

ESTIMATION FOR DEWATERABILITY ON INTERACTION BETWEEN CATIONIC FLOCCULANTS AND IONIC MATERIALS IN DISSOLVING WATER

Young-Han Bae and Sung-Sik Lee[†]

Department of Chemical Engineering, Dong-A University
840 Hadan-2-Dong, Saha-Ku, 604-714, Busan, KOREA

Abstract : Commonly, the flocculant is dissolved in process or recycle water in industrial plant which has many ionic materials. Therefore, the polymer degradation in aqueous solution by chemical, mechanical or bacteriological may occur, sometimes rapidly. Even if the same flocculant is dissolved, the flocculation characteristics and the properties of dissolving polymer varied with the kind of dissolving water. In this study, we try to estimate the interaction between flocculants and ionic materials in dissolving water using self inverting emulsion polymer; polyacrylamide-co-trimethyl ammonium ethyl acrylate chloride flocculants which have varying molecular weights and structures at a several conditions. The polymeric flocculant is dissolved in artificial dissolving water with Potassium Chloride (PC), Calcium Chloride anhydrous (CC), Potassium Hydroxide (PH), Sodium Chloride (SC), Sodium Bromate (SB) and Iron (II) Sulfate Heptahydrate (IS) as ionic sources. Experimental results indicate that the cationic and anionic ions in dissolving water induce the hydrolysis, degradation of cationic functional group and uncoiling of polymeric flocculants, therefore, the flocculation efficiency decreased by undesired polymer. According that result, it is important to estimate not only its structures and physical properties but also the qualities of dissolving water to optimize the efficiency.

Key Words : Flocculant, Flocculation, Dewatering, Dissolving water, Ionic material

INTRODUCTION

A synthetic polyelectrolyte is a polymer derived from petrochemical raw materials, carrying ionic charges along the polymer chains, which make the polymer water soluble¹⁾. And water-soluble polymers have shown many interesting properties leading to a wide variety of industrial and environmental applications. For example, the water-soluble polymeric materials are used in area such as paper products, film coating, membranes and flocculation^{2,3)}.

Polyacrylamides are high molecular weight and water-soluble polymers typically employed

for solid/liquid separation processes. These materials induce flocculation by agglomerating the solids and, hence, improving the dewatering rate of many suspensions.

In recent years, the performance of these flocculants has been improved by "structuring" the linear products through the use of suitable cross-linking/branching agent. Polyacrylamide flocculant is a type of high molecular weight compound that is soluble in water and it has major advantages such as, flexible and effective in treating wastewater, paper, sedimentation, and flotation with wide range of concentrations, due to rapid reaction, low dosage.

Some researchers estimate the floc binding strength, floc strength on shearing or stress and interaction between sludge and polymer as

[†] Corresponding author
E-Mail: hanchemen@yahoo.co.kr
Tel: +82-(0)51-200-7721, Fax: +82-(0)51-200-7728

flocculation aspects and enhanced flocculation by multi component chemicals, dosing sequence, and charge density as chemical aspects⁴⁾.

Generally, the performance factor of flocculant classifies as its structures and physical properties. However, it is possible to estimate the efficiency, when the flocculant is dissolved completely. In general, polymeric flocculants were stable over periods of several months, however, in aqueous solution, chemical, mechanical or bacteriological degradation may occur, sometimes rapidly⁵⁻⁶⁾.

The kind of dissolving water is variable; for example, potable water, process water, underground water, recycling water and river water. And the chemical properties are quite different as location, season, industrial division, and treatment method. Therefore, even if the same flocculant is dissolved, the flocculation characteristics and the properties of dissolving polymer varied with the kind of dissolving water.

The mechanisms of interrelationship between water soluble polymer and materials in a solution can be divided by the poor solubility and degradation by some materials.

The external factors affecting the degradation of water soluble polymers are free radicals, aerobic and anaerobic bacteria, divalent and trivalent ions, and UV radiation.

Especially, the chemical degradation of polymers can be distinguished by processes such as hydrolysis and molecular attack by foreign bodies⁵⁾.

General emulsion flocculant is self-inversing emulsion by inversing agent when it was dissolving. Consequently, the solubility of emulsion type flocculant is depended on the dosage of inversing agent and the properties of dissolving water but that of powder type flocculant is depended on a various physical factors and don't uniform each particles. For that reason, we select the emulsion type flocculant due to emulsion has superior solubility than powder, because of these formulation and micelle effect.

Sludge formed in the biological processing of sewage, human waste, and industrial wastewater

is commonly referred to as organic sludge and generally contains large quantities of negatively charged colloidal matter⁷⁾. Therefore, cationic flocculant generated large floc with the sludge due to the electric attraction.

In this study, we try to estimate the properties and the characteristics of self-inversing emulsion polymerization at various conditions and the interaction between flocculants and ionic materials in dissolving water using ionic metal salt. And the efficiency of drainage for concentrating sludge of sewage and paper plant to ascertain the changes that chemical properties and flocculation characteristics are different to each polymer is estimated.

As the experimental result, the main factor for dissolving water to improve the flocculating and dewatering efficiency is investigated.

MATERIAL AND METHODS

Emulsion Polymerization

The recipes of a series of partially linear polyacrylamide-co-trimethyl ammonium ethyl acrylate chloride (PAMs) produced herein is summarized that the amount of oil phase is approximately 25~35 wt% depending on the monomer phase condition, the monomer concentration of total charge is 35~50 wt.

Acrylamide as base monomer and trimethyl ammonium ethyl acrylate chloride (TMAEAC) as cationic monomer were polymerized by free radical initiation in distilled water at 40~60 °C. Potassium persulfate (Jun Sei, reagent grade) served as the water soluble initiator. Isoparaffinic solvent for Exxon was used as oil phase medium. And Sorbitan monooleate (HLB=4.3), Sorbitan sesquioleate (HLB=3.7), POE (20) sorbitan monostearate (HLB=14.9) and polymeric emulsifier (HLB=6.0) is used as Emulsifier.

The polymerization was carried out in a 1 L round bottomed flask equipped with a mechanical stirrer, nitrogen inlet/outlet, digital thermometer, and so on⁸⁻⁹⁾.

After both monomer phase and oil phase prepared and emulsified using homogenizer,

then Oil-in-Water Emulsion (O/W Emulsion) was generated.

The other polymerization conditions are same; the agitation speed is 300 ± 30 rpm, the peak temperature is $60\pm 5^\circ\text{C}$ and same catalyst system in all formulas.

Polymerization times varied between 40 and 120 min, and the inverting time is 30 min. Molecular weight variations were produced by altering the concentrations of monomer and initiator, and occasionally adding very small amount of ethylene bis-acrylamide as a cross linking agent.

To oxygen free reaction environment, a nitrogen stream was bubbled into the co-monomer solution for 15 min and then a nitrogen blanket was pass over the solution for the duration of the polymerization.

After free radical polymerization, the emulsion is inverted by POE sorbitol hexaoleate as the inverting agent for activation of the polymer dispersion at a level of 2 to 6 w% in the emulsion itself.

The molecular structure of the flocculant depends on the dewatering performances to achieve. Theoretically, the more molecular weight of polymer is increased, the more dewaterability by flocculation is increased. But, a reduction in viscosity of polymer solution after dissolving was seen with all polymeric flocculants.

One of the important properties required in the dissolving process are conductivity and hardness of dissolving water. Polymer in water solutions can be unstable and degradation can result in lower efficiency.

Property Analysis

All solution viscosity were measured at 0.5 w%, $25\pm 2^\circ\text{C}$ in a constant temperature water bath with Brookfield Viscometer, LVTDV-II in these experiments.

The viscosities are compared the original viscosity in de-ionized water at rota 3, 12 rpm, using Brookfield viscometer. Stability factor is calculated by ratio the solution viscosity for each storing time against that on 1 hr after the

polymer dissolved.

The sample was titrated to analyze cationic charge density as colloid equivalent values with an anionic potassium polyvinyl sulfate (PPS) in presence of blue of toluidine as a cationic dye. The end point is determined as the color changed from blue to purple.

The cationic charge density is calculated as followed;

$$\text{Cationic charge density} = \frac{M.V \times 10^{-3}}{5 \times 10^{-3}} \times \frac{1}{400} \times f$$

Here, M.V. means the consumption of PPS at the end point and f is the factor of PPS.

The cationic charge density of 20 mol% polymer has 2.31 meq/g by titration method.

Flocculation Test

Samples of digested and conditioned sludge were taken from two wastewater treatment plant; W paper plant (TS = 25~30 g/kg) and D sewage treatment plant in KOREA (TS = 16~22 g/kg).

