Korean J. Chem. Eng., **18**(6), 965-970 (2001)

Synthesis and Characterization of Polymeric Inorganic Coagulants for Water Treatment

Lim-Seok Kang†, **Seung-Woo Han and Chul-Woo Jung**

Department of Environmental Engineering, Pukyong National University,
559-1, Dae Yeon-3Dong, Nam-Gu, Busan 608-739, Korea

(*Received 13 March 2001 • accepted 23 July 2001*)

Abstract−This research explored the feasibility of preparing and utilizing preformed polymeric solution of Al(III) and Fe(III) as coagulants for water treatment. The differentiation and quantification of hydrolytic Al and Fe species in the coagulants were done by utilizing spectrophotometric method based on the interaction of Al or Fe with ferron as a complexing agent. In addition, ^{27}Al-NMR, FT-IR, and powdered XRD were used to characterize the nature and structure of the hydrolytic species in these coagulants. The properties of the polyaluminum chloride (PACl) and polymeric iron chloride (PICl) showed that the mass fractions of the maximum polymeric Al produced at r(OH/Al)=2.2 and Fe at r=1.5(OH/Fe) were 85% and 20% of the total aluminum and iron in solution, respectively. Coagulation tests were conducted under various coagulant dosages and pHs for each coagulant prepared. In case of PACl coagulants, a coagulation test on Nakdong river waters with three PACls (r=2.0, 2.2, 2.35) showed that the effectiveness of coagulation was in the order, r=2.2>2.0>2.35, corresponding to the order of polymeric aluminum contents. And, for the PICl coagulants, the PICl of r=1.5 was most effective for the removal of turbidity and TOC from the raw water.

Key words: Water Treatment, Polymeric Coagulants, Hydrolytic Species, Coagulation Tests

INTRODUCTION

Coagulation has been used to assist in the removal of particulate and dissolved materials in water treatment. Coagulation requires a unique combination of chemical reactions and physical transport processes which are used to destabilize and aggregate suspended particles and to precipitate or adsorb natural organic substances. Therefore, the effectiveness of coagulation influences the efficiency of subsequent sedimentation and filtration processes [Oh et al., 1999; Hur and Kim, 2000].

Each year, the water industry faces increasingly stringent water quality regulations and ever more challenging treatment objectives. Therefore, it is necessary to control and optimize coagulation process that is essential water treatment unit operation in the treatment sequence. Among the coagulants used, alum has been the most widely used for the treatment of drinking water. Recently, however, existing and potential problems associated with high concentration of residual aluminum and organics in treated water have raised concerns over the use of alum in the treatment of drinking water. Attention is therefore increasingly being focused on alternative coagulants to alum, such as PACl and Fe(III) salt.

Many methods have been utilized for the quantitative determination of soluble Al. Nuclear magnetic resonance (NMR) spectroscopy has been used to examine the structural, kinetic, and equilibrium properties of mononuclear, polynuclear, and complexed aluminum ions and of hydroxyaluminum solid, but it lacks sensitivity for the determination of the mononuclear ion stability constant, relative to other methods. Likewise, Raman spectroscopy can be employed to characterize bonding properties of hydrolyzed Al ion species, but cannot directly supply quantitative estimates of thermodynamic properties for such species. Other spectroscopic techniques (IR, etc.) are similarly ineffective or insensitive owing to their requirements for concentrated solution, solid sample, or magnetic properties. However, the ferron method is considerably more convenient than other methods for differentiating Al (or Fe) species in solution. The chemical properties of PACl are determined with Ferron method assaying each content of the polymeric, monomeric and precipitate Al in synthesized PACl. And the the existence of polymeric Al type in Al_{13} type is also determined to evaluate the chemical properties of PACl [Akitt et al., 1972a, b]. In the case of Murphy [1975a], they were surveying the chemical properties of synthesized PICl by using ferron method.

Recently, also, a common PACl has not been characterized by any methods for Al (Fe) species fraction in domestic. In this research, however, associated chemical testing methods, all of ferron method, Al-NMR, FT-IR, and XRD, were used to get more accurate and scientific analysis data. Comparative studies of these analysis data will be able to optimize the application of coagulants.

Therefore, this research focuses on the synthesis of polymeric metal salts as coagulants. The objectives of this research were (1) to determine appropriate conditions for the production of polymeric metal (Al and Fe) coagulants, (2) to characterize the physical and chemical properties of coagulants prepared, and (3) to evaluate their applications to drinking water treatment.

