

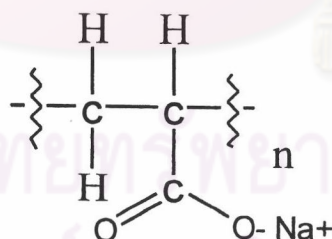
Chapter IV

Results and Discussion

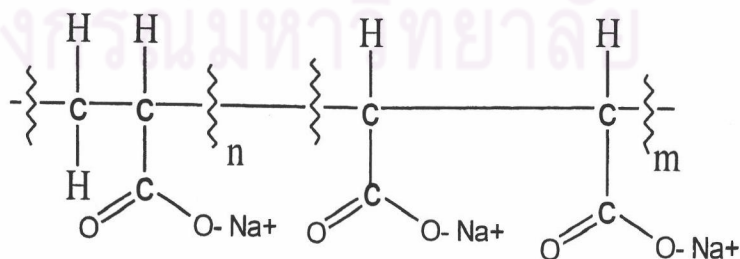
4.1 Prevention of calcium salt precipitation by polyacrylate.

Calcium hypochlorite is one of the most commonly used chlorine compounds. It contains 25 or 70 percent available chlorine. However, it presents an encountered problem since calcium ions tend to precipitate with various anions such as carbonate, sulfate or phosphate. This research attempts to correct this problem. Polyacrylate including its copolymer and terpolymer were chosen to be the trapping agents by chelating with the calcium ions. Acusol445N is one of the trade names of sodium salt of polyacrylic acid while Acusol 479N is the trade name of sodium salt of copolymer of acrylic acid and maleic acid. The terpolymer used in this study is Acumer3100 which is the terpolymer of acrylic acid, sulfonate and nonionic function. Acusol 445N, Acusol 479N and Acusol 3100 will be used to refer to homo-, co- and terpolymer of polyacrylate, respectively, through out this dissertation.

Structure of Acusol445N



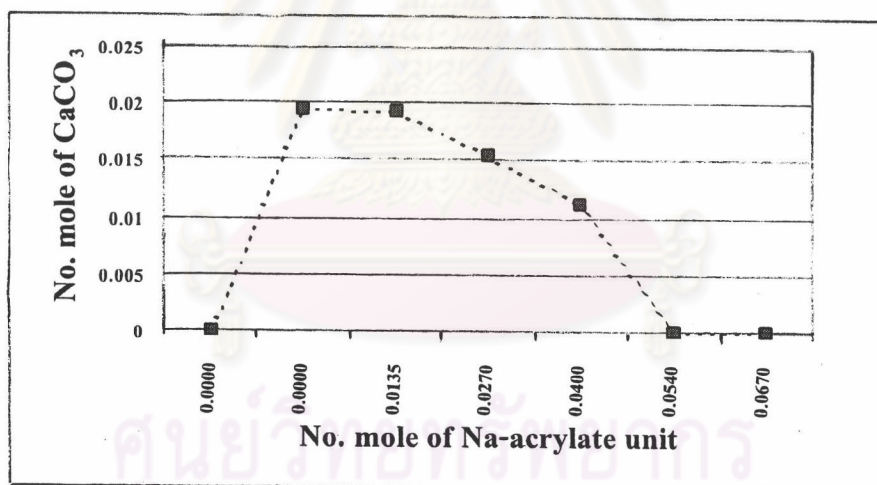
Structure of Acusol479N



This section intends to prove the ability of these polymers to prevent the precipitation of calcium carbonate formed from the reaction of calcium hypochlorite and sodium carbonate. Table 4.1 shows the results of these experiments.

Table 4.1 Prevention of calcium salt precipitation by polyacrylate.

No.	Weight(g) of $\text{Ca}(\text{OCl})_2$	No. mole of $\text{Ca}(\text{OCl})_2$	Weight (g) Na_2CO_3	No. mole of Na_2CO_3	Weight (g) of Acusol 445N	No.moles of Na-acrylate unit	Weight (g) of CaCO_3	No. mole of CaCO_3
1	2.86	0.02	0	0	0	0	0.0030	<0.0001
2	2.86	0.02	2.12	0.02	0	0	1.9542	0.0195
3	2.86	0.02	2.12	0.02	2.86	0.0135	1.9392	0.0194
4	2.86	0.02	2.12	0.02	5.72	0.0270	1.5424	0.0154
5	2.86	0.02	2.12	0.02	8.58	0.0400	1.1236	0.0112
6	2.86	0.02	2.12	0.02	11.44	0.0540	0.0036	<0.0001
7	2.86	0.02	2.12	0.02	14.30	0.0670	0.0027	<0.0001

**Figure 4.1** No. mole of Na-acrylate unit versus no. mole of CaCO_3

2.86 g of commercial calcium hypochlorite in solution gave the amount of insoluble matter of 0.0030 g which is not significant. When calcium hypochlorite was allowed to react with sodium carbonate, calcium carbonate was formed in 97.5 % yield and precipitated out of the solution.