Ten different cationic polyacrylamide flocculant as polyelectrolyte were used, eight samples are lab polymerization sample and others are supplied by Eyang chemical and indicated as Yangfloc C-830SE and C-833SE. Those product were 20 mol% and 60 mol% cationic acrylamide-co-trimethyl ammonium ethyl acrylate chloride polymer and the average molecular weight of that is 8.0×10^6 Daltons and the evaporation residue is 45.3% and 46.3%, respectively.

Before the polymer injected to flocculate suspended solids, the emulsions were made up 0.4 w% solution using tap water.

The water was stirred at 300 rpm and after injecting the solution, mixing was continued for 30 min, 200 rpm at jar-tester. Then the solution aged for another 30 minute.

The flocculation of sludge and polymer was done using 500 mL beaker at 150 rpm using jar-tester.

The drainage of flocculated sludge was dewatered by funnel with belt filtration membrane and digital balance was linked PC. This computer recording of the drainage test is

estimated since the first 10 to 15 sec of the drainage is the most crucial. And the dewatering cake was dried at $120 \pm 2^\circ\text{C}$ using dry oven during 4 hr to measure the water content in cake⁵⁾.

RESULTS AND DISCUSSION

We experiment on the stability of cationic polymer solution with artificial dissolving water of which properties are 5.0 mS/cm of conductivity, 400 mg/L of CaCO_3 hardness, pH 7.5.

Figure 1. shows the stability for various types and charge densities of polymers in the same condition.

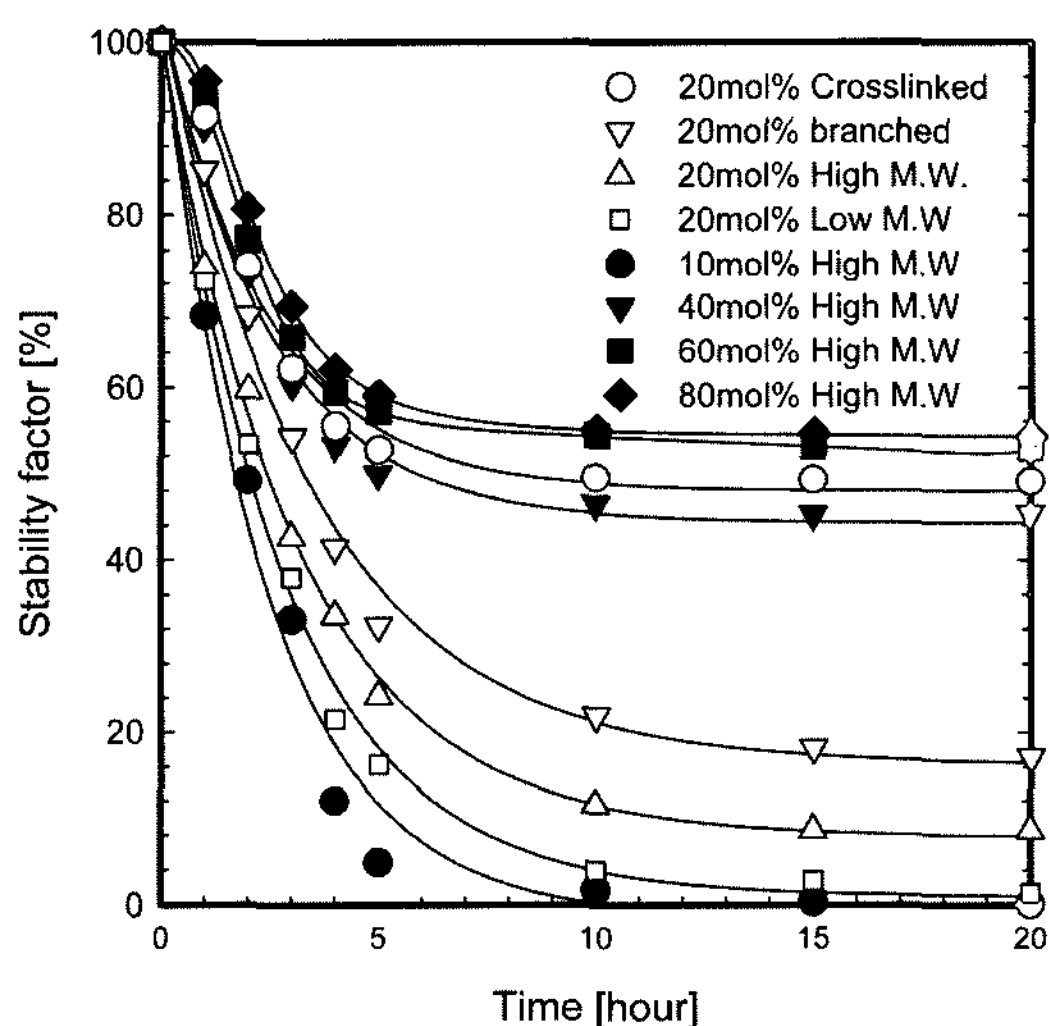


Figure 1. The relationship between the stability of solution and structures/charge density of polymer.

It means that the more the cationic charge density, branch degree or molecular weight of each polymer is higher, the more degradation decreases the tendency.

The difference of stability factor is more than 50% for ionic effect and 20% for branch degree except cross-linking polymer. When the polymer is cross-linked, it is not available to adapt the flocculation due to the high dosage.

Cationic polymer solutions are much less stable than those from nonionic and anionic emulsion, because the hydrolysis of the ester function of the cationic functional group is occurred. A high cationic polymer has a large number of cationic functional group. Therefore, the interaction between cationic group and ionic materials in dissolving water depends on the number of each hydrolyzing site and the interaction both cationic groups is also activated against hydrolyzing reaction.

The cationic charge density as the main factor for flocculation performance not only decreases proportionally to the degree of hydrolysis but very often, depending on the pH and salinity of the water, it may decrease at twice this speed due to the interaction between the anionic groups formed through hydrolysis and the un-hydrolyzed cationic groups is known as the zwitterions effect.

The Effect of Mono-Valent Ions

Various ionic materials in dissolving water have a tendency to decrease the solubility and to attack the ionic functional group during

Table 1. The properties of ionic metal salt

INDEX	Chemical Form	M.W [-]	Conductivity [mS/cm]	pH [-]	Metal ratio [%]	Chemical Name
PC	KCl	74.56	1.739	3.316*	6.35	Potassium Chloride
CC	CaCl_2	110.99	1.726	4.779*	6.57	Calcium Chloride anhydrous
PH	KOH	56.11	3.170	4.549*	11.82	Potassium Hydroxide
SC	NaCl	58.44	1.844	4.685*	6.09	Sodium Chloride
SB	NaBrO_3	150.9	0.616	4.041*	6.11	Sodium Bromate
IS	FeSO_4	278.02	0.591	2.942*	4.73	Iron(II) Sulfate. Heptahydrate
DDW			0.0019		6.06	De-ionized water

* means the conductivity is compensated by metal ratio

dissolving. In order to estimate the interaction influence between ionic materials and polymer, we prepared the artificial dissolving water using metal salt, acid and basic for neutralization which is shown as table 1. When polymer stock solution using de-ionized water are stored in tightly closed, they are stable for 1 months at 25 °C.

Figure 2 and 3 show the dependence the solution viscosity on Sodium Chloride (SC) and Sodium Bromate (SB), respectively. The cationic 20 mol% low molecular weight polymer which is polymerize in lab used to all degradation test.