EXPERIMENT

1. Synthesis of Inorganic Polymeric Coagulants

[†] To whom correspondence should be addressed.
E-mail: kangls@pknu.ac.kr

[‡] Presented at the Int'*l* Symp. on Chem. Eng. (Cheju, Feb. 8-10, 2001), dedicated to Prof. H. S. Chun on the occasion of his retirement from Korea University.

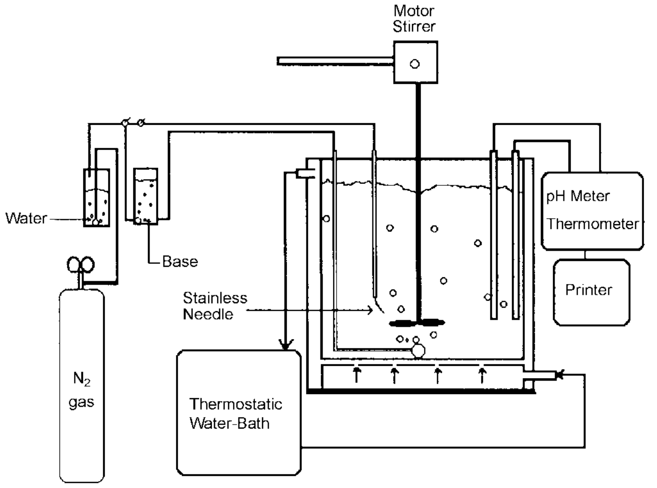

Fig. 1. Experimental apparatus for the preparation of inorganic polymeric coagulants.

PACl (polymeric aluminum chloride) and PICl (polymeric iron chloride) were synthesized by adding a proper amount of base to the supersaturated solution of aluminum chloride or iron chloride in a reactor shown in Fig. 1. A 2-L double walled acrylic vessel was fitted with an acrylic lid on which five inlets were made, and four baffles were glued to the reactor wall. A pH electrode was inserted through one inlet and another one was for an acrylic capillary, through which hydrated high purity N_2 gas was bubbled through the solution to strip off CO_2. Through another port, an acrylic capillary was lowered into the reactor to slowly inject a base solution. The aperture at the tip of the capillary was less than 0.15 mm in diameter to minimize diffusion of the metal solution into the capillary during mixing. A stainless shaft with propeller stirrer was inserted in another port for mixing of solutions. The solution temperature in the reactor was maintained at 20±1 °C by circulating a temperature controlled water through the jacket of the reaction vessel.

For the syntheses of PACl and PICl, 0.2 M $AlCl_3 \cdot 6H_2O$ or 0.2 M $FeCl_3 \cdot 6H_2O$ as precursor, and 0.5 M NaOH or 0.1 M Na_2CO_3 as an added base were used, respectively. For synthesis of PICl, Na_2CO_3 solution was used for neutralization rather than NaOH, because the carbonate reduces the rate of nucleation and precipitation of Fe(III) salt [Schwyn, 1983; Schneider and Schwyn, 1990]. Tables 1 and 2 show the conditions for the synthesis of PACl and PICl, respectively.

Table 1. Conditions for the preparation of PACls

r (OH/Al)	NaOH (M)	$AlCl_3$ (M)	Base injection rate (ml/hr)	Al (M)
0.0	0.5	0.2	50	0.25
1.5				0.12
2.0				0.11
2.20				0.11
2.35				0.10
2.45				0.10
1.0	0.5	0.2	60	0.14
1.0			100	0.14
2.2			60	0.11
2.2			70	0.11
2.2			80	0.11

Table 2. Conditions for the preparation of PICls

r (OH/Fe)	Na_2CO_3 (M)	$FeCl_3$ (M)	Base injection rate (ml/hr)	Fe (M)
0.0	1.0	0.3	70	0.300
0.5				0.279
1.0				0.261
1.5				0.245
2.0				0.231
1.5	1.0	0.3	33	0.245
			70	
			75	
			109.8	
			142.2	

2. Characterization of Polymeric Coagulants

Four different techniques were used to characterize the hydrolyzed speciation of the PACl and PICl solution. One method used a timed colorimetric reaction by using ferron (8-hydroxy-7-iodo-5-quinoline-sulfonic acid) as a coloring reagent to provide a fractionation of hydrolyzed species based on chemical reactivity [Smith, 1971; Bersillon et al., 1980; David and Parker, 1992]. Other instruments used to provide a chemical characterization of hydrolyzed species of Al and Fe salts were FT-NMR (Fourier Transformed Nuclear Magnetic Resonance), FT-IR (Fourier Transformed-Infrared), and XRD (X-ray Diffraction).