Calcium carbonate (MW=100.09) formed in this reaction was found to be 0.02 mole. Various amounts of Acusol 445N were added to the starting solution of calcium hypochlorite before it was allowed to react with sodium carbonate. The number of the repeating unit of sodium acrylate (MW= 94.05) in each amount of Acusol 445N added was calculated. It was found that when Acusol 445N was added in the amount of 0.0135, 0.027, 0.040, 0.054 or 0.067 mole of sodium acrylate, calcium carbonate was formed in 0.194, 0.154, 0.112, 0, 0 mole respectively. One mole of calcium ion reacts stoichiometrically with 2 moles of acrylate moiety. Since calcium carbonate is supposed to form in 0.02 mole, it should require 0.04 mole of acrylate moiety to completely quench the formation of calcium carbonate. However, the experimental results demonstrate that the amount of 0.054 mole of acrylate moiety is required to completely quench the formation of calcium carbonate. It is therefore interesting to note that not every acrylate moiety in polyacrylate forms counter ion with calcium ions. Thus 0.014 mole of acrylate moiety did not form counter ions with calcium ions. This may be due to the arrangement of the monomer unit in polyacrylate. Unfortunately the orientation of polyacrylate was not studied. Debasish Kuila reported that polyacrylic acid is a suitable chelant for calcium ions and the higher chelation values are related to the degree of tacticity and the head-to-tail connection of each monomer unit.²⁰

When calcium hypochlorite was allowed to react with sodium carbonate to produce calcium carbonate which precipitated out of the solution. Acusol 445N was subsequently added to the resulting solution. It was found that the amount of calcium carbonate was reduced however still present in the solution. These results demonstrate that polyacrylate has to be present in the starting calcium hypochlorite before calcium ions can react with carbonate in order to prevent the precipitation of calcium carbonate.

Once calcium carbonate is formed the ability of polyacrylate to trap calcium ions will decrease since the solubility of calcium carbonate is low.

4.2 Determination of weight ratios of mixed solution.

Tables 4.2 , 4.3 and 4.4 shows the comparison of the percent of the insoluble matter at various mixing ratios between calcium oxide or calcium hypochlorite with each polyacrylate polymer.

Table 4.2 Determination of weight ratio of mixed solution;Acusol 445N

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Appearance of mixed polymer with calcium oxide	--	--	--	--	-	+	+
Appearance of mixed polymer with calcium hypochlorite	--	--	--	--	-	+	+
% insoluble matter of mixed polymer with calcium oxide	0.82	0.61	0.47	0.25	0.15	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.73	0.52	0.36	0.12	0.06	<0.01	<0.01

Remark : -- = The solution was hazy.

- = The solution was slightly hazy.

+ = The solution was clear.

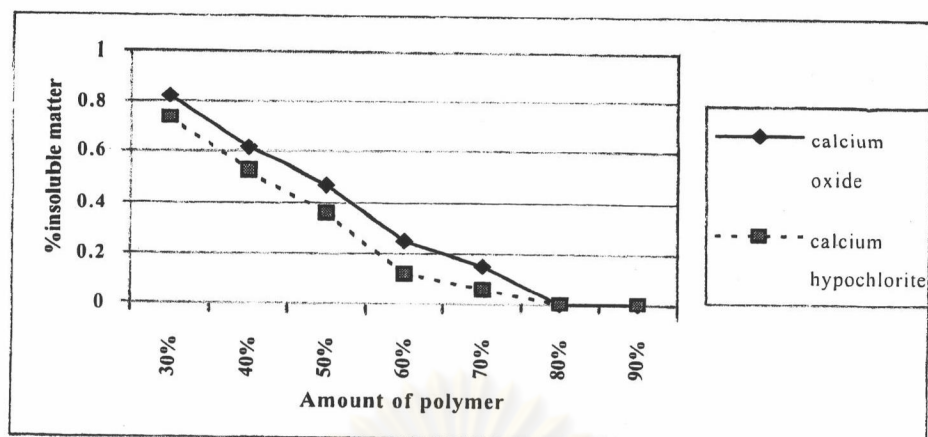


Figure 4.2 %Insoluble matter versus amount of polymer for mixed Acusol 445N with calcium oxide or calcium hypochlorite.

Acusol 445N, was mixed with calcium oxide or calcium hypochlorite at various ratios by weight of polymer, 30%, 40%, 50%, 60%, 70%, 80%, 90%. The mixed sample was dissolved with 50ml distilled water and transferred to a 500 ml volumetric flask and then the distilled water was added to the mark. The percent of insoluble matter for each concentration was determined. It is interesting to note that the percent of insoluble matter decreased while the concentration of polymer increased. The same results were obtained when the polymer was mixed with either calcium oxide or calcium hypochlorite. The percent of insoluble mixed polymer was ranged from 0.82-0.15 or 0.73-0.06 when the homopolymer was mixed with calcium oxide or calcium hypochlorite, respectively. At the concentration of polymer of 80%, there was no observation of insoluble matter in both cases.

Table 4.3 Determination of weight ratio of mixed solution;Acusol 479N,

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Appearance of mixed polymer with calcium oxide	--	--	--	--	-	+	+
Appearance of mixed polymer with calcium hypochlorite	--	--	--	--	-	+	+
% insoluble matter of mixed polymer with calcium oxide	0.99	0.99	0.99	0.63	0.33	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.82	0.69	0.43	0.19	0.06	<0.01	<0.01

Remark : -- = The solution was hazy.

- = The solution was slightly hazy.

+ = The solution was clear.

