the retentate was ejected by pressurized water and air. Feed pressure, raw water turbidity, water temperature, and coagulation pH were monitored continuously, and the data were stored. Coagulant dose was automatically adjusted as a function of raw water turbidity [dosage/(mg-Al/L) = 1.06 for 0–7 NTU, dosage/(mg-Al/L) = 0.151 × turbidity/NTU for 7–14 NTU, dosage/(mg-Al/L) = 0.034 × turbidity/NTU + 1.65 for 14–140 NTU; these formulas were determined from the PACl dosage–turbidity relationship obtained at the Moiwa Water Treatment Plant, which treats the same raw water]. Coagulation pH was controlled at a constant value by the automatic dosage of caustic soda, except for the first set of runs (Run 1). Plant operation was continued either for 25–35 days or until the TMP reached about 100 kPa. In some cases, operation was terminated due to cessation of raw water flow from the Water Quality Center. During plant operation, samples of coagulated waters before direct MF were taken manually and immediately filtered through organic membranes (polycarbonate, Isopore, Millipore Corp.) of the same nominal pore size, 0.1 μm, as that of the ceramic membrane. For some runs, samples were filtered through organic membranes of various molecular mass cutoffs (500 Da, cellulose acetate, Amicon-Y, Millipore Corp; 1, 3, 10, and 100 kDa, regenerated cellulose, Ultracell-PL, Millipore Corp.). In total, eleven runs of parallel filtrations were conducted (Table 2S, supplementary data). Additionally, for supplementary membrane filtrate sampling and foulant analysis, seven pairs of runs were carried out with PACl-60s (sulfated, basicity 60%, Taki Chemical Co.), PACl-65s (sulfated, basicity 65%, Taki Chemical Co.) and PACl-85 (nonsulfated, basicity 85%, Taki Chemical Co.).

2.3. Water quality

The plant treated Toyohira River water that was taken at Moiwa Dam (42.966182N, 141.269428E) and transported to the Water Quality Center through pipelines. The concentrations of dissolved organic carbon (DOC) and aluminum in the water were determined by the UV/persulfate oxidation method (Sievers 900 TOC Analyzer, GE Analytical Instruments, Boulder, CO, USA) and inductively coupled plasma mass spectrometry (ICP-MS, HP-7700, Agilent Technologies, Inc., Santa Clara, CA, USA), respectively. The characteristics of the raw water and the coagulation pH are listed in Table 2S (supplementary data).

2.4. Chemical cleaning of membrane and foulant analysis

After the final hydraulic backwashing in a filtration run, the membrane element was removed from the module and chemically cleaned by repeating the following soak cycle three times: sulfuric acid (0.02 N) for 18 h, Milli-Q water (Millipore Corp.) for 1 min, sodium hypochlorite (1500 mg-Cl_2/L) for 18 h, and Milli-Q water for 1 min. The spent cleaning solutions and Milli-Q

waters were analyzed for organic C (Shimadzu TOC-5000A, Kyoto, Japan), Al, Si, Fe, Mn, and Ca (ICP-MS, HP-7700, Agilent Technologies, Inc.) to determine the concentrations of membrane foulants. Al and Si elemental analyses were conducted on the floc particles retained on the organic membrane filter from the manually collected and filtered samples (PTFE, 0.1 μm, Omnipore, Millipore Corp.) and on the ceramic membrane retentates ejected in the hydraulic backwash process.

3. Results and discussion

3.1. Effect of high-basicity (71%) PACl

Five pairs of runs (parallel filtrations) were conducted with PACl-71s in one line and PACl-51s in the other line. The rates of TMP buildup over the period of operation were lower when feedwater was pretreated with PACl-71s than with PACl-51s (Fig. 2). Even at pH 7.5, which sees more membrane fouling, PACl-71s lowered the rate of TMP buildup (Fig. 2C). Additional runs in which coagulation was conducted at pH 7.0 and pH 7.1 showed similar results, with the TMP following PACl-71s coagulation remaining at a low level throughout the period of operation (Fig. 1S, supplementary data). The consistent results in the five pairs of runs indicate that the difference in the TMP buildups between PACl-71s and PACl-51s was not due to any very slight difference in initial membrane permeability. Moreover, PACl-71s was used in Line B in Runs 1, 2, and 3 and in Line A in Runs 4 and 5. Therefore, the difference in TMP rise is not due to any inherent characteristics of the line, including the membrane element used. We interpret the low rate of TMP buildup in the filtration with periodic backwash as mild irreversible fouling. The high rate of TMP buildup is characterized as severe irreversible fouling. Floc particle size is a key characteristic that affects reversible fouling, but may not be related to irreversible fouling. Fine floc particles were more often observed in the mixing tank after the addition of PACl-71s than after the addition of PACl-51s (Fig. 2S, supplementary data), but addition of PACl-71s yielded a lower rate of TMP rise. The effects of floc particle size are further explored in section 3.3.

The masses of Al and other elements extracted from the fouled membrane by chemical cleaning are shown in Fig. 3. The amounts of Al and Si were the largest among the elements extracted, followed by organic C and Ca, suggesting that the irreversible foulants were mainly composed of these elements. The low relative loadings of organic C indicate natural organic matter (NOM) was not a main cause of membrane fouling: this might be due to the low DOC concentrations in the raw waters (Table 2S). Loadings of Al and Si on the membrane were lower with PACl-71s pretreatment than with PACl-51s pretreatment (Fig. 3S, supplementary data). Therefore, the lower

TMP rise observed with PACl-71s pretreatment could possibly be due to lower loading rates of compounds composed of these elements.

The residual aluminum in the filtrate was lower with PACl-71s pretreatment than with PACl-51s pretreatment (Runs 2-5 of Fig. 4: the comparison in Run 1 was not appropriate because pH was not stable during the experiment and pH of PACl-71s coagulation was often higher than pH of PACl-51s coagulation). This was due to less monomeric aluminum (Ala) in PACl-71s [17]; the percentages of Ala in PACl-71s and PACl-51s are 18.3% and 43.5%, respectively (Table 1S, supplementary data). Similar residual aluminum results were also seen in the filtrates of the manually collected samples through a polycarbonate membrane, which did not exhibit adsorption ability, with fixed straight pores of the size 0.1 μm, the same as that of the ceramic membrane [19] (Fig. 4S, supplementary data). Therefore, it can be interpreted that the concentration of small-size aluminum passing through the ceramic membrane was lower with PACl-71s pretreatment than with PACl-51s pretreatment. Some of the small-size aluminum species passing through the membrane pores might be retained by chance in membrane pores and then foul the membrane. We then thought that the low extent of membrane fouling with PACl-71s pretreatment might have been related to a low aluminum concentration. Molecular weight fractionation with organic MF and UF membranes revealed that the difference in aluminum concentration in the filtrates with the PACl-71s and PACl-51s pretreatments was in the size range >500 Da (Fig. 5S, supplementary data). This result is in accordance with previous jar test results that showed that PACl-71s lowered residual aluminum in the size range >500 Da [17]. The DOC in the filtrate was also lower with PACl-71s pretreatment than with PACl-51s pretreatment (Fig. 6S), and the loadings of organic carbon on the membrane were lower with PACl-71s pretreatment than with PACl-51s pretreatment (Fig. 3S). Therefore, the high NOM removal capability of PACl-71s might also be related to the low rate of TMP buildup.

3.2. Effect of very-high-basicity (90%) PACl

We tested two very-high-basicity (90%) PACls (PACl-90b and PACl-90). PACl-90b had a higher content of Alb, which has a high charge neutralization capacity [20, 21], than PACl-90 or PACl-71s. Kimura, Matsui, Kondo, Ishikawa, Matsushita and Shirasaki [17] reported that very-high-basicity (90%) PACls can decrease the residual Al concentration much more than 71% basicity PACls because 90%-basicity PACls only contain a very small amount of monomeric aluminum species (Ala). Given the lower TMP rise of PACl-71s with respect to PACl-51s, it was suspected that the extent of membrane fouling was related to residual Al concentration in the filtrate, with lower residual leading to lower fouling and less TMP buildup. The percentages of Ala in PACl-90, PACl-90b, PACl-71s, and PACl-51s are 0.4%, 1.2%, 18.3%, and 43.5%,

respectively (Table 1S). Therefore, membrane fouling should be less with PACl-90b and PACl-90 than with PACl-71s. Three pairs of runs were carried out. Results for two pairs of the runs are shown in Fig. 5, and results for the third pair, which had a shorter operational time, are shown in Fig. 7S (supplementary data). In all runs, coagulations with PACl-90b and PACl-90 yielded a similar TMP buildup over the entire operation time as coagulation with PACl-71s. Nonsulfated PACls of basicities 71% and 90% (PACl-71 and PACl-90) also saw no difference in TMP buildup (Fig. 8S, supplementary data). Loadings of Al on the membrane were not different between PACls with basicities of 90% (PACl-90 and PACl-90b) and 71% (PACl-71s) (Fig. 9S, supplementary data).

While further reduction of the residual aluminum concentration (<0.009 mg/L) was successfully achieved – as expected, aluminium concentrations in the filtrates dramatically decreased as basicity increased from 71% to 90% (Fig. 6) – it was not accompanied by a further attenuation of TMP buildup. Thus, increasing basicity to 90% and changing the aluminum species distribution did not further improve permeability. This result suggests that the quantity of small-size aluminum species passing through the membrane pores was not the main cause of the membrane's fouling. Instead, the aluminum species that did not pass through the membrane pores might have caused external membrane fouling by forming a gel layer, which probably consisted mostly of aluminum, on top of the separation layer of the membrane. This differs from pretreatment with a PACl with a basicity of 51%, where external membrane fouling may have been caused by formation of a gel layer and internal membrane fouling could have been caused by internal deposition of aluminum associated with particles smaller than the membrane pore size. Therefore, the characteristics of the membrane foulant might depend on the basicity of the PACl used for coagulation pretreatment. The DOC in the filtrate was slightly higher with 90%-basicity PACl pretreatment than with 71% pretreatment (Fig. 10S). The loading of organic carbon was also slightly higher with 90%-basicity PACl pretreatment. Therefore, the effect of the low aluminum concentration with 90%-basicity PACls might possibly be canceled out with its high DOC, which eventually resulted in the similar TMP buildup rate of PACl-90 to PACl-71s. Experiments using raw water of high NOM concentration are granted to more clearly elucidate the effect of PACl characteristics on the NOM removal and fouling [22].

3.3. Effect of sulfate ion in PACl

Sulfate is often added to PACls because it suppresses charge reversal and enhances flocculation performance [23]. Pretreatment with PACl-90b produced very fine floc particles, whereas pretreatment with PACl-71s produced larger floc particles (Fig. 11S, supplementary data). The very fine floc particles formed by PACl-90b are probably due to the absence of sulfate ion in the

PACl. Therefore, it seemed likely that pretreatment with very-high-basicity (90%) PACls would cancel out the positive effect from the lower residual Al concentration with a possible negative effect from the very fine floc particles.

To further study the effect of floc size on filtration, we compared PACl-71s and PACl-71 – two PACls with the same basicity and aluminum species distribution but with or without the sulfate ion in their structures (Table 1S). PACl-71 formed more very fine floc particles than did PACl-71s (Fig. 12S, supplementary data), however, the TMP variations during filtration were similar (Fig. 7). This result indicates that the very fine floc particles formed by the nonsulfated PACls (PACl-90b and PACl-71) did not have a negative impact on the irreversible fouling, leaving only the positive effect of TMP mitigation. This is further supported by microphotographs that show particles larger than a few microns, much larger than the membrane pore size (0.1 μm), and therefore would not plug the membrane pores. Lastly, the chemical constitution of the irreversible foulant was different from that of the floc particles (see section 3.4) thus floc particles were not directly related to the irreversible fouling. Here we would like to note that our results of the little floc-size effect were obtained on the experiments of dead-end mode filtration. For other hydro-dynamic conditions, such as cross-flow mode, the further study is needed.

So far, the results can be generalized as follows: for a MF system that includes an intensive hydraulic backwash process, coagulants that produce floc particles much larger than the membrane pore size are more than enough for pretreatment. Such a coagulant property is actually required for pretreatment before sedimentation or for enhancing cake layer permeability in membrane systems without a hydraulic backwash. We therefore infer that a high-basicity nonsulfated PACl functions successfully as such a coagulant provided that it retains the capacity to neutralize charge.

Furthermore, inclusion of sulfate ions in PACls with high aluminum content influences the PACls' long-term chemical stability, so the sulfate ion concentration in practically applied PACls with Al content >5% (w/w) is typically limited to a few percent to allow the storage periods >6 months. Therefore, the success of the high-basicity nonsulfated PACl gives merit to its practical application in terms of a long storage period.

3.4. Aluminum and silicate loads on membrane

The spent membrane-cleaning solutions from filtration runs, including short runs terminated forcibly by cessation of raw water supply, were analyzed for the major irreversible membrane

foulants, Al and Si. The ratios of Si/Al were plotted against the basicity of the PACls used for the coagulation pretreatment (Fig. 8). The Si/Al ratios decreased with increasing basicity, suggesting that the characteristics of the membrane foulant differ depending on the basicity of PACl used for the coagulation pretreatment. Therefore, we infer that increasing the PACl basicity not only decreases the concentration of aluminum passing through the membrane and thereby possibly reducing the load of the major foulant, aluminum, but also it changes the characteristics of membrane foulant and through this, may contribute to the attenuation of the TMP buildup.