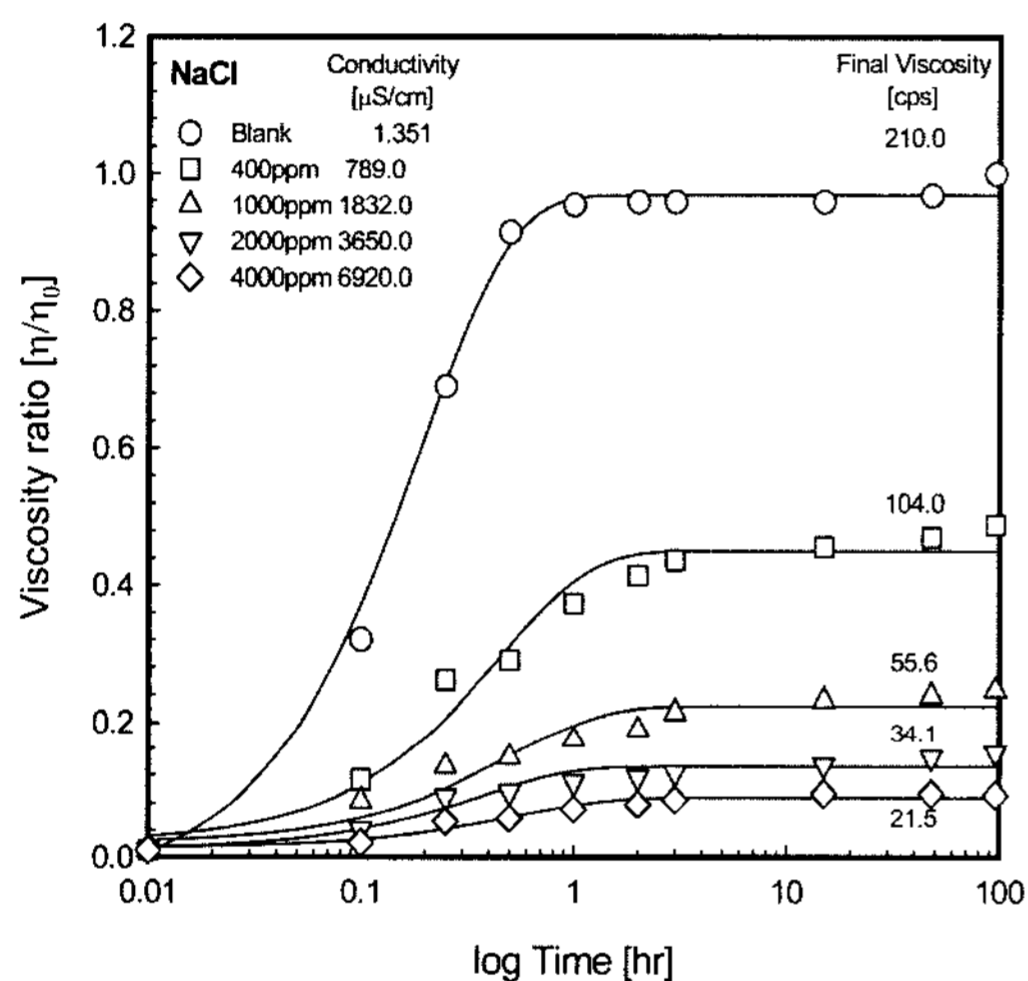


Figure 2. Effect of Sodium Chloride (SC) on viscosity profile of C-830SE.

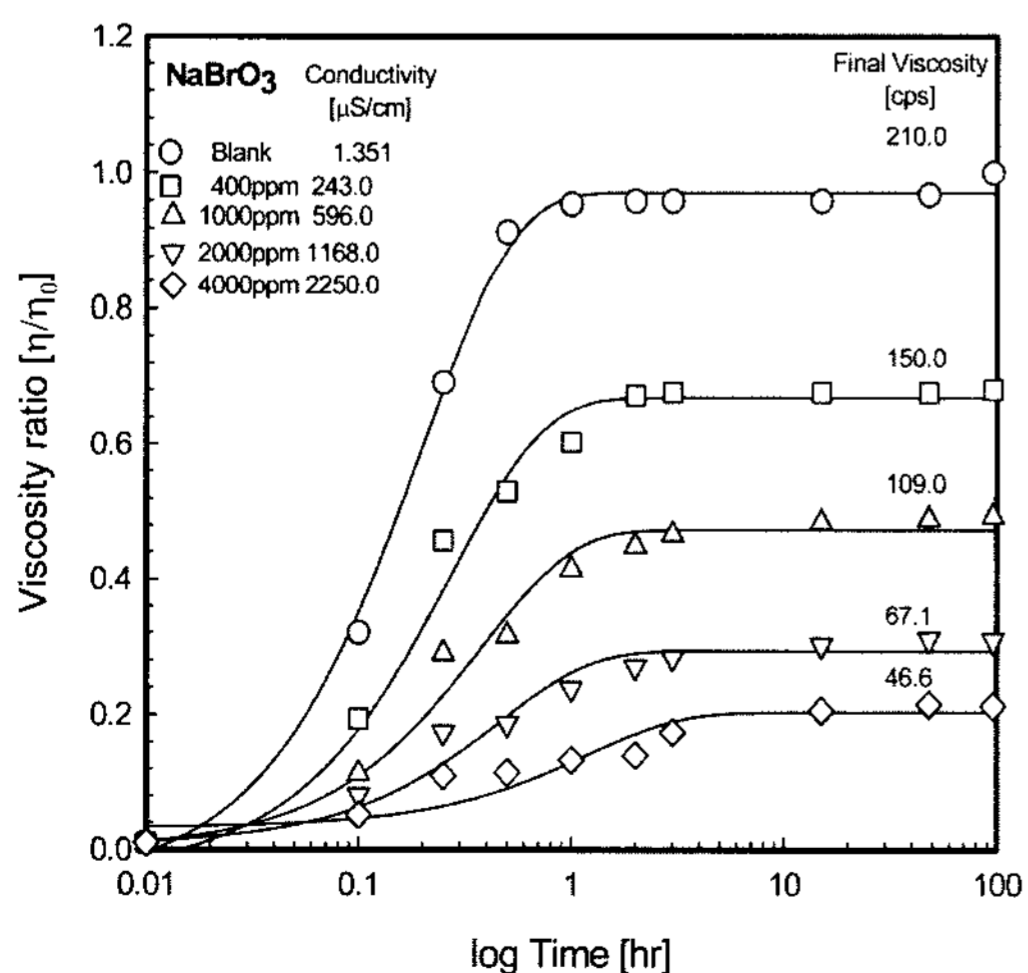


Figure 3. Effect of Sodium Bromate (SB) on viscosity profile of C-830SE.

The viscosity of a solution of a given polymer generally depends on the shear, ionicity, molecular weight, structure, concentration of polymer and so on. And the viscosity of polymer solution represents the stability for storing time on single sample. The functional group of polymer structure is hydrolyzed by free radicals or divalent and trivalent ions chemically.

The sodium ion as the conductivity source in sodium salt derivatives was reduced the solution viscosity for the 0.4% solution from 210 cps to 104 cps for SC and to 150 cps for SB, respectively. The decreased viscosity was proportional to the concentration of sodium ion.

The phenomenon by sodium ion is not the degradation but the aggregation cluster between the swelling polymers according to state of stock solution.

As the result of the observation of the microscope image, the sodium ion interfered with dissolution and uncoiled the polymer drop in water.

The dependence the solution viscosity on Potassium Chloride (PC) is shown as Figure 4.

The potassium ion in potassium salt derivatives was decreased the solution viscosity (88.33% for PC and 69.81% for PH as reduction ratio) by the aggregation cluster for PC and degradation for PH. The low concentration of potassium ion had poor influence. However, the viscosity was decreased sharply at more than 1000 ppm of that. Figure 5. shows the dependence the solution viscosity on Potassium Hydroxide (PH).

Comparing Figure 2. on NaCl and Figure 4. on KCl, the viscosity decreasing profile on sodium ion is two times larger than potassium ion as stable viscosity when the conductivity of SC which is 1.844 mS/cm (4.685 mS/cm) is 10 percent or higher than that of PC which is 1.739 mS/cm (3.316 mS/cm) at same concentration.

The conductivity in parentheses means the conductivity is compensated by metal ratio.

With regard to hydrolytic degradation, the stability of polyacrylamides depends on pH according to their ionic nature. The optimum