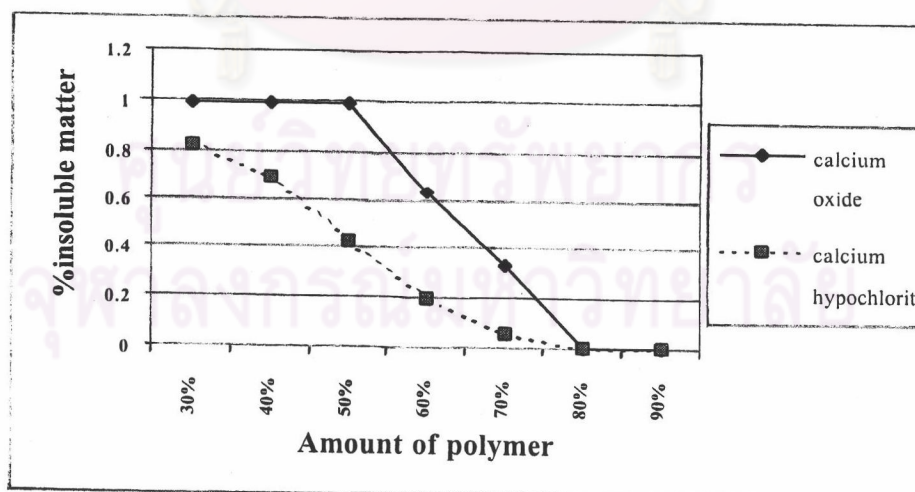


Figure 4.3 %Insoluble matter versus amount of polymer for mixed Acusol 479N with calcium oxide or calcium hypochlorite.

The similar results were also obtained when the reaction was carried out using a copolymer, Acusol 479N. Thus the percent of insoluble mixed polymer decreased while the concentration of copolymer increased. When the concentration of polymer was 80% or more, the insoluble matter cannot be reported.

Table 4.4 Determination of weight ratio of mixed solution; Acumer 3100

Polymer	30%	40%	50%	60%	70%	80%	90%
Amount of polymer (g.)	0.86	1.33	2.00	3.00	4.66	8.00	18.00
Amount of calcium oxide (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Amount of calcium hypochlorite (g)	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Appearance of mixed polymer with calcium oxide	--	--	-	+	+	+	+
Appearance of mixed polymer with calcium hypochlorite	--	--	-	+	+	+	+
% insoluble matter of mixed polymer with calcium oxide	0.53	0.36	0.25	<0.01	<0.01	<0.01	<0.01
% insoluble matter of mixed polymer with calcium hypochlorite	0.32	0.19	0.08	<0.01	<0.01	<0.01	<0.01

Remark : -- = The solution was hazy.

- = The solution was slightly hazy.

+ = The solution was clear.

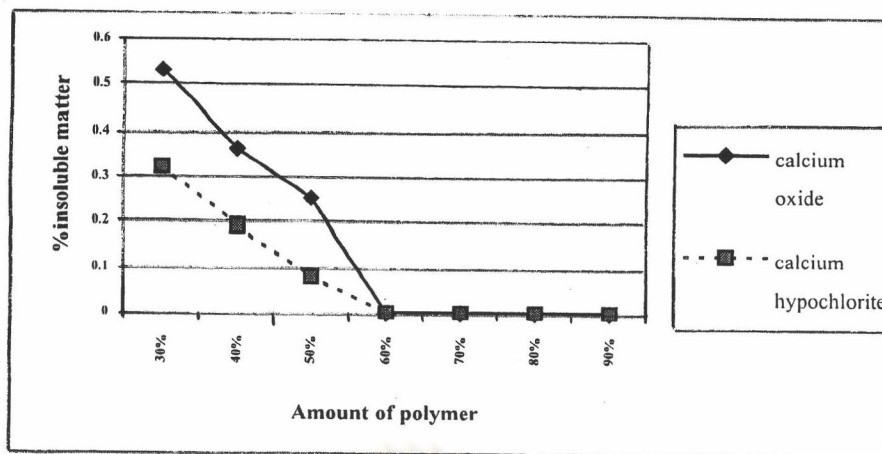


Figure 4.4 %Insoluble matter versus amount of polymer for mixed Acumer 3100 with calcium oxide or calcium hypochlorite.

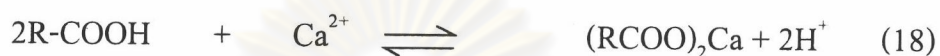
In the case of terpolymer, Acumer3100, the similar results were also observed. Thus the amount of insoluble mixed polymer decreased when the concentration of the terpolymer in the mixture increased. However, the percent of insoluble matter is significantly less than in the case of polyacrylic acid homopolymer and copolymer. Thus at 30% of Acumer3100, the percent of insoluble matter was 0.53 or 0.32 when the polymer was mixed with calcium oxide or calcium hypochlorite, respectively. There was no observation of insoluble matter when the terpolymer concentration was higher than 60 percent.

The ratios at which the mixtures of each polymer and calcium oxide or calcium hypochlorite gave no precipitation were further used in the studying of various effect on the chelations. Thus the percent by weight of Acusol445N, Acusol479N, or Acumer3100 in the mixed solution is 80, 80, or 60 respectively. Ho-Shing Wu studied the reaction of polyacrylic acid (PAA) and CaO.¹⁵ They reported that the mole ratio of CaO to acrylic acid unit in the polymer is 1:2 and the chelation is formed through the partial cross-linking.

The reaction of polyacrylic acid with calcium (II) ion can occur as the following equations 17 and 18. Calcium ions can form strong bonds with the carboxylate groups in the polymer and therefore will not be available to precipitate with carbonate anions in the solution.



or



Harry P. Gregor, Lionel B. Luttinger and Ernst M. Loebel¹⁸ studied the metal-polyelectrolyte complexes [the poly(acrylic acid)-copper complex]. They explain that the reaction of poly(acrylic acid) with metal ion can occur in the form of free carboxylate ion or carboxylic acid as shown in equations 19 and 20.



or



4.3 Characterization of the chelation by FTIR.

Polyacrylic acid and acrylic acid copolymers are soluble in any solvents. Infrared (IR) spectroscopy is a useful tool to confirm the chelation and the formation of the polyacrylic acid – metal oxide composites.