Samples were withdrawn from the reaction vessel at selected values of r(=OH/Al) during neutralization. After a desired period of aging, the speciation of aluminum was determined by the reaction rate of coagulant with ferron. This methodology provides a determination of the fractions of monomeric Al (Al_a), polymeric Al (Al_b), and precipitated Al (Al_c) in a sample. The kinetics of this reaction was monitored spectrophotometrically at a wavelength of 370 nm. In addition, modified ferron technique was employed to evaluate Fe speciation in PICl [Murphy et al., 1975]. The reaction rate was measured at 600 nm to give the distribution of Fe_a, Fe_b, and Fe_c. Total aluminum and iron concentrations were determined by ICP (Inductively coupled plasma, ICAP 61E-Trace analyzer).

Aluminum coordination was determined by using ^{27}Al-NMR. The spectra were obtained by using FT-NMR spectroscopy (JEOL, JUM-ECP 400) operated at 78.2 MHz for ^{27}Al. FT-IR spectrophotometer (Bruker, IFS-88) was used in the range of 4,000-400 cm^{-1}. Samples were prepared for IR analysis by the KBr pellet method. XRD experiments were performed in a diffractometer (Philips, X'Pert) with CuKα radiation.

3. Coagulation Experiments with Inorganic Polymeric Coagulants

Coagulation experiments were carried out using 2 L square jars with six-paddle stirrer (Phipps and Bird). Aliquots (2-L) of each water were dosed with alum, PACls, $FeCl_3$ or PICls coagulant under various coagulant doses and pHs. The solution was rapidly mixed at 250 rpm (G=550 sec^{-1}) for 1 min after coagulant addition, followed by slow mixing at 30 rpm (G=22 sec^{-1}) for 30 min. After 30 min of settling, the supernatant was analyzed for turbidity, TOC,

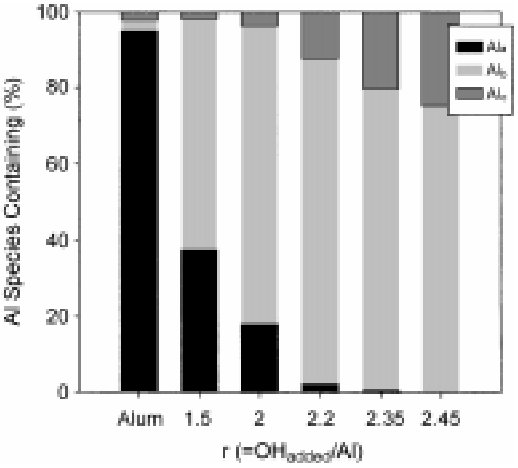

Fig. 2. Distribution of hydrolyzed Al species for each PACl.

UV_{254} absorbance by following Standard Methods [AWWA, 1998].

RESULTS AND DISCUSSION

1. Characterization of Polymeric Coagulants

1-1. Characterization of PACl

The monomeric, polymeric, and precipitated Al species were quantitatively differentiated with the ferron method. As shown in Fig. 2, as the r(=OH/Al) value increased, the speciation of PACl solution was becoming predominantly polymeric species. The fraction of polymeric Al showed a maximum at r=2.2, 85% of the total aluminum in solution, and precipitated Al substantially increased when r was increased above 2.35. This tendency shows that the precipitated Al species were directly transformed from polymeric Al species with increasing r value. However, alum (without added base) was mainly composed of monomeric Al species up to 95%.

^{27}Al-NMR spectra were obtained at 78.2 MHz using $[Al(H_2O)_6]^{3+}$ (1.0 M $AlCl_3 \cdot 6H_2O$ solution in 20% D_2O) as an external reference. Fig. 3 shows peaks whose importance varied with the value of r. The peak appearing at 0 ppm is assigned to the monomeric Al species of the type $Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{2+}$, and $Al(OH)_2(H_2O)_4^{+}$, whereas at r=1.5, the peak at about 3 ppm is assigned to the dimer $Al_2(OH)_2^{4+}$. A signal appears at 62.5 ppm, corresponding to aluminum ions in tetrahedral coordination, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$.

This analysis has provided a direct evidence on the existence of a number of Al polynuclear species in a wide range of hydrolyzed Al solutions. And, this result is consistent with the one obtained from the ferron analysis. Many other investigators also provided definitive evidences for the ubiquitous presence of $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$ species in hydrolyzed Al solutions prepared by a variety of methods [Akitt and Farthing, 1978; Akitt et al., 1972a, b; Bottero et al., 1980]. At r= 2.35, the peak at 0 ppm disappeared but a number of smaller peaks appeared at 0-85 ppm. This phenomenon implies that the precipitated Al species were directly transformed from polymeric Al species rather than from monomeric Al species.