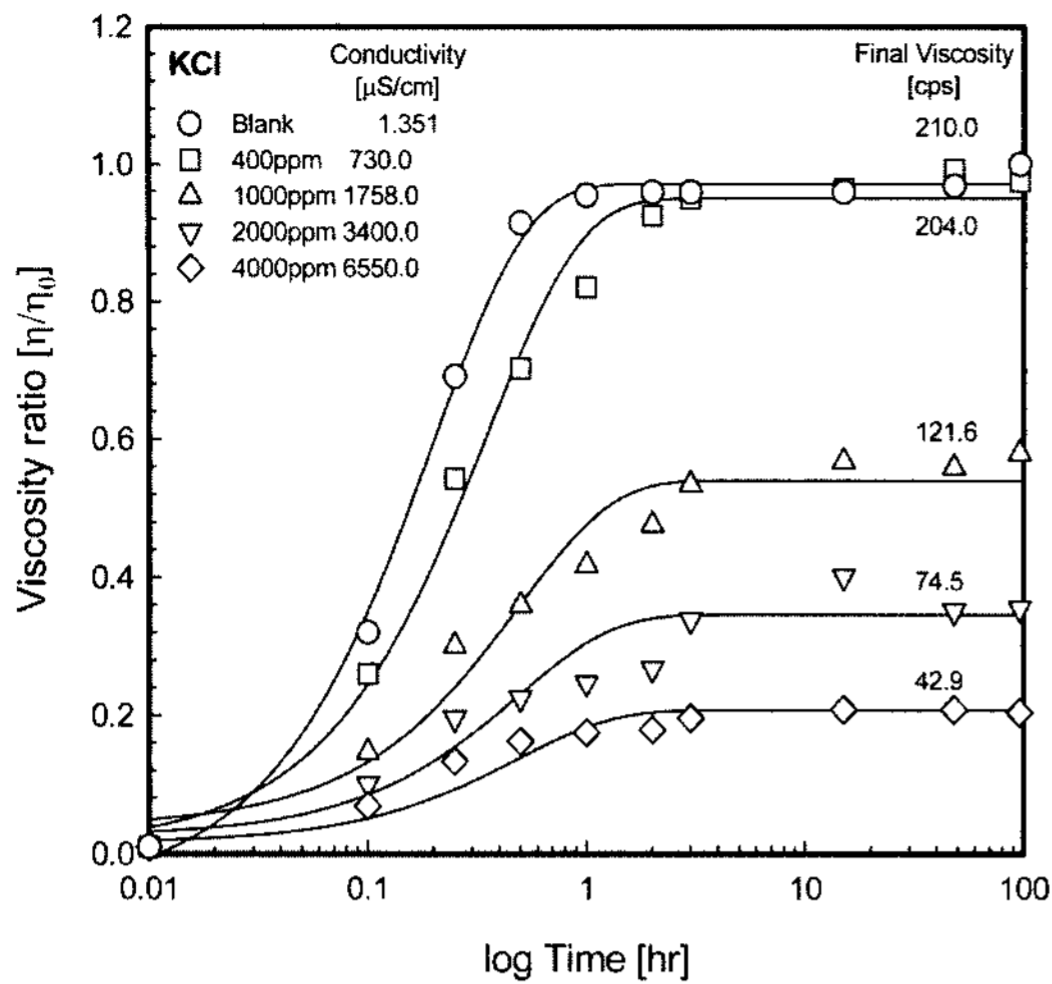


Figure 4. Effect of Potassium Chloride (PC) on viscosity profile of C-830SE.

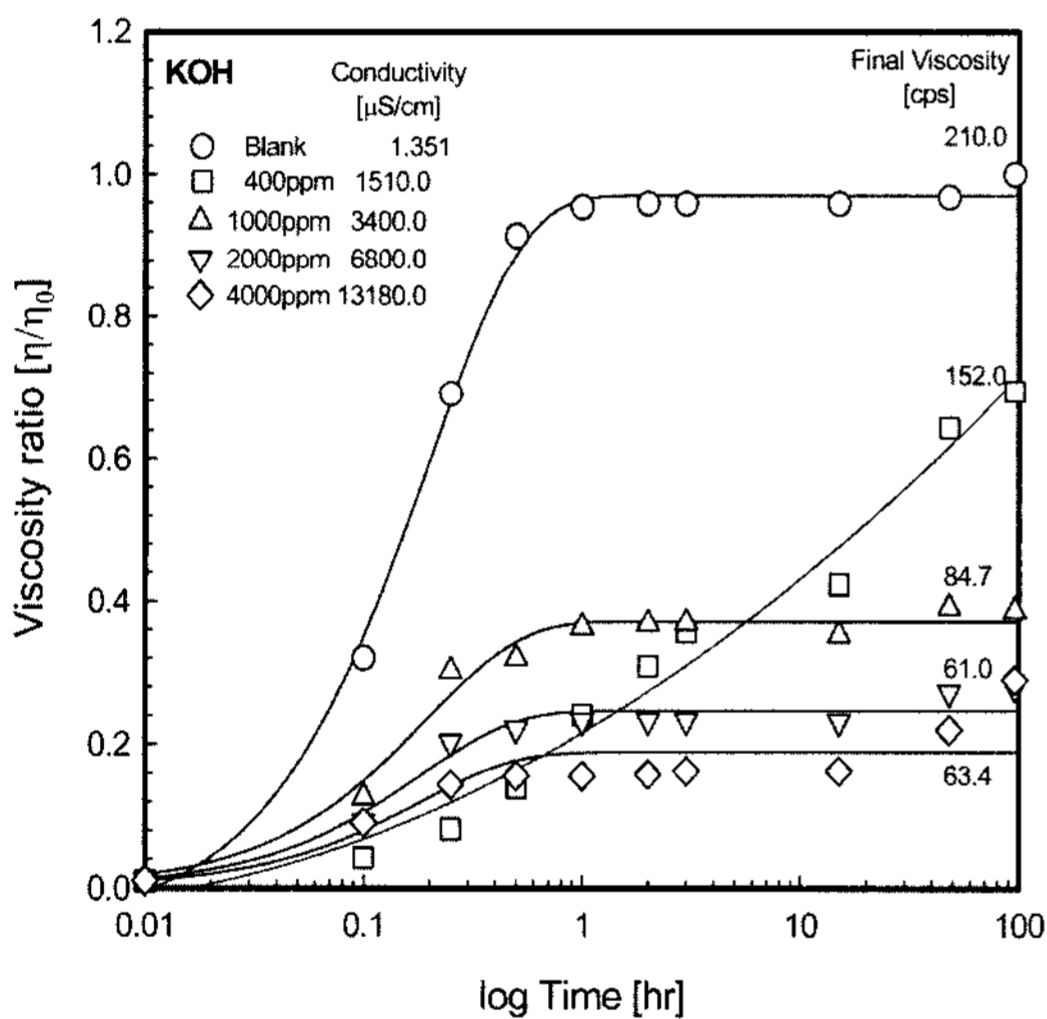


Figure 5. Effect of Potassium Hydroxide (PH) on viscosity profile of C-830SE.

pH is stable for cationic polymer is range from pH 4 to pH 6 as an empirical fact. In case of the dissolving water on potassium hydroxide, the pH of solution is more than pH 11 and high degree of electrolytic dissociation and the degradation of polymer on hydrolytic degradation is forced not only potassium ion but high pH value for OH radicals.

As the result, potassium ion has stronger degradation influence than sodium ion and their colloid equivalent values did not change as 2.1 meq/g.

The Effect of Divalent and Trivalent Ions

Generally the hardness shall be below 100 mg CaCO₃/L, and desirably 50~100 mg CaCO₃/L. The hardness of over 100 mg CaCO₃/L and below 50 mg CaCO₃/L will reduce their solubilities.

Figure 6. and Figure 7. reveal the dependence the solution viscosity on Calcium Chloride (CC) and Iron (II) Sulfate Heptahydrate (IS), respectively.

The effects of Ca²⁺ as divalent ion in Calcium Chloride anhydrous (87.58% for CC as reduction ratio) are similar to that of Na⁺. But

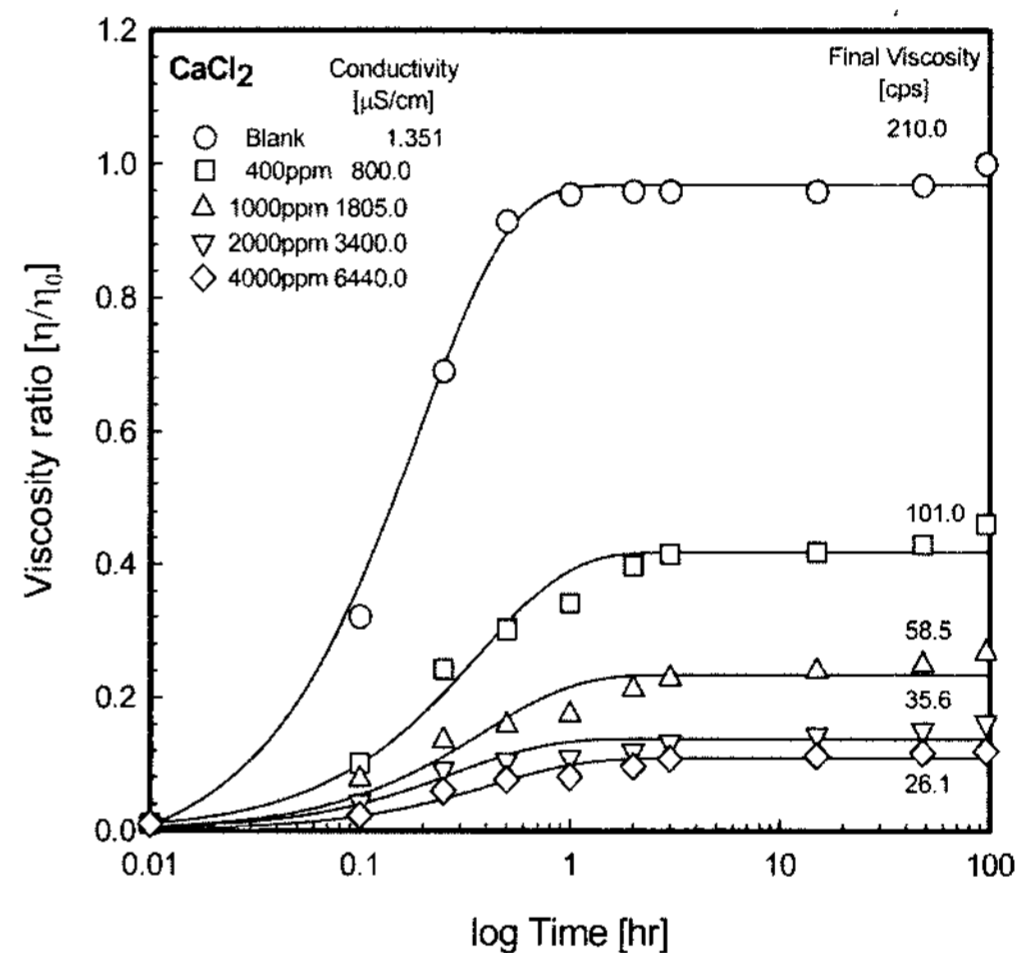


Figure 6. Effect of Calcium Chloride (CC) on viscosity profile of C-830SE.

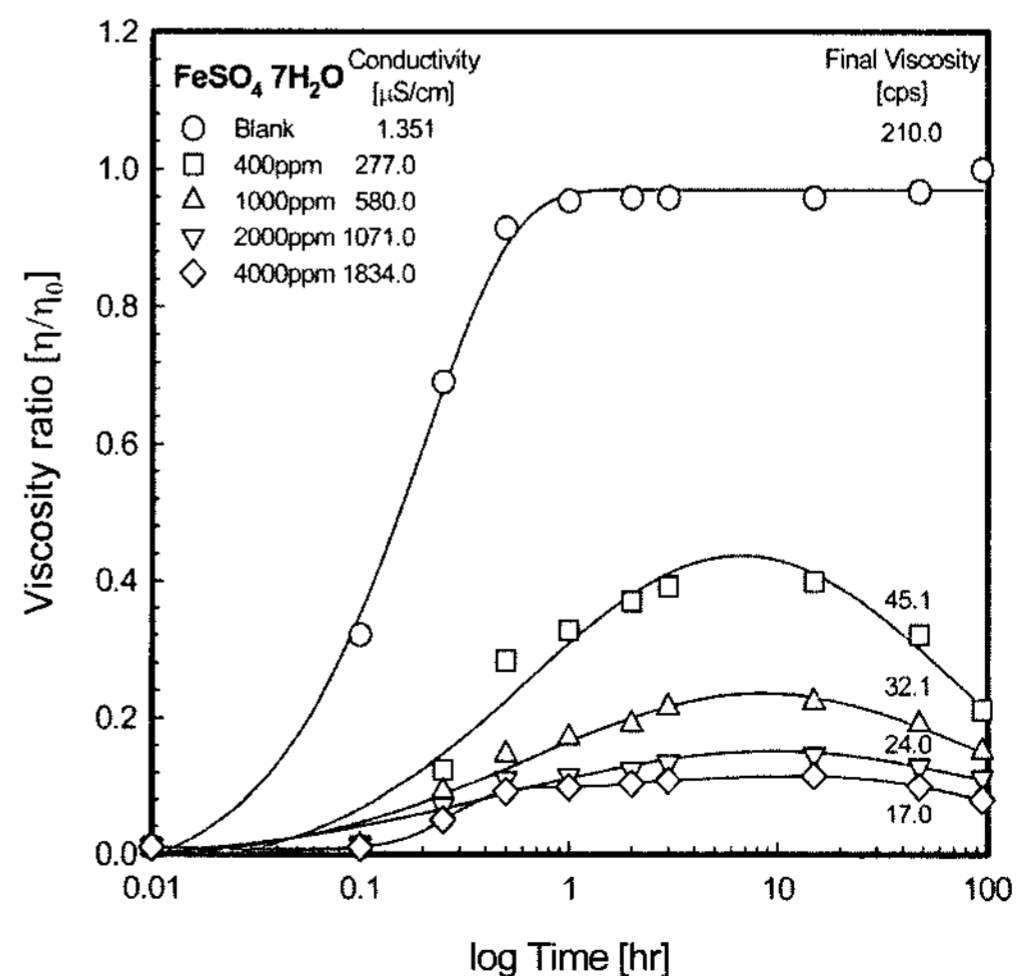


Figure 7. Effect of Iron(II) Sulfate Heptahydrate (IS) on viscosity profile of C-830SE.

the iron ion as trivalent ion generated the pin floc with polymer particle by the coagulation. In a consequence of that, the viscosity decreasing profile and degradation of polymer was higher than other metal ions.

Polyacrylamides in solution are sensitive to free-radical chain degradation. Free radicals are formed in water by a number of oxidizing and reducing agent; metal ions as iron ion and alkali ions.

Because of the presence of divalent and trivalent ions in inorganic salts formulated as the high hardness, it is useful to inverses and dissolves the polymer under a low dissolving rate. But the solution is easily degraded by divalent and trivalent ions and their colloid equivalent values did change under less than 1.0 meq/g by hydrolysis and degradation; 0.52 meq/g for IS and 0.87 meq/g for PH.

And the stronger ionic polymer requires the shorter dissolving time by a frequent interaction between ionic material in dissolving water and ionic functional group in polymer structure, because the polymer is easily uncoiled and dissolved in dissolving water by the ionic force. Consequently, the C-833SE has the high stability for those conditions (48% for IS as maximum reduction ratio)

The lower hardness for absence of ion in inorganic salts formulated leads to that result; the lower the salt concentration, the longer the dissolving time, due to the ionic interaction is poor.

Multivalent metal ions have a much more profound effect in lowering polymer solution viscosity because single multivalent metal ion causes that the ionic polymer coil up by ionic interaction in polymer solution.

The Effect of pH and Anionic Ion

Figure 2, and 3 show the dependence on the effect of anionic ions.

When the conductivity of SB is 0.616 mS/cm (4.041 ms/cm) and is one over three times for that of SC, the viscosity decreasing profile on SC shows rather insignificant influence than

that of SB. It means that the concentration of cationic ion has stronger influence on the degradation of flocculant than the kind of anionic ion.

The effect of pH and anionic ion for dissolving water using HCl and NaOH showed the Figure 8. In case of pH 2.0, the polymer has very poor solubility and low viscosity by the aggregation cluster. But the viscosity of polymer solution was decreased rapidly at base range by degradation.

There are many hydroxyl radicals or negative charged materials in dissolving water.

The addition of simple strong acid (e.g. HCl) to the dissolving water causes a weak contraction of the polymer conformation. But the contraction effect is increased as the polymers coil up by interaction between Cl^- ion and cationic functional group of polymer in low pH. Therefore, the viscosity of dilute polymer solution is rapidly fall as the ionic strength of the solvent increases.

In case of the addition of strong basic (e.g. NaOH), the polymer micelle is opened by inversing agent in the early stage and the viscosity of polymer solution is relative high value. However, the viscosity of that is rapidly decreased by ions of the basic material as the dissolving polymers coil up with a plenty of OH^- ion.

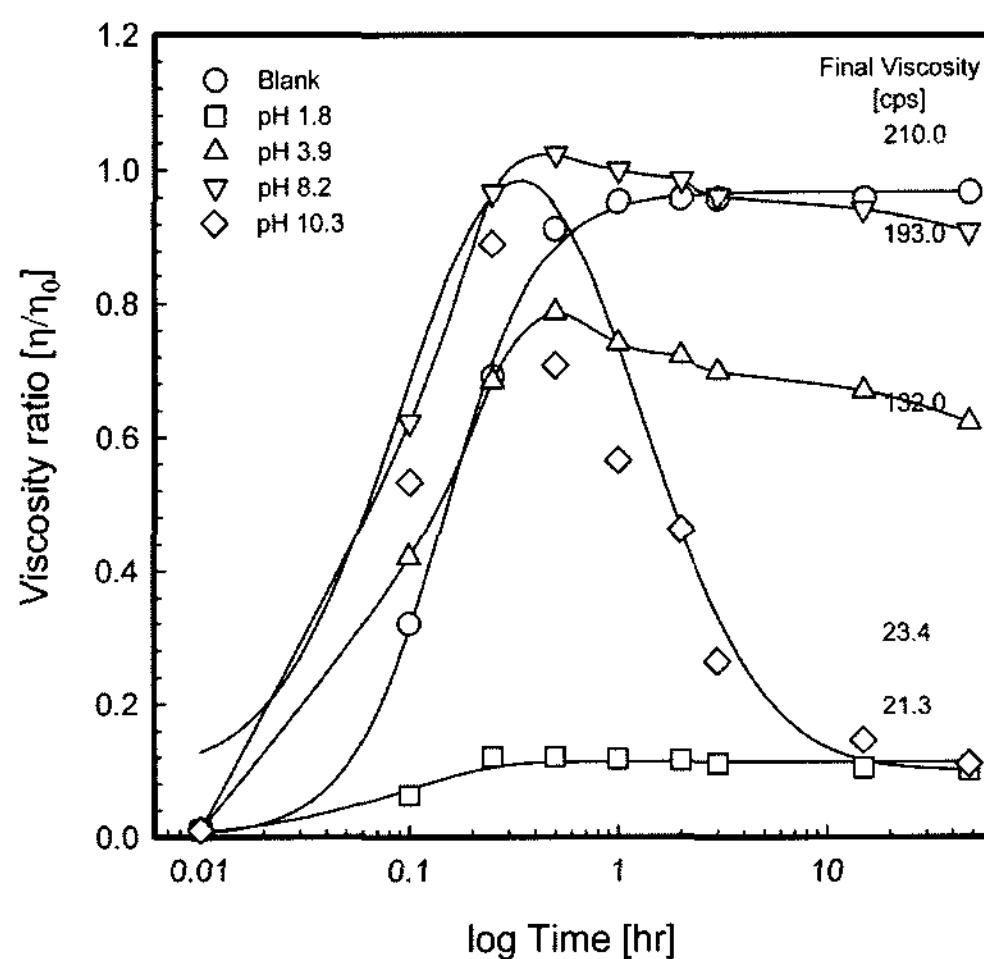


Figure 8. Effect of pH on viscosity profile of C-830SE.

The hydroxyl radical occur the hydrolysis reaction. As the result, the polymers lose the cationic functional group.

Figure 9. shows the summary for effect of ionic material on solution viscosity.

In this figure, SC and PC have higher intercept and slope. For that reason, when SC and PC is existed at high concentration in dissolving water, its viscosity and dewaterability of the polymeric flocculant is decreased.

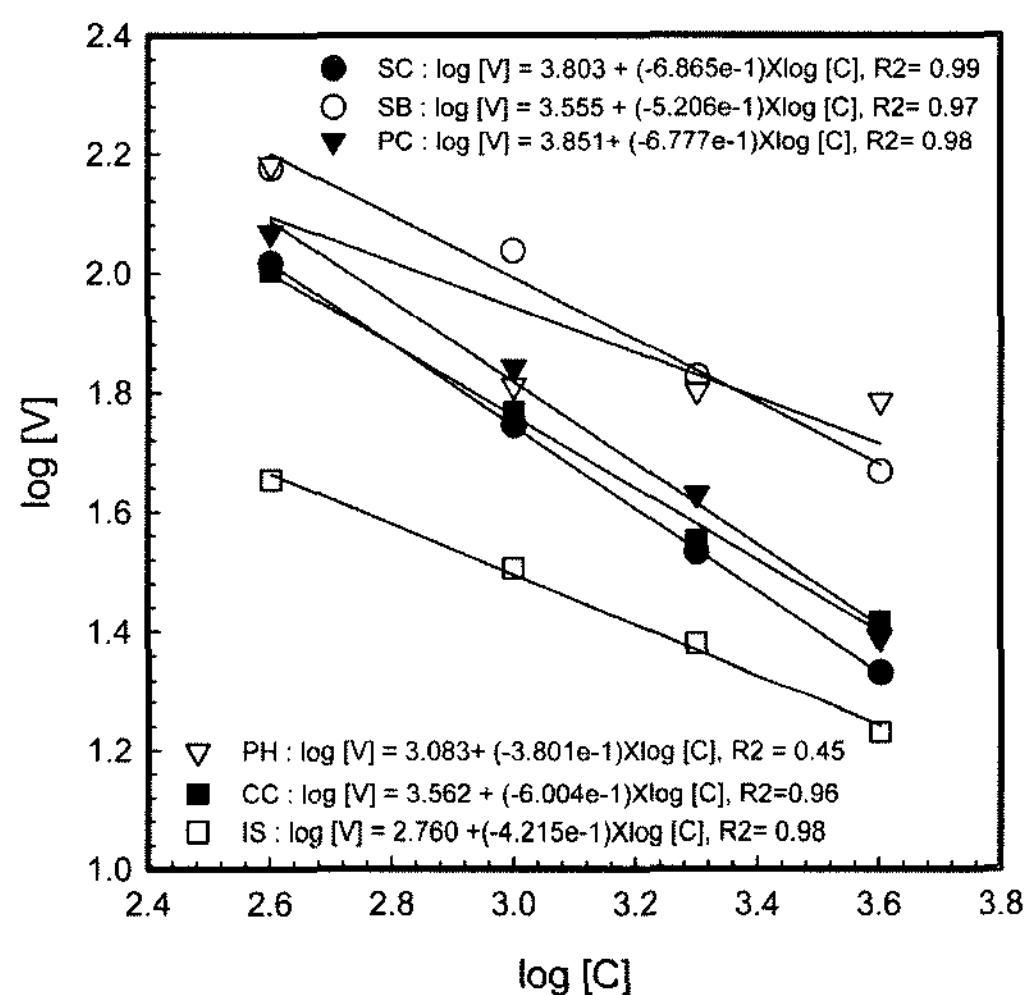


Figure 9. Dependence for the solution viscosity on various kinds of metal salt.

The Relationship Between Degradation and Dewatering Drainage

The efficiency of flocculation to separate the suspended solid (SS) in the water is measured by the size of the flocs and their drainage characteristics, the amount of flocculated matter in suspension and the turbidity of the supernatant liquid. In the flocculation, three main factors are involved; the molecular weight, the concentration and the ionic charge of polymer itself.

Generally, the more the dissolving and stocking time is increased, the less the efficiency for dewatering is decreased. We used the condensation sludge of W paper plant and D sewage plant to estimate the performance of polymer.

The properties of sludges are 2.71% and

1.84% of total solid, 1.43 mS/cm and 3.150 mS/cm of conductivity, 245 mg/L and 320 mg/L of CaCO₃ hardness, pH 7.14 and 7.76 and 72.1% and 62.3% of volatile suspended solid as organic materials in total solid, respectively. We select the cationic 25 mol% low molecular weight polymer as the optimum ionic charge by testing all range of cationic polymer with the same molecular weight for a drainage test of two sludges.

The performances of each experimental condition showed the Figure 10, 11, 12 and 13.

The optimum charge and dosage are cationic 10~25 mol% and 130~150 mg/L for conditioning sludge for W paper plant in our experiment using the jar test which is one standard method for accomplishing the performance test of flocculant.

SC and SB don't have any effect for drainage performance. The viscosity reduction by degradation for PC is ordinary. But, dewatering efficiency of that has lower performance than other conditions as shown Figure 10. In case of multivalent ions, the dewatering efficiencies are sharply decreased by more than 20%. It means the multivalent ions react with the functional groups of polymer structure as hydrolysis.

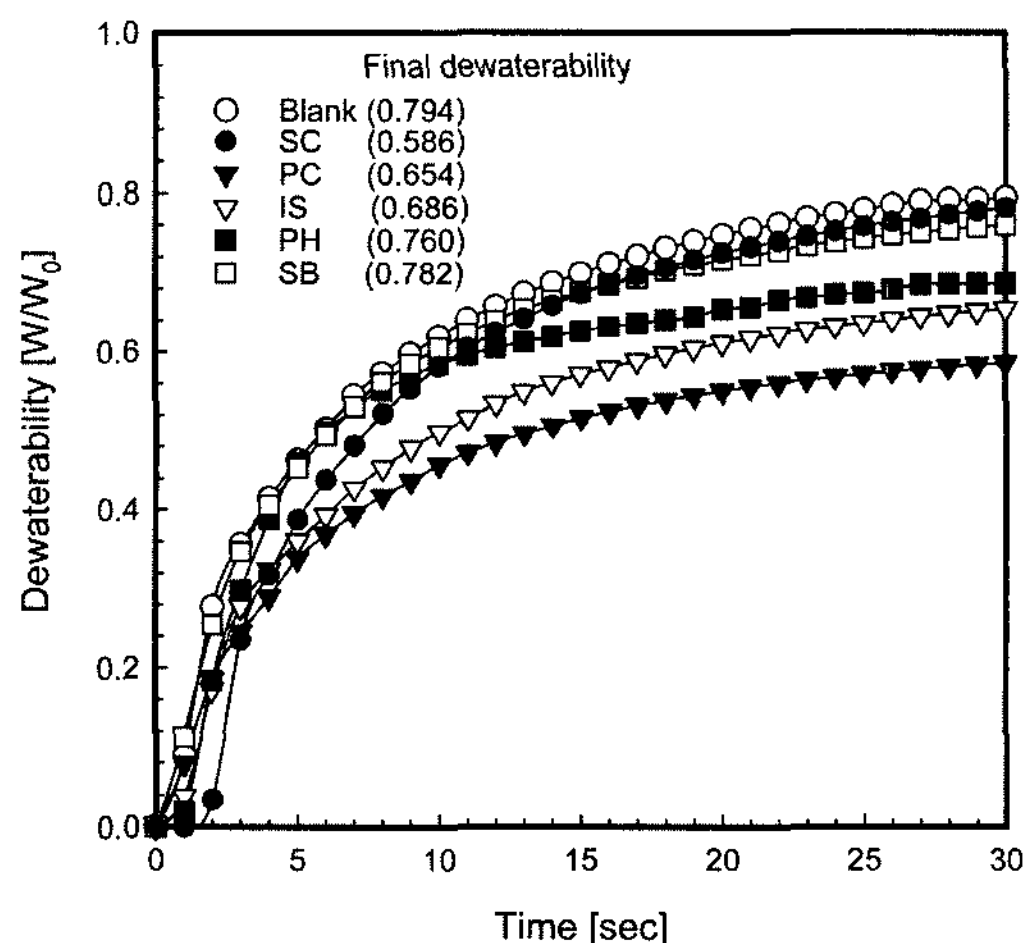


Figure 10. Drainage test on various kinds of metal ion for W paper sludge (Dosage: 140 mg/L, Jar-tester condition: 150 rpm, 30 sec).

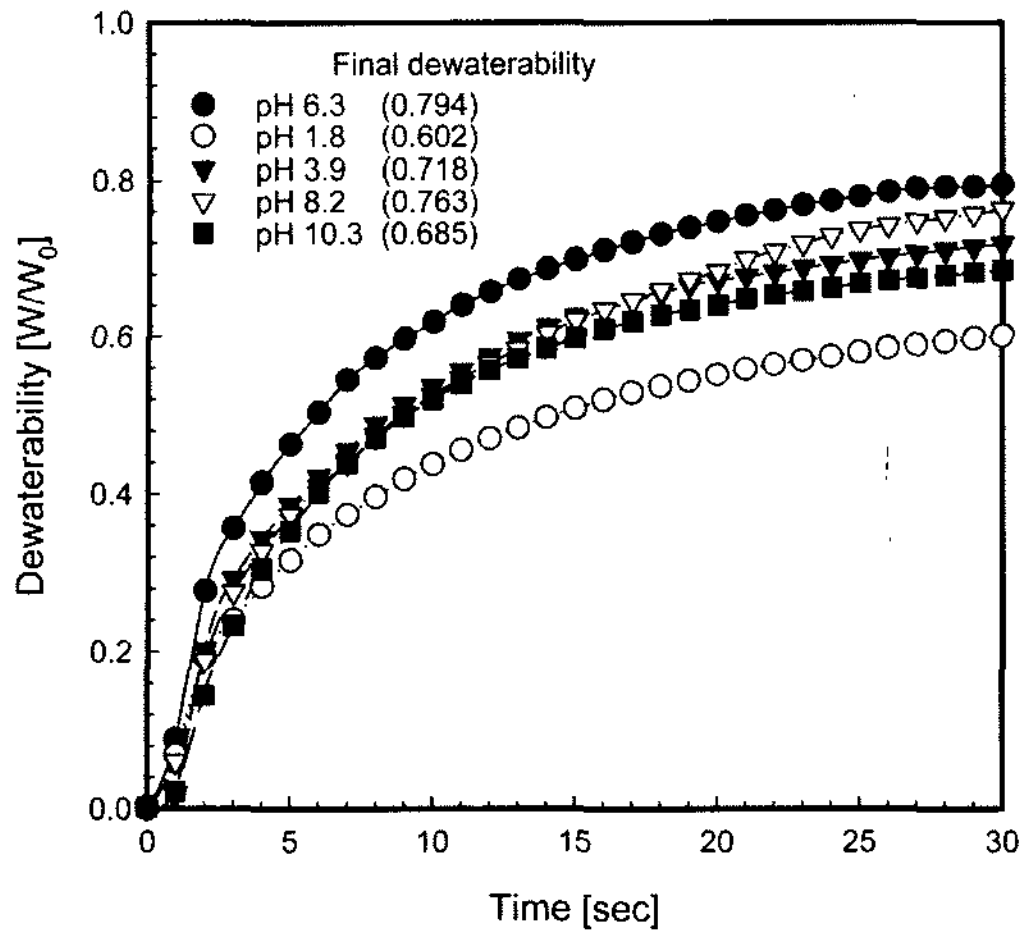


Figure 11. Drainage test on the pH of dissolving water for W paper sludge (Dosage: 140 mg/L, Jar-tester condition: 150 rpm, 30 sec).

Then the polymers lose the cationic charge on its chain. In consequence of interaction, the polymer has not enough cationic charge and generated weak flocs on an absence of bridging effect by free charge.

Although the polymer has relative high viscosity, the degradation polymer by ionic material in dissolving water has poor efficiency for dewatering and dosage because the loss of activated functional group.

As the result to estimate the effect of pH change by acid and base on drainage efficiency for W paper plant, the optimum pH of dissolving water was weak acidic as blank which is followed as Figure 11. The drainage efficiency is decreased in the below pH 2 and over pH 10 due to the cationic functional group in polymer structure is activated in acidic and neutral pH.

And the pH of polymer solution for PH is 11.82. But the performance was more than pH 10.3 in that condition and sludge. It is the evidence that the potassium ion is weaker inhibitor than sodium ion.

Metal salt and H⁺ ion interfered with polymer dissolving to generate the aggregation cluster and iron ion was formed the floc between iron ion and polymer as coagulant. But OH⁻ ion led to degrade the functional

group of polymer and other anionic ion showed a poor affect to polymer dissolving and performance.

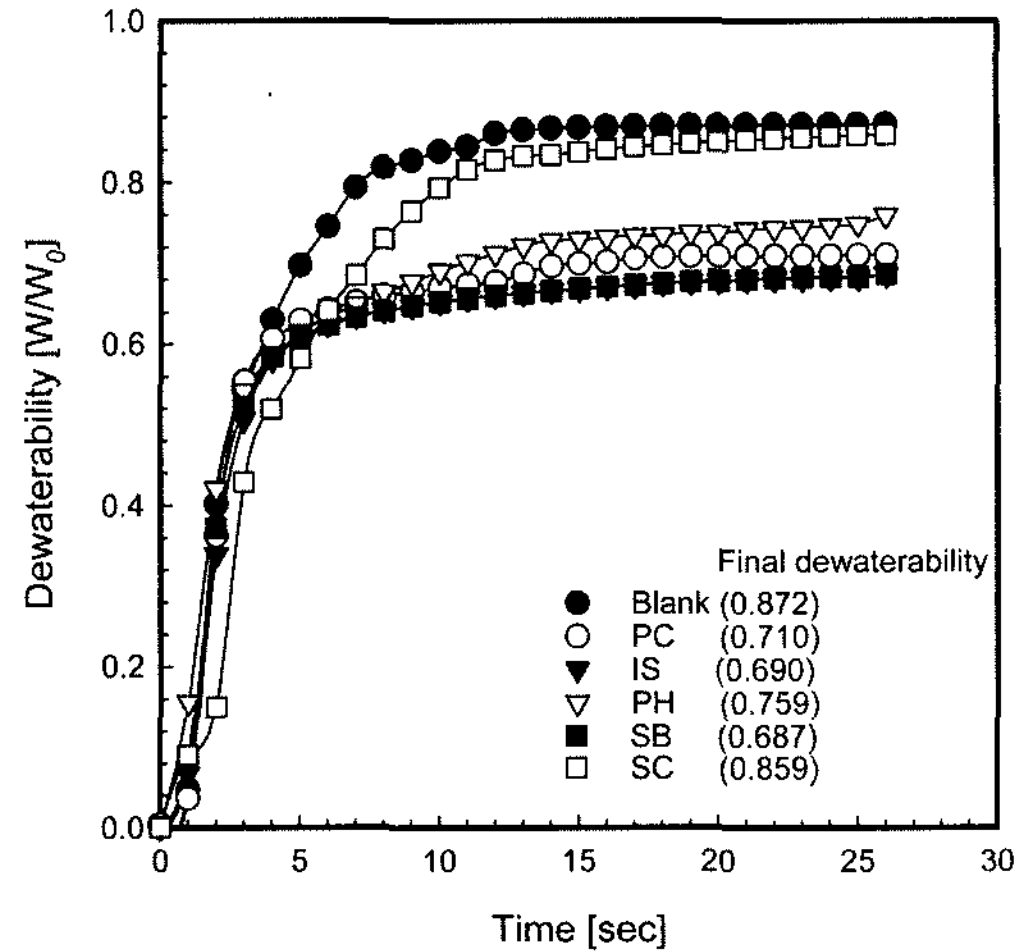


Figure 12. Drainage test on various kinds of metal ion for D sewage sludge (Dosage: 210 mg/L, Jar-tester condition: 150 rpm, 30 sec).