The polymer solution was transferred to a barium fluoride liquid cell with diameter 32 mm. and thickness 3 mm. (Perkin-Elmer 1760X). The IR spectra of the polymer solutions were recorded and the according solvent was used as a background. Figure 4.1 shows the IR spectra of the homopolymer Acusol445N, the resulting mixture

of Acusol445N with CaO and the resulting mixture of Acusol445N with $\text{Ca}(\text{OCl})_2$. The spectra display band at $3200\text{-}3500\text{ cm}^{-1}$ due to OH stretching, 2990 cm^{-1} (aliphatic C-H stretching), 1720 cm^{-1} (characteristic stretching, COOH group), 1560 cm^{-1} (asymmetry COO^- stretching), 1450 and 1400 cm^{-1} (scissors and bending vibration of CH_2 and CHCO).

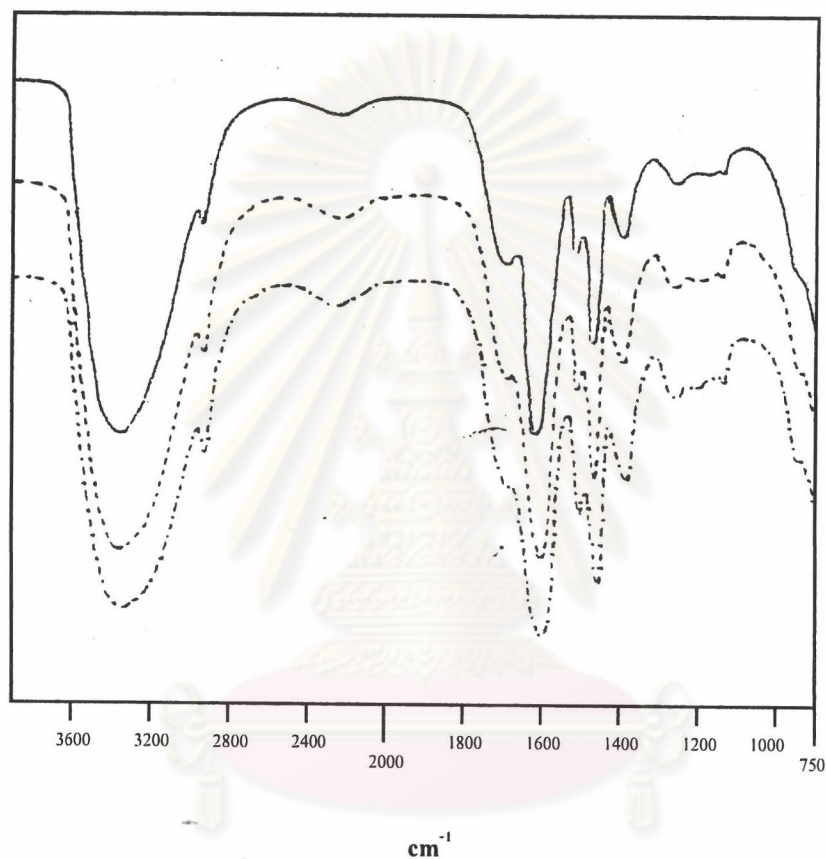


Figure 4.5 IR Spectra of homopolymer, Acusol445N;

- polyacrylate, sodium salt
- polyacrylate with CaO
- o-o-o-o-o polyacrylate with $\text{Ca}(\text{OCl})_2$

Ho-Shing Wu¹⁵ reported that the chelation between polyacrylic acid with metal oxide was confirmed by IR spectroscopy by showing that the absorption band at 1717 cm^{-1} due to the carbonyl absorption in carboxylic acid functionality in polyacrylic acid

disappeared while a new absorption band at 1560 cm^{-1} due to the carboxylate absorption appeared. Unfortunately, Acusol445N used in this study is in the form of sodium salt of polyacrylic acid. The IR spectrum of Acusol445N exhibits a weak absorption at 1720 cm^{-1} due to the carbonyl absorption of COOH and a strong absorption at 1560 cm^{-1} due to the carbonyl absorption of COO^- . It is therefore demonstrated that Acusol445N is in equilibrium in aqueous solution between its acid form and its carboxylate form as shown below.



Figure 4.5 demonstrates that the intensity of the absorption band at 1720 cm^{-1} in the reacted Acusol445N with CaO or $\text{Ca}(\text{OCl})_2$ decreases. Even though the change in absorption is very small it is possible to say that calcium ions can form chelation with the carboxylate in Acusol445N.

The pH of the resulting solution of Acusol445N and CaO is 11. This is due to the formation of $\text{Ca}(\text{OH})_2$ after CaO is dissolved in water. The reaction of $\text{Ca}(\text{OH})_2$ with Acusol445N generates 2 moles of NaOH.

For reaction of calcium oxide and the polymer as equation;



On the other hand, in the case of calcium hypochlorite, the pH of the mixture is 7. The hydrolysis of $\text{Ca}(\text{OCl})_2$ produces HOCl and $\text{Ca}(\text{OH})_2$. $\text{Ca}(\text{OH})_2$ subsequently reacts with sodium acrylate polymer and results in the formation of calcium acrylate chelate and one mole of NaOH . NaOH is then neutralized with hypochlorous acid generated from the hydrolysis of $\text{Ca}(\text{OCl})_2$.