The feed water to the membrane contained aluminum and silicate at very different concentrations. The aluminum concentration (around 1.2 mg/L on average) was much lower than the Si concentration (around 6.6 mg/L), and the Si/Al molar ratio was about 5.3 for the feed water. The Si/Al ratios of the irreversible membrane foulant varied from 0.5 to 0.2, depending on the basicity of the PACls. Since most of the aluminum in the feed water to the membrane was in a suspended form (floc), whereas the silicate was in a soluble form, a small portion of the silicate might have been incorporated into the aluminum that precipitated after the PACl was dosed. However, the extent of incorporation is low for high-basicity PACl because the aluminum was pre-neutralized in the PACl solution. The Si/Al ratio of the irreversible membrane foulant at each basicity was also higher than that of the floc particles that were ejected by the hydraulic backwash, the highest ratio of which was 0.2. The difference of the Si/Al ratio suggests that the irreversible foulant did not originate from floc particles, even though the irreversible foulant also consisted mostly of aluminum. Adding to the fact that floc size did not affect the extent of irreversible fouling, this further shows that floc particles are not directly related to irreversible fouling.

The higher Si/Al ratios of the irreversible foulant for the lower-basicity PACls suggest that Si plays a role in membrane fouling. A stability diagram (Geochemist's Workbench, ver. 6, RockWare, Inc., Golden, CO, USA) for the chemistry of the membrane feedwater suggests that kaolinite [$Al_2Si_2O_5(OH)_4$] was the final stable species; the aqueous solubility of kaolinite is much lower than that of gibbsite [$Al(OH)_3$] [24]. The Si/Al molar ratio of kaolinite is 1.0, a value closer to that of the irreversible foulant than to that of the floc particles. We infer that aluminum silicate hydroxide, which is chemically similar to kaolinite but amorphous, probably accumulated on top of and inside the membrane, thereby irreversibly fouling the membrane.

Quantification of total foulant loads sheds light on its relationship to TMP rise, however, it requires information about the chemical structures of the foulants and such information is scant. The total loads shown in Fig. 9 were calculated on the assumption that the Si existed mainly in compounds characterized by the stoichiometry of $Al_2Si_2O_5(OH)_4$, the surplus of Al over Si was in the form of $Al(OH)_3$, Ca was in the form of $Ca(OH)_2$, Mg was in the form of $Mg(OH)_2$, Fe was in

the form of $Fe(OH)_3$, and Mn was in the form of $MnO(OH)_2$. Carbon was assumed to account for 50% of the organic matter [25]. The positive correlation between the total foulant loading and TMP suggests that the quantity of total foulant loading is an index for TMP. However, the correlation was not high (r = +0.35, Fig. 9). When compared at the same loading, the TMPs of direct MF after coagulation with normal basicities (50% and 60%) were higher than the TMPs associated with high and very-high basicities (>70%). This correlation suggests the rise in TMP may to some extent be related to the quantity of total foulant loading on the membrane, but altogether, the characteristics of membrane foulants depend primarily on the PACls used for coagulation pretreatment.

4. Summary

(1) In ceramic MF with PACl coagulation pretreatment, long-term development of TMP caused by hydraulically irreversible fouling followed the order PACl-90b = PACl-90 = PACl-71s < PACl-51s. Use of high-basicity (71%) PACl coagulant (PACl-71s) reduced hydraulically irreversible fouling and attenuated long-term development of TMP compared with normal-basicity (51%) PACl coagulants (PACl-51s). The use of very-high-basicity (90%) PACls (PACl-90b and PACl-90), however, did not result in a reduction of long-term TMP buildup beyond that obtained with PACl-71s.

(2) Aluminum concentrations in the filtrates were in the following order: PACl-90 = PACl-90b < PACl-71s < PACl-51s. This order paralleled the order of Ala content in the PACls. The lower aluminum passage following pretreatment with a high-basicity PACl correlated with less membrane fouling. PACl-90 and PACl-71s exhibited similar long-term TMP buildup, suggesting that the characteristics of the membrane foulant differed from the normal basicity PACl of 51%. This conclusion was also supported by the fact that the Si/Al ratio of hydraulically irreversible foulants, which consisted mostly of Al and Si, decreased with increasing basicity of the PACl used for coagulation pretreatment.

(3) The hydraulically irreversible foulants differed in terms of Si/Al ratios compared to floc particles. Additionally, while floc size was a function of the concentration of sulfate ions and polymeric species in the PACls, it did not affect the reduction of hydraulically irreversible fouling. Therefore, the floc particles were not directly related to hydraulically irreversible fouling.

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Appendix. Supplementary Information

Table 1S–2S and Figs. 1S–12S are available in the online version.

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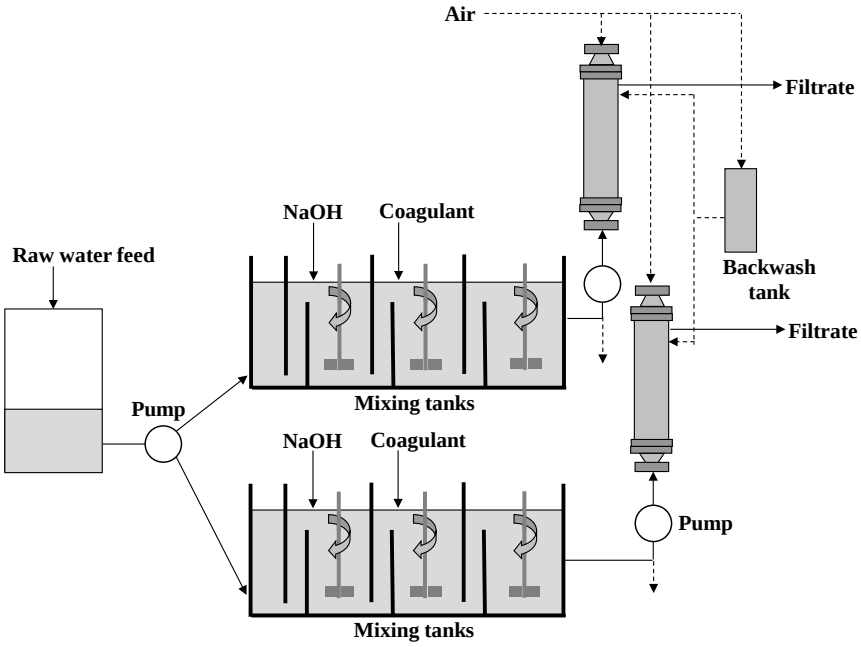

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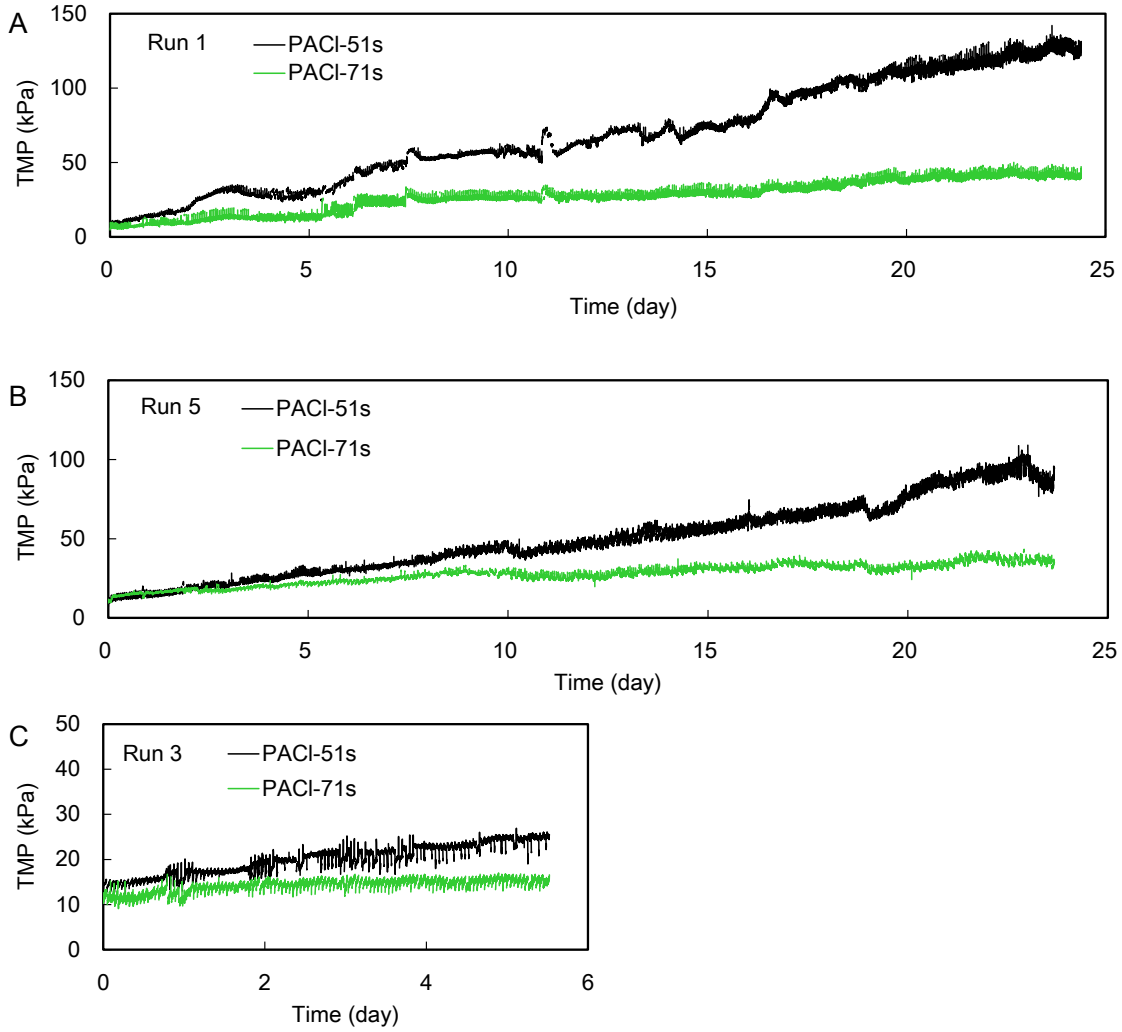

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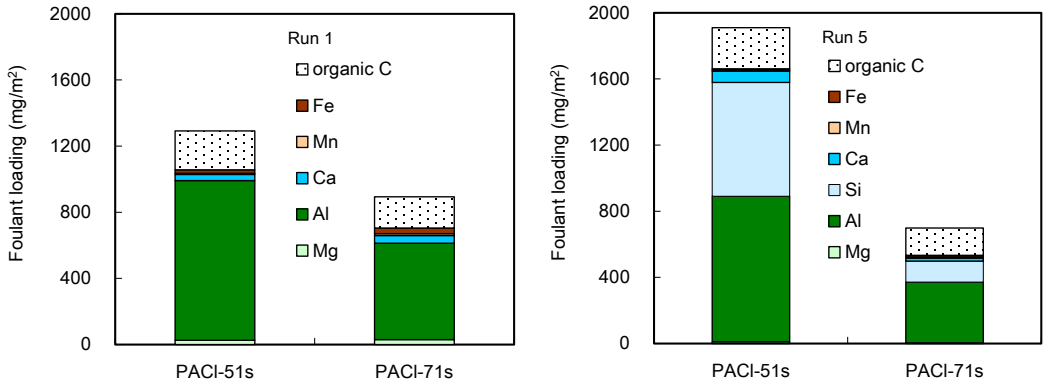

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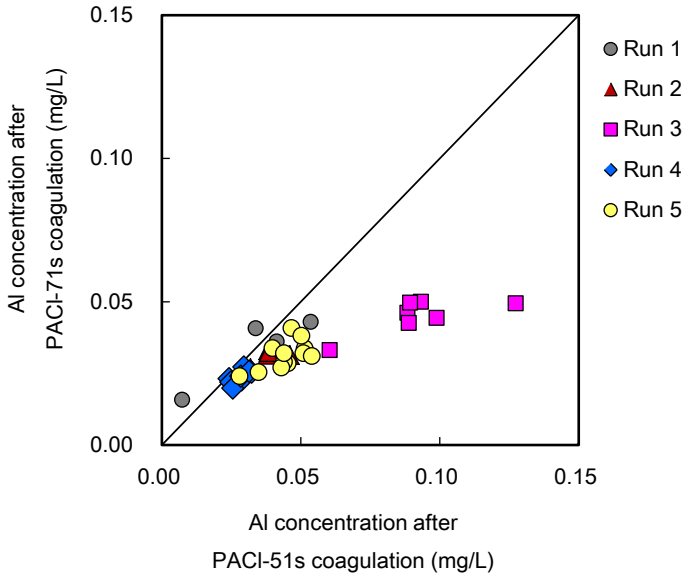