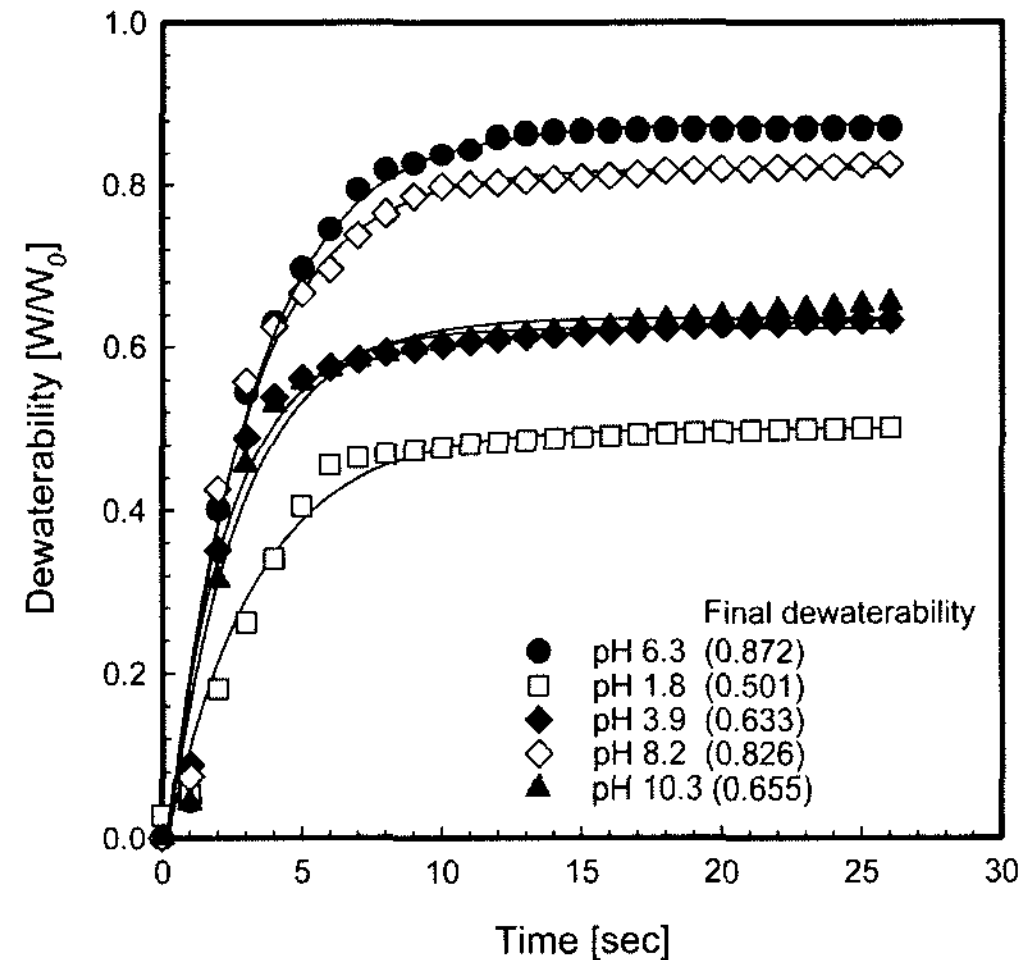


Figure 13. Drainage test on the pH of dissolving water for D sewage sludge (Dosage: 210 mg/L, Jar-tester condition: 150 rpm, 30 sec).

Figure 12 and 13 show the drainage test result for D sewage sludge.

In case of D sewage plant, the optimum charge and dosage are cationic 20~50 mol% and 200~220 mg/L for conditioning sludge in our experiment.

Only SC has good drainage performance. Other test showed lowering of efficiency about 20%. The difference of drainage was bigger than that of W paper and was range from 10 to 40% for each condition because the optimum charge for sewage is higher than that for paper and the degradation and hydrolysis effect is stronger.

Accordingly, the drainage is depended on the net charge balance of polymer and SS to generated floc and the polymer solubility and it is important to know how to dissolving polymer to optimize the dewatering and dissolving system.

CONCLUSIONS

Self inversing emulsion polymers as flocculant are polymerized and estimated the dissolution and flocculation characteristics to estimate the relational efficiency of dewatering system.

As the result for estimation the interaction between flocculants and ionic materials in dissolving water, the ionic material in dissolving water was shown two type interactions on emulsion flocculant as followed.

1. Generation of the aggregation cluster
: The ion interacted the surfactant which is to emulsify and inverse the micelle or the swelling polymer.
2. Degradation of functional group
: It means that the polymer has a lower charge density than original that.
Therefore it forms a weaker and smaller floc because the polymer doesn't generate an ionic bond.

In experimental condition, metal ions and H^+ ion interfered with polymer dissolving to generate the aggregation cluster and iron ion was formed the floc between iron ion and polymer as coagulant. And OH^- and Cl^- ion leaded to degrade the functional group of polymer and other anionic ion showed a poor affect to polymer dissolving and performance.

The cationic PAMs lose the cationic charge on its chain by multivalent ions, hydroxyl

radicals or negative charged materials. In consequence of interaction, the polymer has not enough cationic charge and generated weak flocs on an absence of bridging effect by free charge. The dewaterability of that is decreased by that effect.

And, although the polymer has relative high viscosity, it has poor efficiency for dewatering and dosage because the loss of activated functional group.

Finally, the difference of drainage for sewage sludge was bigger than that of paper sludge and was range from 10 to 40% for each condition due to the bigger degradation and hydrolysis effect for sewage sludge. And, the dewaterability is proportioned to viscosity reduction not on metal ions but on pH.

It is important to know how to select the optimized polymer and the dissolving water to optimize the dewatering and dissolving system.

ACKNOWLEDGEMENTS

We extend our thanks to Eyang chemical. Co., Ltd. for their assistance and practical input to these studies.

REFERENCES

1. Mortimer, D. A., "Synthetic Polyelectrolytes -A Review," *Polymer International*, **25**, 29-41, (1991).
2. Zayas, T., Percino, M. J., Cardoso, J. and Chapela, V. M., "Novel water soluble polyelectrolyte with arsenic acid group for flocculation application," *Polymer*, **41**, 5505-5512, (2000).
3. Banister, S. S. and Pretorius, W. A., "Optimization of primary sludge acidogenic fermentation for biological nutrient removal," *Water SA*, **24**(1), 35-41, (1998).
4. Lee, C. H. and Liu, J. C., "Sludge dewaterability and floc structure in dual polymer conditioning," *Advances in environmental research*, **5**, 129-136, (2001).
5. SNF, Polyacrylamide Emulsion Handbook,

- 1-2, (2002).
6. Branham, K. D., Snowden, H. S. and McCormick, C. L., "Water-soluble copolymer. 64. Effect of pH and composition on associative properties of amphiphilic acrylamide/acrylic acid terpolymer," *Macromolecules*, **29**, 254-262, (1996).
7. Watanabe, Y., Kubo K. and Sato, S., "Application of amphoteric polyelectrolytes for sludge dewatering," *Langmuir*, **15**, 4157-4164, (1999).
8. Blackley, D. C., *Emulsion Polymerization*, Applied Sci. Pub. (1982).
9. Chern, C. S., Chen, T. J., Wu, S. Y., Chu, H. B. and Huang, C. F., "Semibatch seeded emulsion polymerization of acrylic monomers: Bimodal particle size distribution," *Macromolecular Science*, **7**, 1221-1236, (1997).