For reaction of calcium hypochlorite and the polymer as equation;

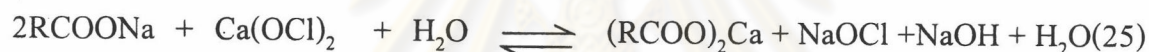


Figure 4.6 shows the Fourier transform infrared spectra of the copolymer Acusol 479N, the copolymer with calcium oxide and the copolymer with calcium hypochlorite. The spectra display bands at $3200\text{-}3500\text{ cm}^{-1}$ due to OH stretching, 2990 cm^{-1} (aliphatic C-H stretching), 1720 cm^{-1} (characteristic stretching, COOH group), 1560 cm^{-1} (asymmetric COO^- stretching), 1450 and 1400 cm^{-1} (scissors and bending vibration of CH_2 and CHCO), 1170 cm^{-1} (CO stretching of neighboring carboxyl group).

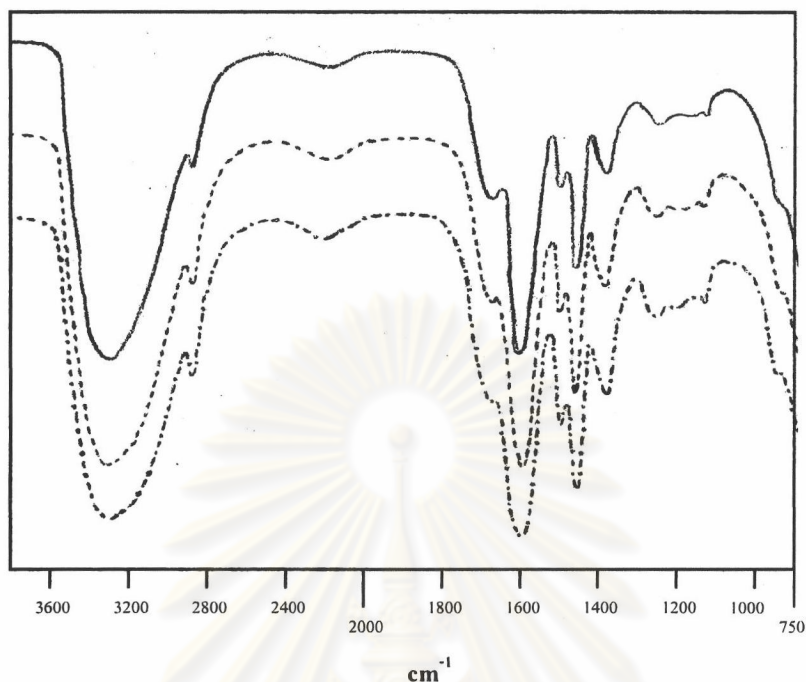


Figure 4.6 IR Spectra of copolymer, Acusol479N;

- polyacrylate, sodium salt
- polyacrylate with CaO
- o-o-o- polyacrylate with Ca(OCl)₂

Analogous results were obtained in this reaction. IR spectra exhibit strong absorption bands at 1560 cm^{-1} (COO^- group) and weak absorption bands at 1720 cm^{-1} . The intensity of the carbonyl absorption of the carboxylic acid at 1720 cm^{-1} of polyacrylate decreases due to the chelation with Ca(II) ion.

Analogously, the pH of the solution of Acusol479N and CaO was 11 while the pH of the calcium hypochlorite mixture was 7. It is due to the hydrolysis of each calcium salt. Hydrolysis of CaO produces Ca(OH)_2 and Ca(OH)_2 react with Acusol479N generates 2 moles of NaOH. While Ca(OH)_2 and HOCl are generated

upon hydrolysis of $\text{Ca}(\text{OCl})_2$. $\text{Ca}(\text{OH})_2$ subsequently reacts with Acusol479N and results in the formation of calcium acrylate chelate and one mole of NaOH . NaOH is then neutralized with hypochlorous acid.

Figure 4.7 shows the Fourier transform infrared spectrum of the terpolymer Acumer 3100 with calcium oxide and the terpolymer with calcium hypochlorite. The spectra exhibit bands at 3500 cm^{-1} (OH stretching), 2966 cm^{-1} (CH aromatic), 1720 cm^{-1} (characteristic stretching, COOH group), 1652 cm^{-1} (characteristic stretching COO^-), 1546 and 1453 cm^{-1} (C=C stretching, aromatic), 1222 , 1183 (S=O).

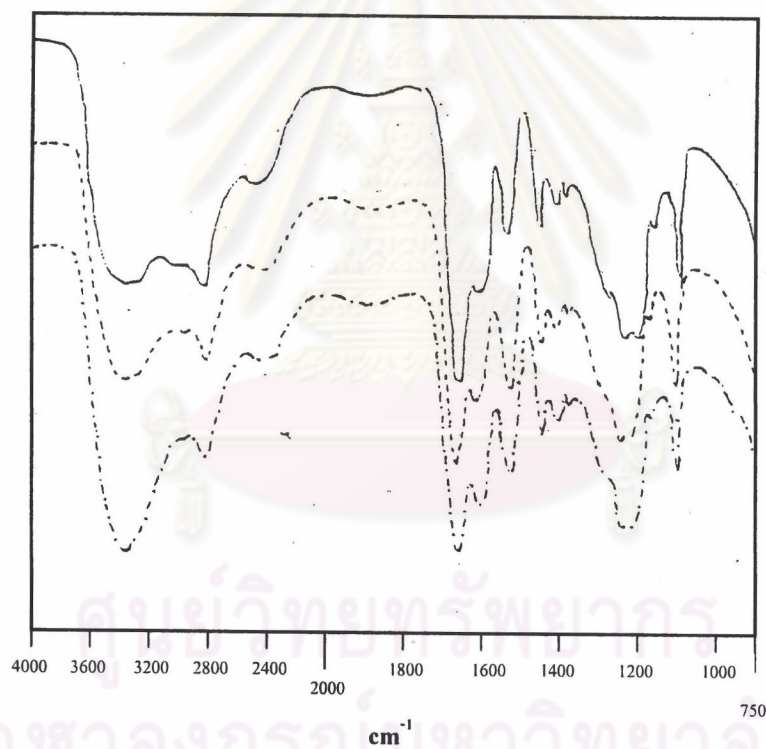


Figure 4.7 IR Spectra of terpolymer, Acumer3100;