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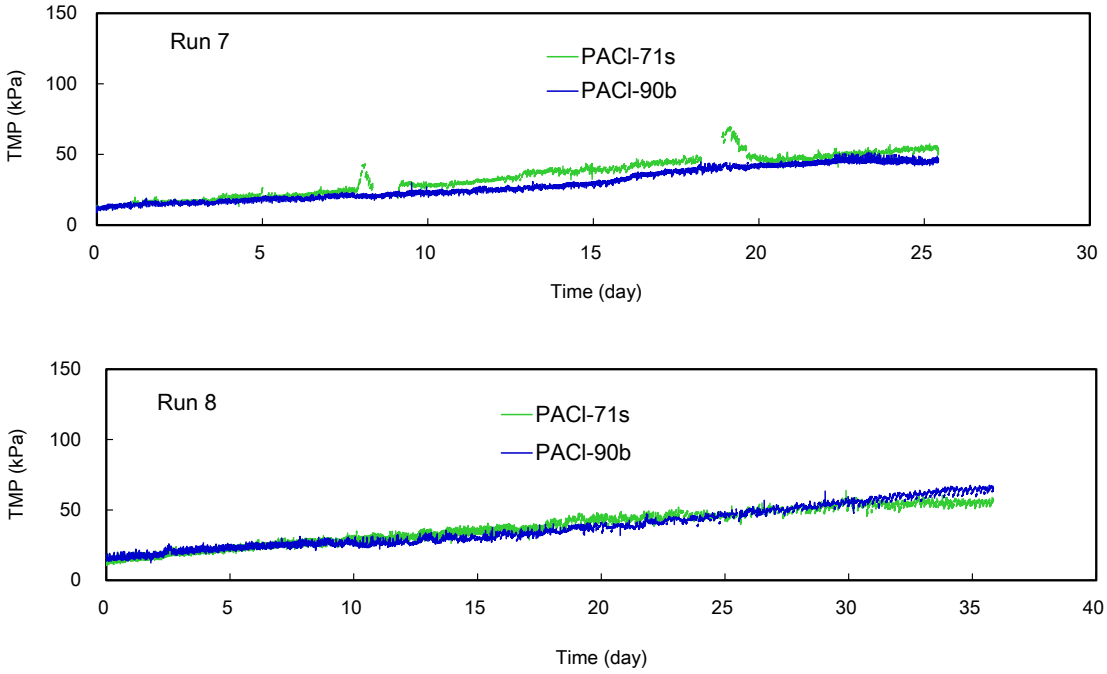

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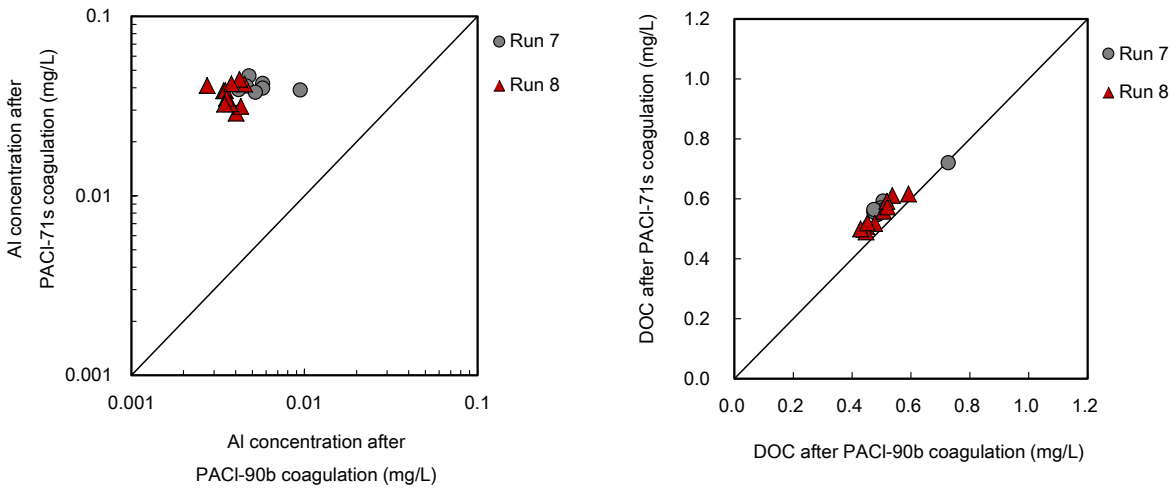

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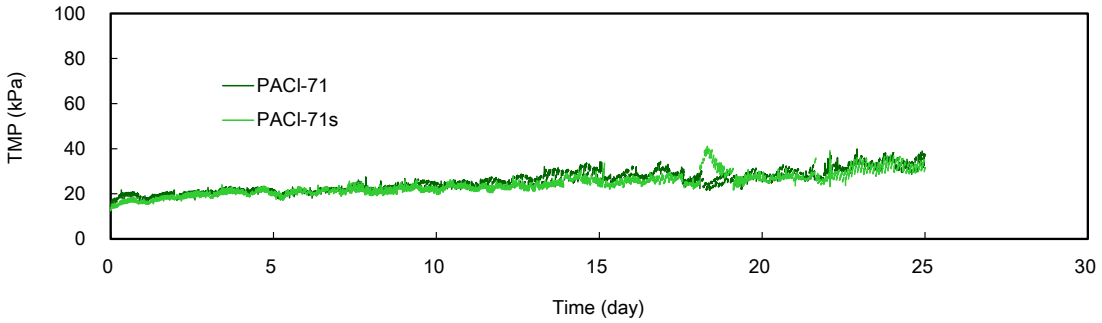

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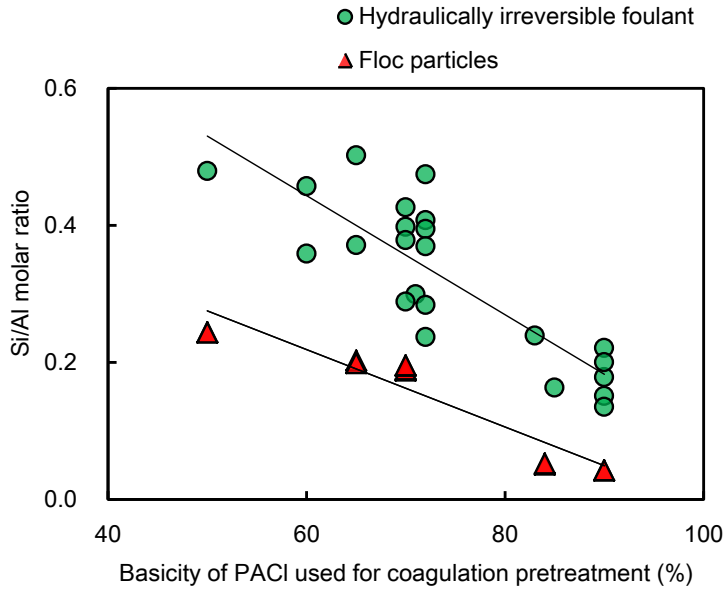

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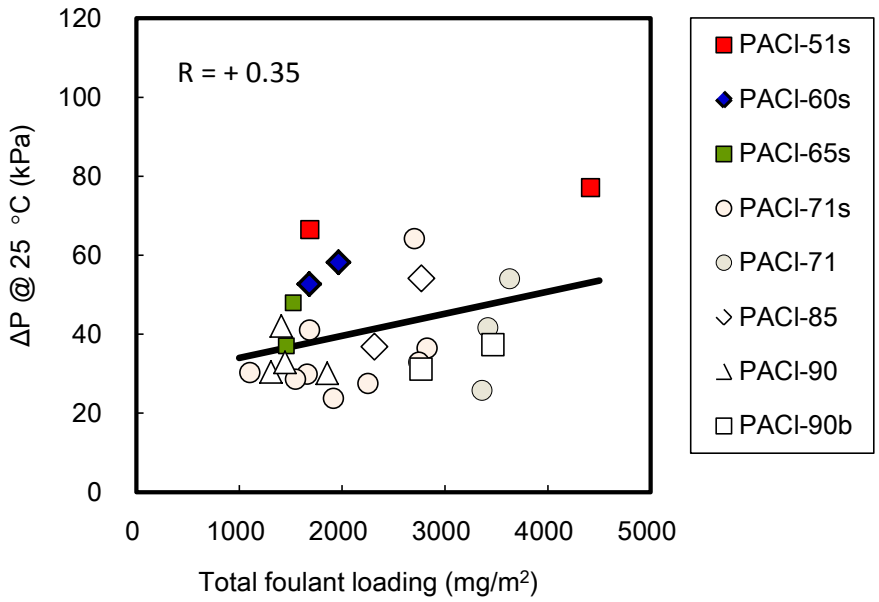

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