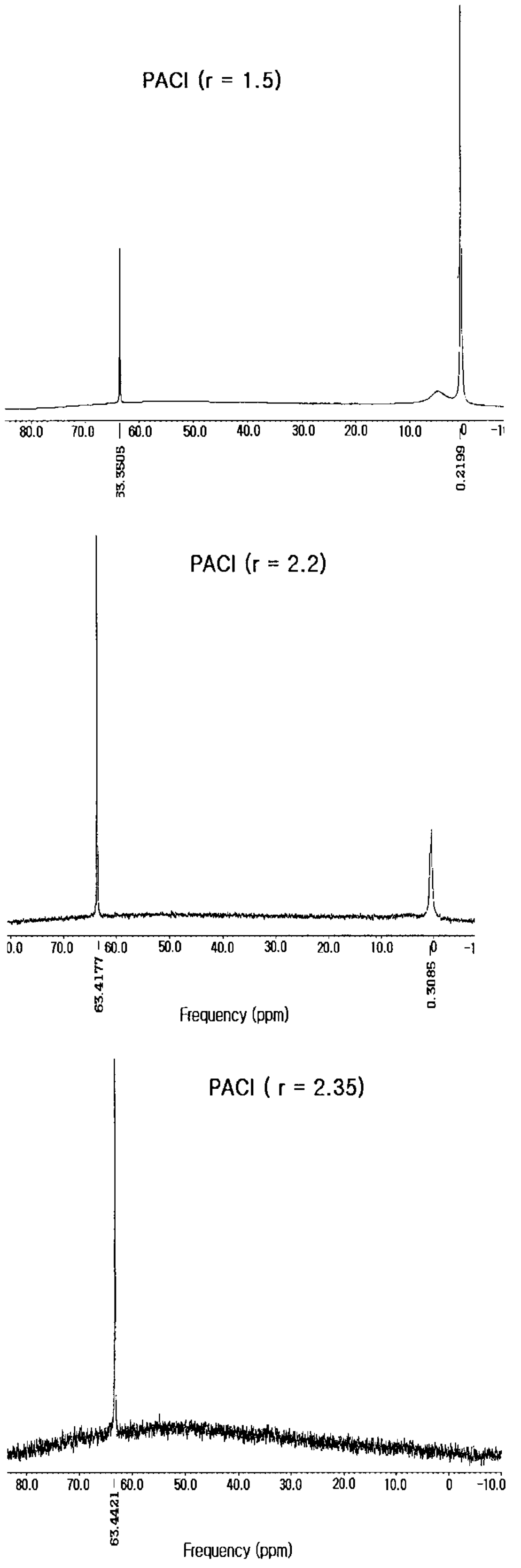

Fig. 3. ^{27}Al NMR spectra of PACl with varying r values.

In order to corroborate the hydrolyzed species of the PACls determined, we took FT-IR spectra of the PACls. Fig. 4 shows the FT-IR spectra of the Al species of the PACls with different r values. The bands were formed at 600, 800, 1,200, and 1,600 cm^{-1}. With increasing r, the peaks at 600 and 800 cm^{-1} diminish. The bands at 600, 800, and 1,200 cm^{-1} were assigned to the complexes of coordi-

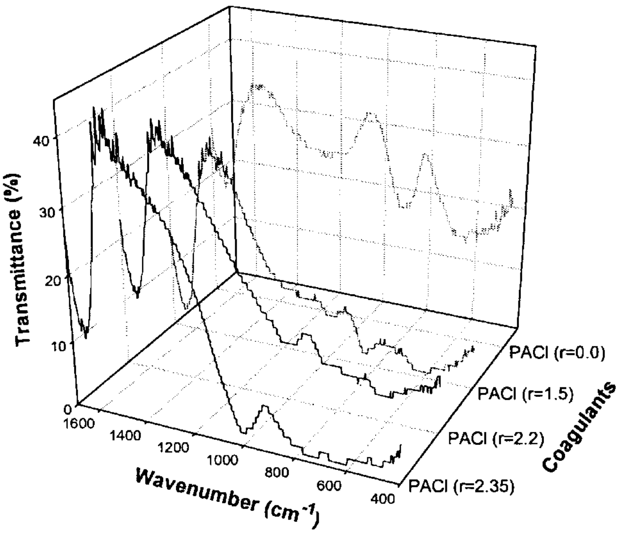

Fig. 4. FT-IR spectra of the products of hydrolyzed aluminum in each PACl.

nated H_2O to Al(III) and the band at 1,600 cm^{-1} represents free H_2O molecule.

Therefore, it is believed that the peaks becoming smaller at 600, 800, and 1,200 cm^{-1} were resulted from the chemical exchange between the hexaaquo- and the mono- and dihydroxo monomeric Al(III) species due to hydrolysis on base addition (i.e., increasing r value) according to the reactions (1) and (2),

$$Al(H_2O)_6^{3+}+H_2O \rightleftharpoons Al(OH)(H_2O)_5^{2+}+H_3O^+ \qquad (1)$$

or

$$Al(OH)(H_2O)_5^{2+}+H_2O \rightleftharpoons Al(OH)_2(H_2O)_4^{+}+H_3O^+ \qquad (2)$$

With increasing r, consequently, the band at 1,000 cm^{-1} represents the polymeric Al(III) with higher OH^- and less H_2O content per mole of aluminum than monomeric Al(III). Park et al. [1994] also reported that at an extent of decomposition of 33.4%, a band appeared at 980 cm^{-1} indicating the formation of basic aluminum chloride.

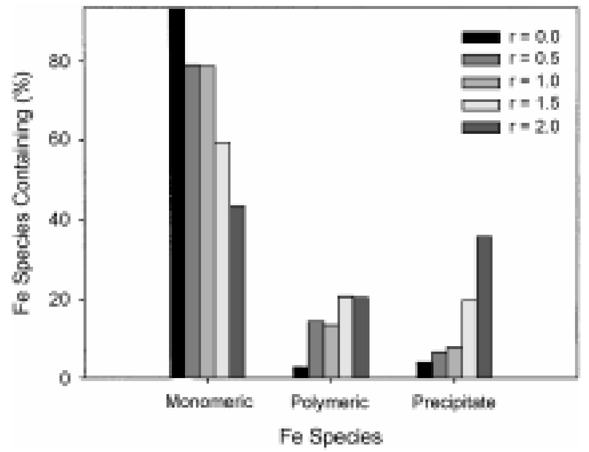

Fig. 5. Distribution of hydrolyzed Fe(III) species for a variety of PICls.

1-2. Characterization of PICl

Fig. 5 shows the result of ferron analysis for Fe(III) solutions neutralized partially with Na_2CO_3 solution. As the r value increased, monomeric Fe species substantially decreased and the fraction of polymeric Fe produced at r=1.5 showed a maximum at 20% of the total iron in solution, and the precipitated Fe was dramatically increased with increasing r above 2.0. This tendency indicates that the precipitated Fe species were directly transformed from the monomeric Fe species due to rapid hydrolysis reaction. However, $FeCl_3$ (r=0.0) was predominantly monomeric, the monomer content of which is as high as 93%.

Fig. 6 shows the FT-IR spectra of the Fe species of the PICls with different r values. The bands appeared at 600, 850, 1,160 and 1,600 cm^{-1}. As r value increased, the bands at 600, 850 and 1,160 cm^{-1} became smaller. The bands at 600, 850 and 1,160 cm^{-1} represent the complexes of coordinated molecures of H_2O of hydration to Fe(III) and the band at 1,600 cm^{-1} represents free H_2O molecule. As r value increased, the bands at 600, 850 and 1,160 cm^{-1} diminished due to the polymeric Fe(III) with higher OH^- and less H_2O per mole of

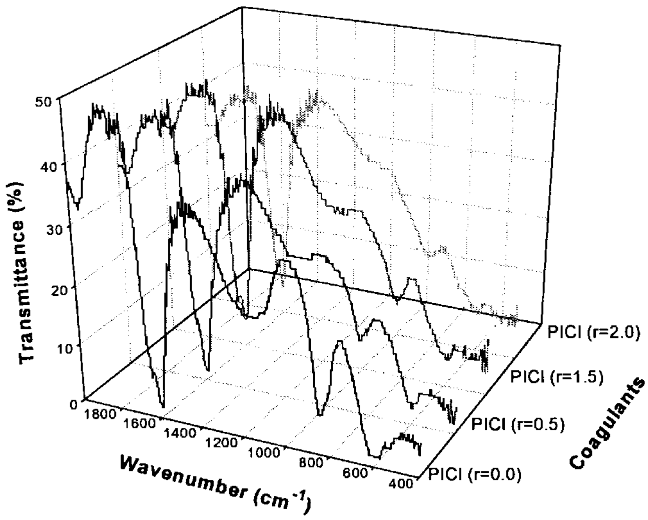

Fig. 6. IR spectra of the hydrolyzed iron in PICl.

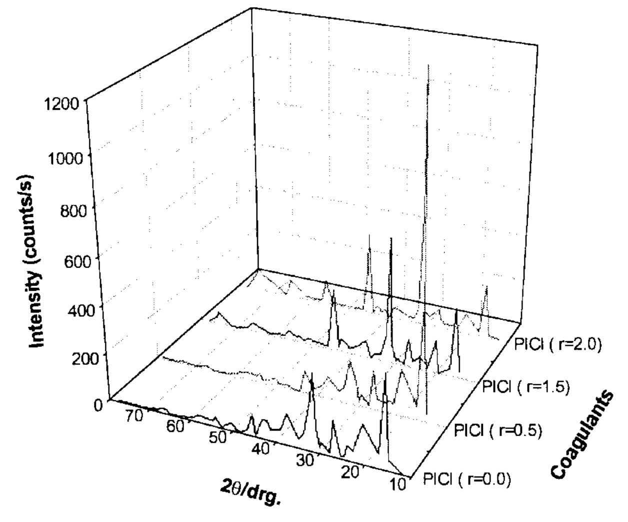

Fig. 7. XRD patterns of the PICls at different r.

Fe(III) than monomeric Fe(III). Therefore, the band at 1,600 cm^{-1} of base is due to the replacement of initial H_2O molecules contained in $Fe(H_2O)_6^{3+}$ by OH^- ion.

More quantitative correlations between the composition of the hydrolyzed Fe(III) and the various r values were obtained from the XRD peak intensities. Fig. 7 shows XRD patterns of the PICls synthesized under different r. The peaks were observed at 2θ=16°, 2θ=27°, 2θ=32°, and 2θ=47°. As seen in this figure, the increase of r reduces the peak intensity at 2θ=16° but increases the peak at 2θ=32°. From the XRD results, we can infer that the polymeric Fe species were directly transformed from the monomeric Fe species by the addition of base.

2. Coagulation Tests with Inorganic Coagulants

Coagulation experiments with the synthesized PACls and PICls coagulants were carried out using Nakdong river water. Figs. 8 and 9 show the TOC and turbidity removal efficiency of alum, $AlCl_3$ (r=0.0), and PACls (r=2.0, 2.2, 2.35) coagulants as a function of coagulant dose. As shown in these figures, the PACl (r=2.2) coagulant shows the most efficient TOC and turbidity removal among the coagulants used, due to its highest amount of polymeric Al species contained in the PACl (r=2.2). Also, comparing three PACls (r=2.0, 2.2, 2.35), the effectiveness of TOC coagulation represents as r=2.2>2.0>2.35, which is also the order of higher polymeric aluminum contents.

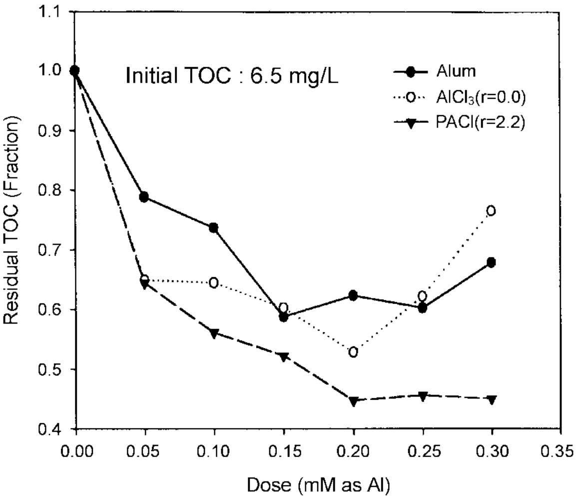

Fig. 8. Comparison of Alum, $AlCl_3$, and PACl coagulants for TOC removal as a function of coagulant dose.

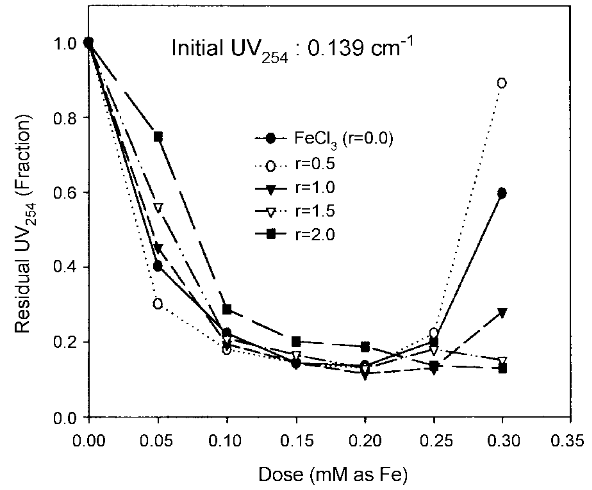

Fig. 10. Comparison of PICl coagulants with different r values for UV_{254} removal as a function of coagulant dose.

Fig. 10 shows UV_{254} removal efficiency of $FeCl_3$ (r=0.0) and PICls (r=0.5, 1.0, 1.5, 2.0) coagulants as a function of coagulant dose.

As shown in Fig. 10, the PICl (r=2.0, r=1.5) coagulants show more efficient UV_{254} removal than $FeCl_3$ and PICl (r=0.5, r=1.0) due to a higher polymeric Fe species contained in PICls (r=2.0, r=1.5). In addition, PICls (r=0.0, r=0.5 and r=1.0) coagulants show the decreased UV_{254} efficiency at high coagulant dose due to the restabilization of organic matters.

Fig. 11 shows turbidity removal and zeta potential change as a function of coagulant dose. As shown in Fig. 11, PICl (r=1.5) is most effective in the turbidity removal than the other coagulants at small coagulant dose. Also, the PICl containing higher amount of

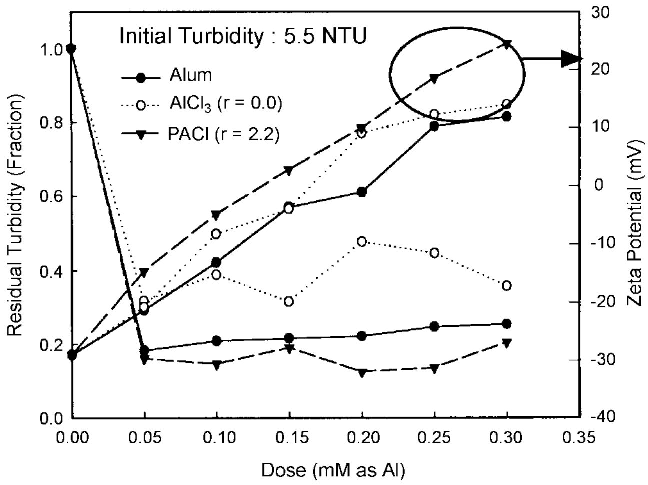

Fig. 9. Comparison of Alum, $AlCl_3$, and PACl coagulants for turbidity removal and zeta potential change as a function of coagulant dose.

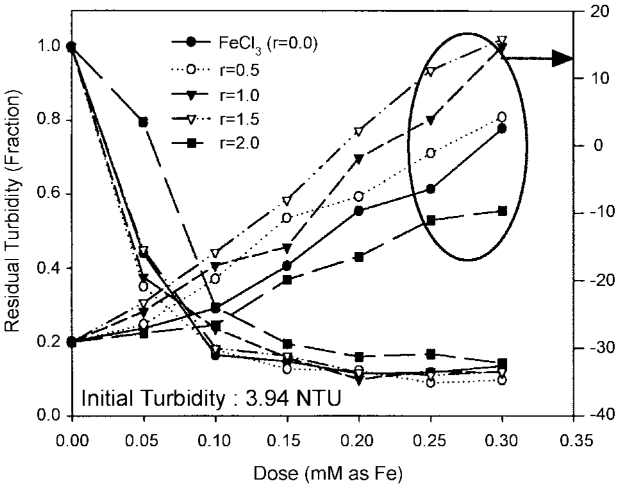

Fig. 11. Comparison of PICl coagulants with different r values for turbidity removal and zeta potential change as a function of coagulant dose.

polymeric Fe species attained more effective charge neutralization for the removal of turbidity in raw water.

CONCLUSIONS

The following conclusions are drawn from this research:

1. The fraction of polymeric Al showed a maximum at r=2.2, 85% of the total aluminum in solution, and precipitated Al substantially increased when r increased above 2.35.

2. ^{27}Al-NMR spectra were recorded for Al hydrolysis species under different r values. A peak appearing at 0 ppm is assigned to the monomeric Al species of the type $Al(H_2O)_6^{3+}$, $Al(OH)(H_2O)_5^{2+}$, and $Al(OH)_2(H_2O)_4^{+}$. A signal appears at 62.5 ppm, corresponding to aluminum ions in tetrahedral coordination, $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$. As the r value increased, polymeric Al species was detected at 63.4 ppm.

3. The characrerization of PICl showed that as the r value increased, monomeric Fe species substantially decreased and the fraction of polymeric Fe showed a maximum at r=1.5, 20% of the total iron in solution, and the precipitated Fe was dramatically increased with increasing r above 2.0.

4. FT-IR and powdered XRD spectra were used to determine Fe hydrolysis species under different r values. As r values increased, bands at 600, 850 and 1,160 cm^{-1} diminished due to the polymeric Fe(III) with higher OH^- and less H_2O per mole of Fe(III) than monomeric Fe(III). A powdered XRD intensity indicated that the polymeric Fe was directly transformed from monomeric Fe by the addition of base.

5. The coagulation tests for the synthesized PACls showed that the PACl (r=2.2) coagulant showed the most efficient TOC and turbidity removal among the coagulants used due to its highest amount of polymeric Al species contained in the PACl (r=2.2).

6. For the coagulation tests using synthsized PICls, the PICl (r=2.0, r=1.5) coagulants showed more efficient UV_{254} removal than $FeCl_3$ and PICl (r=0.5, r=1.0) due to a higher polymeric Al species contained in PICls (r=2.0, r=1.5), and PICl (r=1.5) was the most effective in the turbidity removal and charge neutralization.

ACKNOWLEDGEMENT

This work was supported by grant No. R02-2000-00357 from the Basic Research Program of the Korea Science & Engineering Foundation.

REFERENCES

Akitt, J. W. and Farthing, A., "New Al NMR Studies of the Hydrolysis of Aluminum Ions," *J. Mag. Reson.*, **32**, 345 (1978).

Akitt, J. W., Greenwood, N. N. and Khandelwal, B. L., "Aluminum-27 Nuclear Magnetic Resonance Studies of Sulphato-Complexes of the Hexa-Aquo Aluminum Ion," *J. Chem. Soc. Dalton Trans.*, 1226 (1972a).

Akitt, J. W., Greenwood, N. N., Khandelwal, B. L. and Lester, G. D., "^{27}Al Nuclear Magnetic Resonance Studies of the Hydrolysis and Polymerisation of the Hexa-Aquo Aluminum(III) Cation," *J. Chem. Soc. Dalton Trans.*, 604 (1972b).

APHA-AWWA-WEF, "Standard Methods for the Examination of Water and Wastewater," *APHA AWWA WEF.*, 20th eds. (1988).

Bersillon, J., Hsu, P. and Fiessinger, F., "Characterization of Hydroxy-Aluminum Solution," *J. Soil. Sci. Soc. of Amer.*, **44**, 3 (1980).

Bottero, J. Y., Cases, J. M., Fiessinger, F. and Poirer, J. E., "Studies of Hydrolyzed Aluminum Chloride Solutions I. Nature of Aluminum Species and Composition of Aqueous Solutions," *J. Phys. Chem.*, **84**, 2933 (1980).

David, R. and Parker, D. R., "Identification and Quantification of the Al_{13} Tridecameric Polymeric Polycation using Ferron," *Environ. Sci. Tech.*, **26**(5), 908 (1992).

Hur, J. M. and Kim, S. H., "Combined Adsorption and Chemcial Precipitation Process for Pretreatment or Post-Treatment of Landfill Leachate," *Korean J. Chem. Eng.*, **17**, 4 (2000).

Murphy, P. J., Posner, A. M. and Quirk, J. P., "Chemistry of Iron in Soils. Ferric Hydrolysis Products," *Australian J. Soil Res.*, **13**, 189 (1975).

Oh, M. H., So, J. H., Lee, J. D. and Yang, S. M., "Preparation of Silica Dispersion and its Phase Stability in the Presence of Salts," *Korean J. Chem. Eng.*, **16**, 4 (1999).

Park, K. Y., Lee, K. C. and Kim, J. K., "Manufacture of PAC (Polyaluminum Chloride) by Partial Decomposition of Aluminum Chloride Hexahydrate," *HWAHAK KONGHAK*, **32**, 5 (1994).

Schneider, W. and Schwyn, B., "The Hydrolysis of Iron in Synthetic, Biological, and Aquatic Media," Aquatic Surface Chemistry (Stumm, W. eds.), John Wiley and Sons, N.Y. (1990).

Schwyn, B., "Die Hydrolyse von Eisen(III) β-Eisenoxyhydroxid: Von der Keimbildung bis zur Koagulation," Ph.D. dissertation No. 7404, ETH, Zürich, Switzerland (1983).

Smith, R. M., "Relation Among Equilibrium and Nonequilibrium Aqueous Species of Aluminum Hydroxy Complexes," Nonequilibrium Systems in Natural Water Chemistry (Gould, R. F. eds.), A.C.S. Advances in Chemistry Sereis No. 106, Washington, D.C., 250 (1971).