- polyacrylate, sodium salt
- polyacrylate with CaO
- - - - - polyacrylate with $\text{Ca}(\text{OCl})_2$

IR spectra of the terpolymer Acumer 3100 are quite different from the homo- and copolymer of polyacrylate. The structure of Acumer3100 contains acrylic acid, sulfonate and nonionic moieties. The pH of the Acumer3100 solution is 2.5 which is quite acidic. It is interesting to note that the intensity of the absorption band at 1720 cm^{-1} is much stronger than the absorption band at 1650 cm^{-1} . This suggests that the acid-base equilibrium in Acumer3100 lies towards the carboxylic acid functionality.



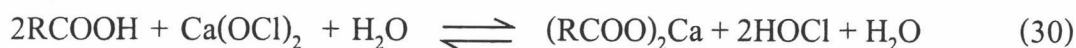
When Acumer3100 was allowed to react with CaO or $\text{Ca}(\text{OCl})_2$ the IR spectra demonstrate that the intensity of the absorption band at 1650 cm^{-1} increases. It is due to the chelation between the carboxylic acid moieties with calcium ions.

Since pH of the starting Acumer3100 is quite acidic, the pH of the resulting solution of Acumer3100 and CaO or $\text{Ca}(\text{OCl})_2$ is 7 or 4, respectively. This is due to the hydrolysis of each calcium salt. Hydrolysis of CaO produces $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ react with Acumer3100 and results in the formation of calcium acrylate chelate. While $\text{Ca}(\text{OH})_2$ and HOCl are generated upon hydrolysis of $\text{Ca}(\text{OCl})_2$, $\text{Ca}(\text{OH})_2$ subsequently reacts with Acumer3100 and results in the formation of calcium acrylate chelate and two moles of HOCl .

For reaction of calcium oxide and the polymer as equation;



For reaction of calcium hypochlorite and the polymer as equation;



Ho-Shing Wu¹⁵ and team studied the polyacrylic acid-metal oxide composites by infrared spectroscopy. They used aqueous polyacrylic acid (25% by weight of solid PAA, average molecular weight of 90,000) and metal oxide powder. They reported that IR spectrum of unreacted polyacrylic acid display bands at 2990cm^{-1} (CH_2), 1717cm^{-1} (stretching, COO^-), 1235 and 1170cm^{-1} (OH bending and CO stretching of neighboring carboxyl group). The spectra of the treated metal oxides exhibited bands at 1560cm^{-1} (asymmetric COO^- stretching), 1415cm^{-1} (symmetric COO^- stretching), 1455cm^{-1} (CH_2 deformation). The characteristic stretching band of the carboxyl group shifted from 1717 to 1560cm^{-1} due to the chelation of carboxylic acid with metal oxide. Furthermore, the doublet at 1235 and 1170cm^{-1} in the unreacted polyacrylic acid disappeared. A new peak at 1300cm^{-1} appeared. This occurrence indicates that polyacrylate ions were present in the PAA-metal oxide material. (shown in Figure 4.8).

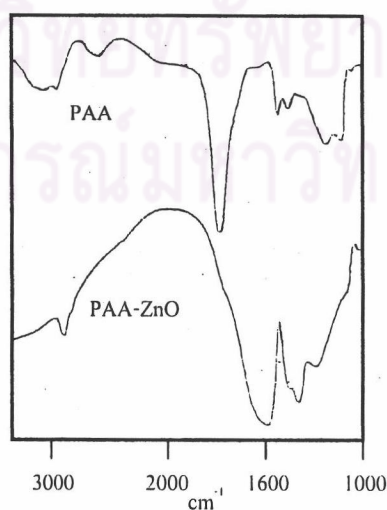


Figure 4.8 FT IR spectrum of pure polyacrylic acid and PAA-ZnO.¹⁵

4.4 The effect of solvent on reactivity of the reaction.

Ho-Shing Wu¹⁵ and team reported that lipophilic solvents including toluene, chlorobenzene, hexane, benzene, and dichloromethane, were introduced to the reaction system. Even though the resulting solution became a two-phase system. The conversion of carboxylate group was the same as that of the homogeneous system. The IR spectra of the resulting mixture demonstrate the same pattern. Thus, the absorption band at 1720 cm^{-1} shifted to 1560 cm^{-1} due to the chelation of polyacrylic acid with metal oxide. The same results were also obtained in this research, regardless of the solvent system. We also determined the effect of the lipophilic solvent; benzene, toluene, xylene, on the chelation of calcium ions with each polymer and similar results were obtained. It was reported that polyacrylate can disperse in high polar solvent such as water, methanol because each polymer coil can be stabilized through electrostatic repulsion among the charge of the hydrophilic groups.¹² When we use lipophilic solvents, the interaction between the nonpolar solvent and acrylate polymer is not available. Thus the electrostatic on the polymer chain can not be stabilized by the lipophilic solvent, it is therefore precipitate out of the solution. We indeed observed that polyacrylates lose its dispersing ability in lipophilic solvent.

For hydrophilic solvent, Ho-Shing Wu¹⁵ found that the order of conversion of the carboxylate group for CaO is $\text{H}_2\text{O} = \text{CH}_3\text{OH} > \text{no extra solvent}$ as shown in Figure 4.9.

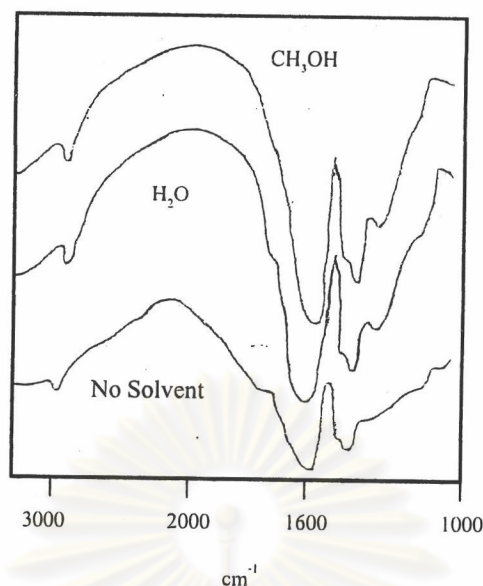


Figure 4.9 IR spectrum of PAA-ZnO for solvent effect : 30 degree celcius , 400 rpm, 30 min; PAA 1 ml, ZnO 0.28 g, solvent 10 ml.¹⁵

Effects of hydrophilic solvents on the amount of insoluble matter were determined when each polymer, Acusol445N, Acusol479N, or Acumer3100 was allowed to react with either calcium oxide or calcium hypochlorite. Table 4.5 shows the experimental results. Since lipophilic solvents are immiscible with water and it is not practical to use these solvents in many applications. Therefore water and methanol are chosen for this investigation. The weight ratios of each polymer to calcium oxide or calcium hypochlorite was chosen from section 4.2 to give no precipitation. Thus Acusol445N or Acusol479N was mixed with either calcium oxide or calcium hypochlorite with the weight ratio of 4. While the ratio of Acumer3100 to calcium oxide or calcium hypochlorite was 1.5. The results demonstrate that water is the best solvent system and there is no precipitation observed. On the other hand, the polymer cannot completely quench the precipitation in methanol solvent.

Table 4.5 Effects of solvents on the amount of insoluble matter.

Polymer	Metal oxide or Hypochlorite	Solvent	Insoluble matter(%)
Acusol 445 N	Calcium hypochlorite	H ₂ O	0
Acusol 445 N	Calcium oxide	H ₂ O	0
Acusol 445 N	Calcium hypochlorite	CH ₃ OH	0.13
Acusol 445 N	Calcium oxide	CH ₃ CH	0.23
Acusol 479 N	Calcium hypochlorite	H ₂ O	0
Acusol 479 N	Calcium oxide	H ₂ O	0
Acusol 479 N	Calcium hypochlorite	CH ₃ OH	0.32
Acusol 479 N	Calcium oxide	CH ₃ OH	0.53
Acumer 3100	Calcium hypochlorite	H ₂ O	0
Acumer 3100	Calcium oxide	H ₂ O	0
Acumer 3100	Calcium hypochlorite	CH ₃ OH	0.10
Acumer 3100	Calcium oxide	CH ₃ OH	0.11

The chelation of polyacrylate to calcium (II) ion in methanol solvent was slow and incomplete. Since methanol solvent has bulky group(CH₃ group) and it can resist the dissociation of sodium ions from carboxylate group. Consequently, The carboxylate anions are less available to bind to calcium (II) ion under this condition. Debasish Kuila²⁰ and team explained that the counterions (Na⁺ ions) screen the charge of the ionized carboxylate and lead to the recoil of the polyelectrolyte chain which not only hinders available free carboxylate but also prevents the diffusion of the doubly charge calcium into the coiled chain to reach the carboxylates.

Water is the good solvent for the chelation. The water in the polymer solution consists of “bulk” water and “hydration” water which surround polymer molecules. It is also acting as the “interstitial” water in compartmentalized spaces surrounded by the

polymer network. Moreover Na^+ ions tend to form NaOH by the hydration water and allowed polyacrylate anions to chelate with calcium(II) ions.

4.5 The effect of pH on reactivity of the reaction .

Effects of pH on the reactivity of reaction were also investigated. The results are shown in Table4.6

Table 4.6 Effect of pH on the amount of insoluble matter.

Polymer	Metal oxide or Hypochlorite	Insoluble matter (%)			
		pH3	pH7	pH11	pH14
Acusol 445 N	Calcium hypochlorite	0.16	0	0.62	0.81
Acusol 445 N	Calcium Oxide	0.37	0.07	0	0.70
Acusol 479 N	Calcium hypochlorite	0.18	0	0.70	0.91
Acusol 479 N	Calcium Oxide	0.56	0.28	0	1.01
Acumer 3100	Calcium hypochlorite	0	0.21	0.40	0.55
Acumer 3100	Calcium Oxide	0.14	0	0.53	0.68

The chelation of polyacrylate; Acusol 445N or Acusol 479N with calcium hypochlorite is complete at pH7, whereas Acusol 445N and Acusol 479N with calcium oxide was complete at pH11. In the case of Acumer3100 with calcium hypochlorite, the reaction is complete at pH3, whereas Acumer3100 with calcium oxide is complete at pH7. When the mixture was made acidic by HCl, percent insoluble matter were increased. It is due to the reaction of polyacrylate anion with H^+ (from acid) instead of calcium (II) ion. Interestingly, when the solution was made basic by NaOH, percent insoluble matter were also increased. Debasish Kuila²⁰ and team explain that the coil expansion of polymer ceases when a critical amount of counterions (Na^+ from the base)

screen the charges of the ionized carboxylate and further addition of the base leads to the recoil of the polyelectrolyte chain that not only hinders available free carboxylate but also prevents the diffusion of doubly charged calcium into the coiled chain to reach the carboxylates. When the reaction takes place in solution, calcium may be bound to both a carboxylate anion and a hydroxide ion. As concentration of hydroxide increase, it will compete with polymer chain to attach calcium (II) ions and produced Ca(OH)_2 which precipitate out of the solution.

4.6 The effect of temperature on reactivity of the reaction .

Effects of temperature on the reactivity of the chelation were also studied. Acusol445N, Acusol479N or Acumer3100 was allowed to react with CaO or Ca(OCl)_2 at 25, 50 and 90 °C. Table4.7 shows the amount of insoluble matter observed at each reaction temperature.

Table 4.7 Effect of temperature on the amount of insoluble matter.

Polymer	Metal oxide or Hypochlorite	insoluble matter (%)		
		25°C	50°C	90°C
Acusol 445 N	Calcium hypochlorite	0	0.06	0.12
Acusol 445 N	Calcium oxide	0	0.13	0.22
Acusol 479 N	Calcium hypochlorite	0	0.08	0.19
Acusol 479 N	Calcium oxide	0	0.23	0.43
Acumer 3100	Calcium hypochlorite	0	0.01	0.07
Acumer 3100	Calcium oxide	0	0.03	0.09

The chelations of polyacrylate; Acusol 445N, Acusol 479N and Acumer3100 with calcium hypochlorite or calcium oxide were complete at low temperature (25

degree celcius). Percent insoluble matter increased the temperature was increased to 50 and 90 °C. S.M. Rabie¹⁷ and team studied the reaction between MgO and an aqueous solution of polyacrylic acid at different temperatures, 0, 25, 50, 90 °C. The IR spectra of the samples show a strong absorption at the frequency of 1565 cm⁻¹ and medium absorption at 1400 cm⁻¹ which are due to asymmetric and symmetric stretching vibration of the COO⁻ structure, respectively. The spectrum of Mg-polycarboxylate prepared at 25°C shows a very weak shoulder at 1725 cm⁻¹, whose intensity slightly increases with raising the temperature to 50 and 90°C and decreases with lowering the temperature to 0°C (Figure 4.10 This result gives strong evidence that the rate of reaction depends on the temperature of reaction, it is enhanced as the temperature is lowered.

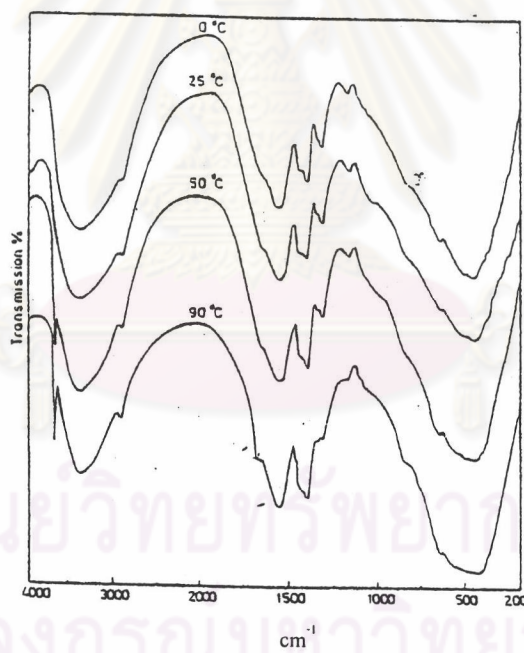


Figure 4.10 IR spectra of polyacrylate cement containing MgO at different temperatures.¹⁷

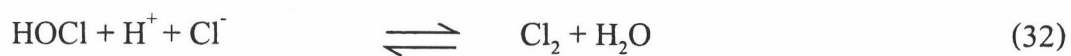
4.7 Determination of heat stability of the chelation of calcium hypochlorite with polyacrylate and acrylate copolymers

Table 4.8 Effect of heat stability of the chelation of calcium hypochlorite with polyacrylate and acrylate copolymers.

Mixture	Before heated (ppm.)	After heated(ppm.)	%Reduction
Calcium hypochlorite with acusol 445N	987	858	13.94
Calcium hypochlorite with acusol 479N	970	820	15.43
Calcium hypochlorite with acumer3100	841	439	47.78

The percents of available chlorine of the mixtures of Acusol445N, Acusol 479N and Acumer3100 with calcium hypochlorite before heating are in the range of 841 – 988 ppm which are about the same. When the mixtures were heated the percents of available chlorine are reduced in all cases. However, the percent of reduction is significant in the case of Acumer3100. Thus, the percents of reduction of Acusol445N and Acusol479N are 14 and 15, respectively while the percent of available chlorine in the chelation of Acumer3100 is reduced by 48 percent. These results demonstrate that the chelation of calcium hypochlorite with Acusol445N or Acusol479N can tolerate the heating to some degree. On the other hand, the mixture of calcium hypochlorite with Acumer3100 is thermally unstable.

The reaction between Acumer3100 with calcium hypochlorite is acid – base reaction. Hydrolysis of calcium hypochlorite produces hypochlorous acid and calcium hydroxide. In the presence of strong acid, hypochlorous acid can decompose to free chlorine. This reaction is activated by heat.



Acumer3100 contains high amount of acidic groups which will increase the decomposition of hypochlorous acid to free chlorine. As a result the amount of available chlorine in the case of Acumer3100 is reduced greatly after heating.



ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย