

# Effects of Surfactant Addition on Dewatering of Alum Sludges

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**Abstract:** In Taiwan, surfactants are frequently used in the flotation process to aid in solid/liquid separation. Their effect on the dewatering of alum sludge was investigated. Various amounts of cationic and anionic surfactants were added to sludge samples, and the dewatering characteristics of the sludge and the water content of sludge cakes were evaluated. Both surfactants improved the dewatering of the sludge by lowering the specific resistance to filtration, decreasing the bound water content, and increasing the dewatering rate of the sludge. Different combinations of anionic and cationic surfactants and polyelectrolytes were also experimented on to study the effect of surfactant addition on the dewatering characteristics of polyelectrolyte-conditioned sludge. Experimental results indicated that both cationic and anionic surfactants adversely affected the dewatering of the conditioned sludge. The addition of surfactant to the oppositely charged polyelectrolyte proved to be most detrimental to sludge dewatering due to the precipitation between surfactant and polyelectrolyte. The addition of cationic surfactant to the cationic polyelectrolyte-conditioned sludge had the least effect.

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## Introduction

Currently, approximately 170,000 tons of sludge are produced annually in the water treatment plants of Taiwan. This amount is expected to increase significantly due to the increasing demand for better quality water by the people of Taiwan. The majority of Taiwan water treatment utilities use alum as the coagulant for removing particulate impurities. After gravity concentration, the alum sludge still contains more than 85% water, which amounts to a tremendous volume of sludge. Therefore, finding a means to effectively reduce the water content of sludge in an economical way is vital in sludge disposal.

For years, polyelectrolyte conditioning has been the most popular practice for improving the dewatering property of sludge. Despite its efficiency in sludge conditioning, the cost for polyelectrolytes and the concern for their possible pollution of surface waters have detracted from their applicability. Many researchers have been searching for alternatives in reducing sludge water content.

Sludge dewatering characteristics are also greatly affected by the quality of the raw water. Our previous studies revealed that

the presence of algae in sludge significantly affects their dewatering properties (Pan et al. 1999). Several waterworks (WTP) in southern Taiwan utilize source waters containing algae. To remove the algae, the plants use dissolved air flotation (DAF) thickening to concentrate the WTP residual. Often, they add surfactants in the sludge thickener to facilitate solid/liquid separation. Surfactants are also organic pollutants commonly found in raw waters. Most of them are anthropogenic discharges of chemical detergents upstream of the source water. The inclusion of surfactants in the sludge may affect dewatering.

Somasundaran et al. (1994) discovered that an optimal amount of surfactant promoted the stretching of the polyelectrolyte molecule, while the curling of polyelectrolyte molecules was observed in the overdosing of surfactants. It is generally believed that polyelectrolytes condition sludge through charge neutralization and bridging. Since the degree of expansion of polyelectrolyte molecules is critical in the bridging effect, there is reason to believe that the addition of surfactants can change the dewatering characteristics of the conditioned sludge. In analyzing the interaction of surfactants and polyelectrolyte in solutions, Goddard also discovered that the adsorption of surfactants on the polyelectrolyte surface caused the structure of the polyelectrolyte to branch out (Goddard 1985). Also, surfactants adsorbed on the surface of the sludge particles in various ways depending upon their concentration. As a result, they affect the interaction between the polyelectrolyte and the sludge particle. Chitikela et al. (1997) indicated that more cationic polyelectrolyte was needed to achieve the same dewatering efficiency if the sludge system contained anionic surfactant.

The evidence mentioned above suggests the need to evaluate the effect of surfactants on sludge conditioning. In this study, the alum sludge was first treated with surfactants of different charges, followed by the conditioning with various amounts of cationic or anionic polyelectrolytes. The dewatering characteristics, dewatering rate, and the mechanism of the interaction between surfactants and polyelectrolytes were investigated.

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**Table 1.** Characteristics of Typical Alum Sludge Samples Collected from Feng-Yuan and Hsin-Chu Waterworks

Sample number	Hydrogen ion concentration	Total organic carbon ( $\mu\text{g}$ of C/g)	Volatile Solids (mg/L)	Total solids (mg/L)	ZP (mV)
1 <sup>a</sup>	7.04	56.1	375.1	41,253	-19.5
2 <sup>b</sup>	6.77	62.4	119.8	39,412	-20.6
3 <sup>b</sup>	6.89	77.9	144.7	38,164	-27.3

<sup>a</sup>Collected from the Feng-Yuan Waterworks.

<sup>b</sup>Collected from the Hsin-Chu Waterworks.

## Methods and Materials

### Sludge Sample, Surfactant, and Polyelectrolyte

Alum sludge samples were collected from the thickening tanks of the Feng-Yuan Waterworks in Taichung, which is severely contaminated by algae, and the Hsin-Chu Waterworks in Hsin-Chu, Taiwan. The solids content and other basic properties of sludge samples are listed in Table 1.

Both cationic and anionic surfactants were explored in this study. The cationic surfactant was cetyltrimethyl-ammonium bromide (CTAB) of molecular weight (M.W.) 364.45 g/mol. Its critical micelle concentration (CMC) is  $9.2 \times 10^{-4}$  M in D.I. water at 25°C. The anionic surfactant was dodecylsulphate sodium salt (SDS) with an average M.W. of 288.38 g/mol and a CMC of  $8.2 \times 10^{-3}$  M in D.I. water at 25°C.

Polyelectrolytes chosen in this study were PC-325 and PA-220, purchased from the Taiwan Polymer Company. The charge densities of the cationic polyelectrolyte (PC-325) and the anionic polyelectrolyte (PA-220) are 25 and 20%, respectively. They are copolymers of acrylamide and acrylic acid, with a similar average M.W. of  $1.1 \times 10^7$  to  $1.2 \times 10^7$  g/mol. Polyelectrolyte solution (0.1% by weight) was freshly prepared as recommended by the manufacturer before each trial.

### Sludge Conditioning

One liter of sludge sample was poured into the mixing chamber, followed by the surfactant addition, and was immediately mixed at a paddle rotation speed of 100 revolutions per minute by a Hsiangtai DE-CD-4T. The mixing times were fixed at 60 min to ensure the complete reaction between the surfactant and the colloidal particles. Samples were then withdrawn for the measurements of zeta potential (ZP), capillary suction time (CST), specific resistance to filtration (SRF), water contents of sludge cakes, and bound water content, which will be explained in detail below. After the mixing of the surfactant and the sludge, the polyelectrolyte was added and mixed for another 60 s. The reaction times of 60 min and 60 s were determined from the results of preliminary experiments. All experiments were conducted at 25°C.

### Zeta Potential Measurement

The surface potential of sludge particles was measured with a Zeta-Meter System 3.0, a product of the America Zeta-Meter Inc.

### Dewaterability Measurement

Sludge dewaterability was evaluated with CST, SRF, dewatering rate, and dry solid contents of pressed sludge cakes. CST was measured with a Triton CST apparatus Model 200 fitted with a 1.8-cm-diameter cylinder and Whatman No. 17 filter paper. A standard Buchner funnel test apparatus with a 9-cm Buchner fun-

nel and Whatman No. 42 filter paper was used for the SRF determination. The sludge samples were filtered under a pressure of 100 kPa using a sample volume of 100 mL. Filtrates were collected and the volume was recorded as a function of time. The sludge cake remaining from the filtration was dried at 105°C for 24 h and its dry weight was used to calculate the water content of the sludge cake as well as the dry solid base for bound water content. A laboratory scale mechanical press filter with pressure of 557 kPa and Whatman No. 1 filter paper was used to simulate the press filter used in conventional water treatment plants. The dry solid content of the filtered cake was also determined following the same procedure as that for SRF cakes. The detailed experimental procedure for the measurements can be found in the study of Wu et al. (1997).

### Bound Water Content Measurement

In the study of the relationship between the water distribution and the dewatering efficiency of the sludge, Vesilind and Hsu (1997) suggested that bound water content can be used as the limit of mechanical dewatering for sludge. Therefore, the bound water content is used as another index for sludge dewaterability. The bound water content was analyzed with a dilatometer. The detailed procedure for bound water measurement can be found in the work by Wu et al. (1997), in which a dilatometer and an expression test were employed. Fifteen grams of sludge sample were introduced into a dilatometer, and the remainder of the volume was filled with an indicator fluid. Mineral oil (Shell Donax TG) was used as the indicator fluid described by Robinson and Knocke (1992). Dry ice in an ethanol bath was used to lower the sample temperature from 20 to -20°C. The initial and final liquid levels on the dilatometer during the cooling period were recorded and the frozen water content was determined by using

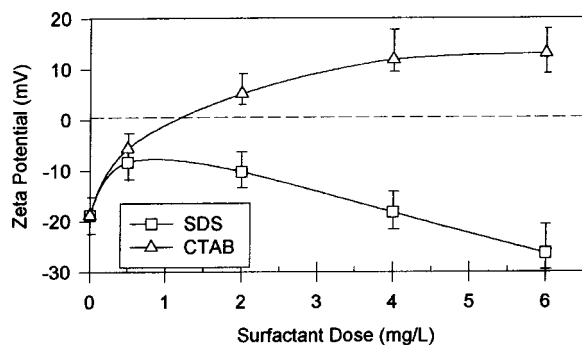
$$\text{frozen water content} = (\Delta L + W \times A) / B \quad (1)$$

where  $\Delta L$  = difference in liquid level from 20 to -20°C;  $W$  = weight of oil used;  $A$  = concentration coefficient of the oil for each dilatometer; and  $B$  = expansion coefficient of sludge filtrate. The total water and the dry solid contents of the sludge were determined by drying at 105°C for 24 h. The amount of bound water was calculated by subtracting the frozen water content from the total water content.

## Results and Discussion

### Effect of Surfactants on Sludge Dewatering

Various amounts of cationic and anionic surfactants, namely, CTAB and SDS, were added to sludge samples, and their effects on the dewatering characteristics of the sludge as well as the water contents of sludge cakes were evaluated.



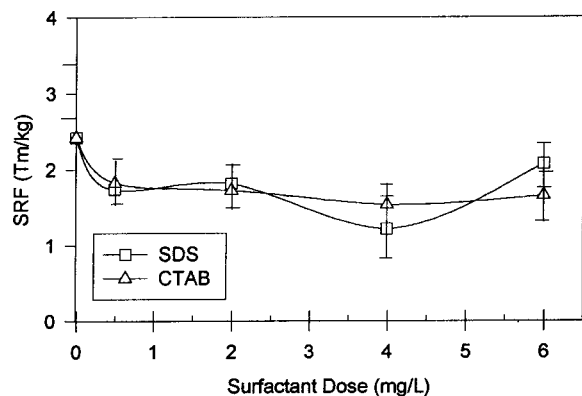
**Fig. 1.** Effect of surfactants dosing (0–6 mg/L) on zeta potential of alum sludge

### Effect of Surfactants on Zeta Potential

The effect of surfactant addition on *zeta potential* of the sludge was quite significant. Fig. 1 shows the zeta potential of the sludge at various amounts of surfactants. The zeta potential of the original sludge was  $-18.5$  mV. The addition of cationic surfactant (CTAB) raised the zeta potential, an indication that the surfactant was specifically adsorbed on the sludge floc. With the addition of the anionic surfactant, the zeta potential first increased and then gradually decreased. The initial increase in the surface charge may be due to the immediate replacement of more numbers of charged ions  $[\text{Al}(\text{OH})_4^-]$  from the floc surface by the less densely charged species (surfactant ion) of greater polarity. After mixing for 60 min, sludge suspensions in both experiments turned yellowish brown. The coloring of the sludge suspension is evidence of the displacement of the coloring material by the surfactant.

### Effect on Specific Resistance to Filtration

Since the belt press is the most popular means for sludge dewatering in Taiwan, and its mechanism of filtration is very similar to that of the SRF measurement, SRF results were chosen for comparisons of sludge dewaterability. Results shown in Fig. 2 suggest that both the cationic and the anionic surfactants benefit dewatering. The addition of a small amount of surfactant, 0.5 mg/L, immediately dropped the SRF of the sludge by approximately 30%, although no further improvement in SRF was observed at a higher dosage of surfactants. Similar results have been reported by Christensen and Dick (1985) who concluded that a filtration me-



**Fig. 2.** Effect of surfactant dosing (0–6 mg/L) on specific resistance to filtration of alum sludge

**Table 2.** Effect of Surfactant Dosing (0–6 mg/L) on  $T_{85\%}$  of Sludge

Dosage (mg/L)	$T_{85\%}$ (s) <sup>a</sup>	
	SDS	CTAB
0	292	292
0.5	228	264
2	180	113
4	69	42
6	168	42

<sup>a</sup> $T_{85\%}$ : time (s) to collect 85% of the expressible water from the conditioned sludge.

dium of low specific resistance ( $\alpha$ ) would result in small SRFs. Later, Wu et al. (1997) also suggested that since the filtration rate of a uniform filtration medium was much slower during the beginning of the filtration, lower resistance was measured, which resulted in smaller SRF.

### Effect on Dewatering Rate

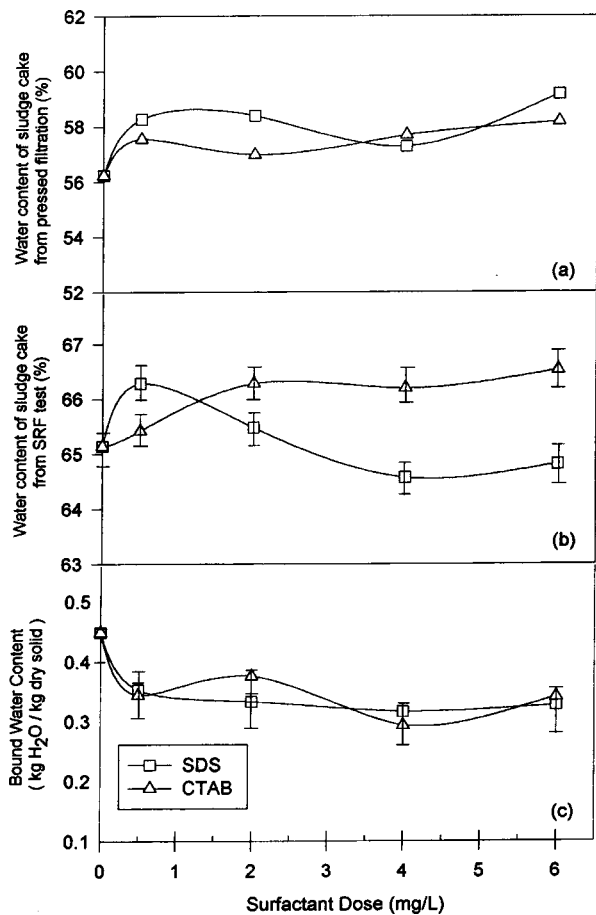
The dewatering rate is another criterion in designing a sludge dewatering device. To determine the dewatering rate, the amount of water collected from the press filtration was monitored. For comparison,  $T_{85\%}$  in seconds was defined as the time to obtain 85% of the maximum expressible water from the conditioned sludge.

The results are summarized in Table 2. It is obvious that the addition of both surfactants improves the dewatering rate and the rate of increase is proportional to the amount of surfactants added for up to 4 mg/L. This can be explained by the change in the structural strength of the sludge flocs. Under the pressure applied on the press filtration, the flocs are pressed and deformed, which causes the cake void to close and subsequently restrain the water filtration. Surfactants help to maintain the structural frame of the aggregated flocs which sustains the strength and the permeability of the flocs.

### Effect on Water Content of Sludge Cakes

To further understand the influence of surfactants on mechanical dewatering, the water content of sludge cakes remaining after the vertical press filtration and after the SRF test, as well as the bound water content, were analyzed. The results, as shown in Fig. 3, indicate that more water was retained in sludge cakes as the result of surfactant addition. This result also echoes the study by Wu et al. (1997) who pointed out that faster filtration does not guarantee drier cakes.

Vesilind and Hsu (1997) suggested that the limit of sludge dewaterability can be represented by the bound water content. Since neither the SRF test nor laboratory scale press filtration reflects the pressure applied for sludge dewatering in plant operations, bound water content may be an alternative for predicting the performance of mechanical dewatering. Bound water analysis, as depicted in Fig. 3(c), indicates that surfactants lower the bound water content. This may be explained by a theory proposed by Hunter (1986), suggesting that when the hydrophobic surface interacts with the hydrophobic end of the surfactant, the water originally adsorbed on the sludge surface is expelled, resulting in a lowered bound water content.



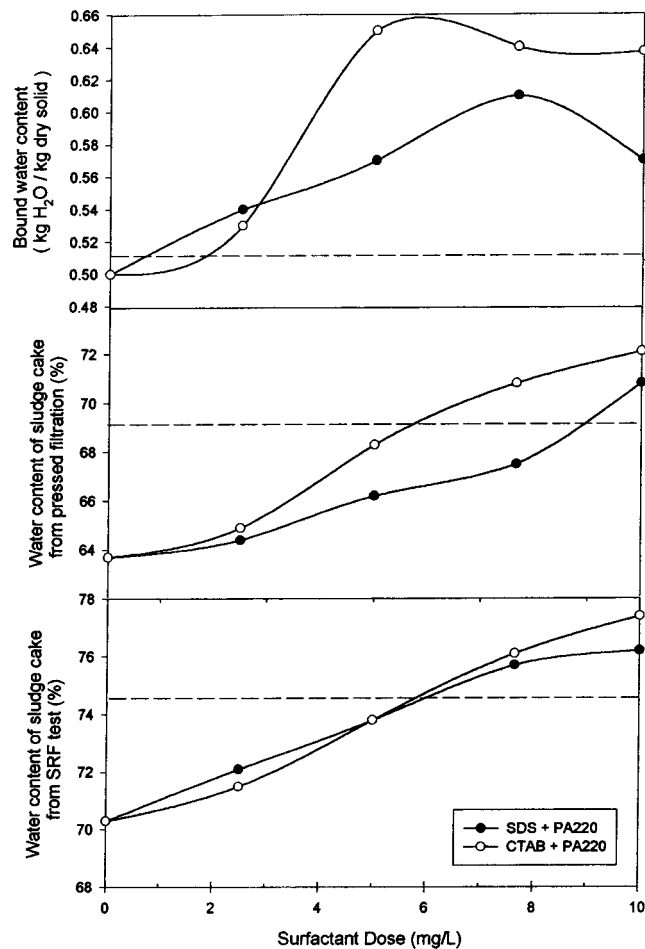
**Fig. 3.** Effect of surfactant dosing (0–6 mg/L) on water contents of sludge cakes and bound water content

### Effect of Surfactants on Sludge Conditioning by Anionic Polyelectrolyte

The alum sludge used in this study was collected from the Hsin-chu Waterworks. Surfactants in various amounts were added to the sludge samples before the addition of the anionic polyelectrolytes SDS to study their effect on conditioned sludge.

### Effects on Zeta Potential

Jar tests of CST determinations were first performed to estimate the optimum dosage of PA220. An optimum dosage of 12 mg/L was determined, which was used for both studies involving cationic and anionic polyelectrolytes. Fig. 4 shows the change in zeta potential of the anionic polyelectrolyte-conditioned sludge when surfactants were added. The conditioning by PA220 changed the sludge surface toward more negative potential, from  $-27.3$  to  $-35$  mV. The additions of cationic and anionic surfactants affect the zeta potential in a nearly linear fashion. At 10 mg/L of CTAB, the surface regained its zeta potential ( $-27.0$  mV), showing the neutralization of the two oppositely charged species. In the trial of CTAB+PA220, a grayish-white filament was observed around the mixing blade, as shown in Fig. 5, which suggests the coprecipitation of the anionic polyelectrolyte (PA220) and the cationic surfactant (CTAB). This phenomenon was more obvious when the mixing time for the surfactant was shortened from 60 to 30 min, indicating that 30 min is not enough

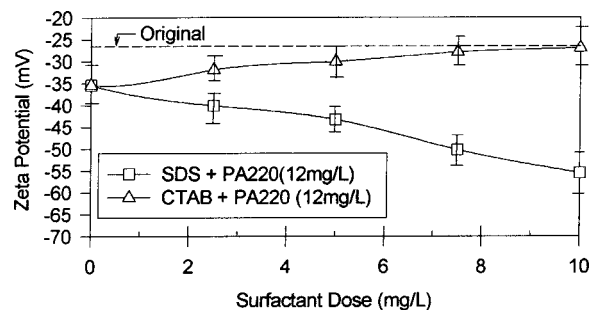


**Fig. 4.** Effect of surfactant dosing on zeta potential of PA220-conditioned alum sludge

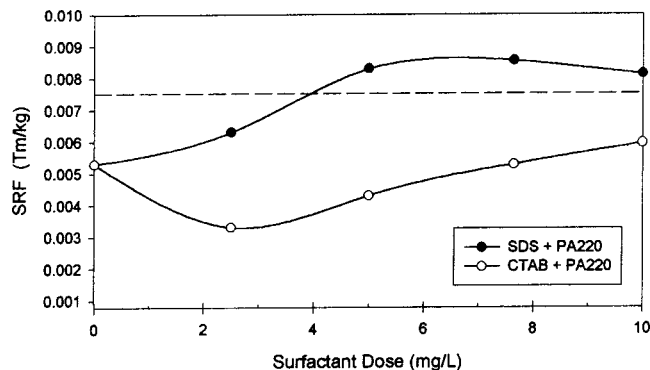
for the surfactant and the sludge particle to reach equilibrium. No filament was found in the combination of SDS and PA-220.

### Effect on Specific Resistance to Filtration

The effect of surfactants on the dewaterability of the anionic polyelectrolyte-conditioned sludge is presented in Fig. 6. The SRF of the unconditioned sludge is indicated by the dashed line. Without surfactants, 12 mg/L of PA220 improved the dewaterability, as shown by the decrease of SRF from 0.0076 to 0.0052 T m/kg. When the anionic surfactant SDS was added, the SRF



**Fig. 5.** Filamentous substances formed in CTAB+PA220-conditioned alum sludge



**Fig. 6.** Effect of surfactant dosing (0–6 mg/L) on specific resistance to filtration of PA220-conditioned alum sludge

increased with the dosage, similar to the variation in zeta potential (Fig. 4). A two-stage change was observed when the cationic surfactant CTAB was added. When a small amount of CTAB (2 mg/L) was added, the stronger attraction between the CTAB and PA220 facilitated the bridging effect of polyelectrolytes, which enhanced the formation of larger flocs and, consequently, a lower SRF. When more CTAB was added, PA220 was consumed by the excess amount of CTAB, as evidenced by the formation of filamentous substance. This coprecipitation of surfactant and polyelectrolyte caused the increase in SRF.

#### Effect on Dewatering Rate

To determine the dewatering rate, the amount of water collected from the expressed filtration was monitored with time. For the benefit of comparison, a  $T_{85\%}$  was defined as the time to collect 85% of the maximum expressible water from the conditioned sludge. The result is summarized in Table 3. The  $T_{85\%}$  of the original sludge was 251 s, and the addition of PA220 reduced it to 73 s. Although the dewatering rate of the system with either surfactant was still much faster than the unconditioned sludge, the best result could be obtained by use of PA220 alone.

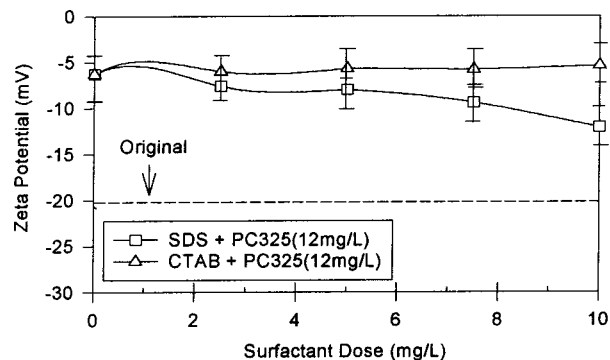
#### Effect on Water Contents of Sludge Cakes

The amount of water remaining in the sludge cakes obviously depends upon the choice of a mechanical dewatering device. The effect of surfactant dosing on water contents of sludge cakes by the SRF test and by laboratory scale press filtration were determined and compared with the bound water content, as shown in

**Table 3.** Effect of Surfactant Dosing (0–10 mg/L) on  $T_{85\%}$  of Sludge

Surfactant dosage (mg/L)	Polyelectrolyte		PC325 (12 mg/L)	
	PA220 (12 mg/L)			
	SDS	CTAB	SDS	CTAB
0	73	73	68	68
2.5	78	79	74	64
5	93	87	95	71
7	100	102	116	76
10	111	119	137	82
Original sludge	251		251	

Note:  $T_{85\%}$ : time (s) to collect 85% of the maximum expressible water from the conditioned sludge.



**Fig. 7.** Effect of surfactant dosing on water contents of PA220-conditioned sludge cakes and bound water content of PA220-conditioned sludge

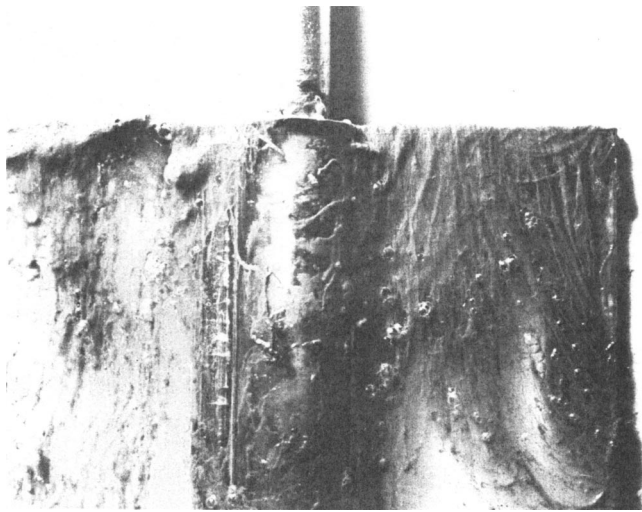
Fig. 7. Results of the three tests were fairly consistent. The changes in water contents of sludge cakes from the SRF test and press filtration as surfactants were added indicate that more water molecules were retained in the flocs. At around 6 mg/L, both surfactants completely offset the improvement in cake water contents by PA220.

The application of anionic polyelectrolyte, PA-220, had a very limited effect on the bound water content [Fig. 7(a)], in which the dashed lines represent the raw sludge. Both CTAB and SDS, however, increased the bound water content significantly. Somnandaran et al. (1994) proposed that the flocs of minimum bound water content formed at optimum dosage. The addition of surfactant shifts the optimum dosage, and therefore results in a higher bound water content. The exceedingly high bound water with CTAB + PA220 was probably due to experimental error caused by the water trapped between filaments of coprecipitation.

#### Effect of Surfactants on Sludge Conditioning by Cationic Polyelectrolyte

#### Effects on Zeta Potential

For the benefit of comparison, the amount of PC325 used in this experiment was fixed at 12 mg/L as well. When only PC325 was added, the zeta potential was raised from  $-20.3$  to  $-6.6$  mV, as shown in Fig. 8, indicating the charge neutralization of colloid particles by the cationic polyelectrolyte. The zeta potential became slightly more negative with the addition of SDS, and there was almost no change by CTAB addition. However, neither



**Fig. 8.** Effect of surfactant dosing on zeta potential of PC325-conditioned alum sludge

reached charge neutralization. The filamentous precipitate similar to that shown in Fig. 5 was observed in the SDS+PC325 trial.

#### Effect on Specific Resistance to Filtration

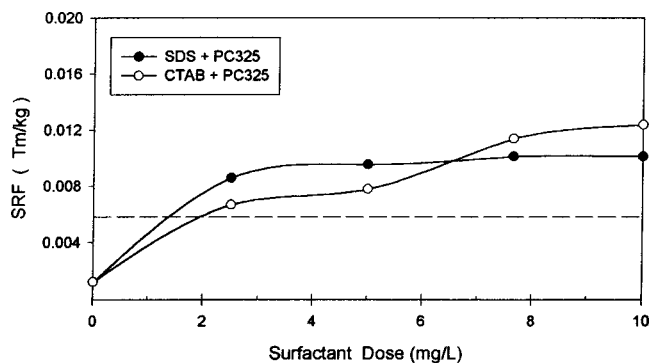
These filamentous substances interfered with the filtration of the sludge as evidenced by the increased SRF (Fig. 9). Since the mechanism of PC325 conditioning involves both charge neutralization and bridging, the effect of the same positively charged CTAB is not as significant as its effect on PA220, in which bridging is the cause for sludge conditioning.

#### Effect on the Dewatering Rate

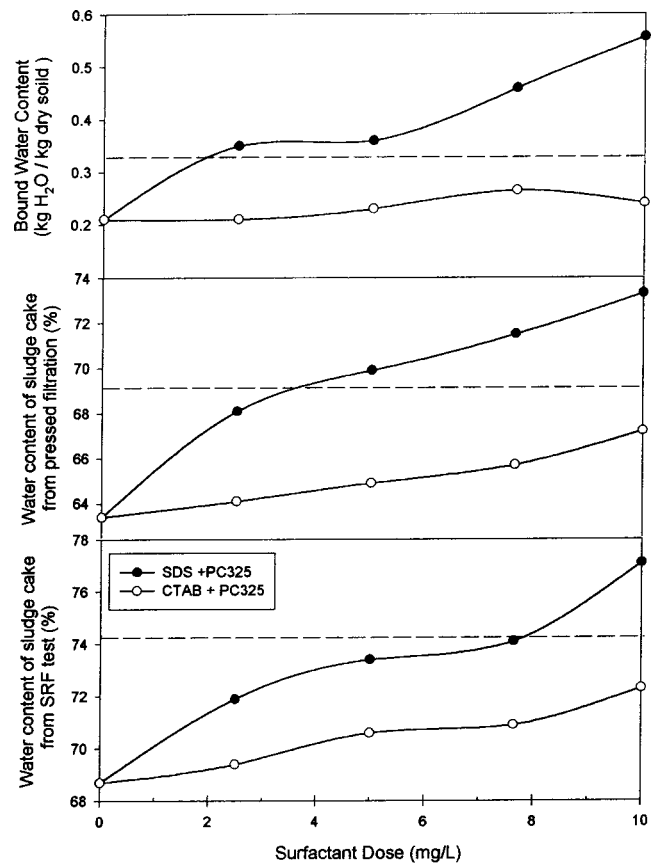
The effect of surfactants on  $T_{85\%}$  of PC325-conditioned sludge is also presented in Table 3. PC325 improved the dewatering rate dramatically. The  $T_{85\%}$  of the original sludge was enhanced from 251 to 68 s. The addition of SDS impaired the dewatering rate in proportion to the amount added, while no effect was observed with the addition of CTAB.

#### Effect on Water Contents of Sludge Cakes

By the same token, the effects of CTAB on water contents of sludge cakes and bound water content, shown in Fig. 10, are not



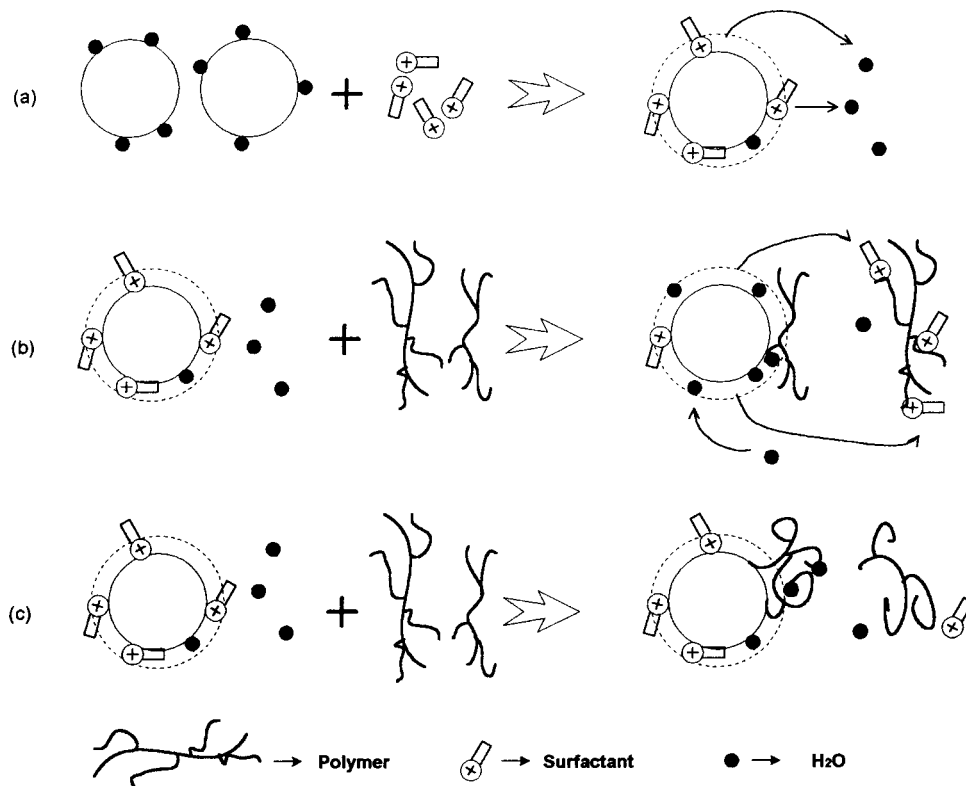
**Fig. 9.** Effect of surfactant dosing on specific resistance to filtration of PC325-conditioned sludge



**Fig. 10.** Effect of surfactant dosing on water contents of PC325-conditioned sludge cakes and bound water content of PC325-conditioned sludge

as obvious as those of SDS. The effect of SDS appears to be proportional to their dosage. The filamentous coprecipitate of SDS and PC325 apparently help the flocs retaining more water in the structure.

To explain the variation in the bound water condition, the following mechanism, as illustrated in Fig. 11, is proposed. (1) When CTAB was added, due to the hydrophobic interaction, part of the hard-to-remove bound water was expelled from the surface, leaving sludge with less bound water; (2) When polyelectrolyte of opposite charge, PA220, was added, it replaced the adsorbed surfactant, which coprecipitated the excess amount of polyelectrolyte. At the same time, water molecules returned to the surface and raised the bound water content; and (3) When polyelectrolyte of the same charge, PC325, was added, a small amount of surfactant promoted the stretching of the polyelectrolyte. The combined effect of surfactant and polyelectrolyte expelled more water molecules from the surface. However, at a higher concentration, competitive adsorption occurred between the two. Because of the weak bondage between the surfactant and the sludge particle, surfactant was expelled. The polyelectrolyte, under the influence of such a high concentration of surfactant, formed a curled configuration enclosing water molecules. When this structure approached the surface of the sludge particles, it brought the water molecule back to the sludge, resulting in an increase in the bound water content.



**Fig. 11.** Proposed mechanisms for water movement at interface of floc surface and polyelectrolyte under influence of surfactant

## Conclusions

Experimental results indicate that the presence of surfactants in a sludge system improves the sludge quality in terms of filterability, dewatering rate, bound water content, and solids content of sludge cakes as long as no polyelectrolyte is added. It is also evident that the types of surfactant charge have a minimal effect on sludge conditioning and dewatering. Surfactants and polyelectrolytes of opposite charge applied together produce a filamentous substance which impairs the filterability of the sludge. The best sludge dewatering takes place in the system with optimum combination of cationic surfactant (CTAB) and cationic polyelectrolyte (PC325). Surfactants had a negligible effect on the dewatering rate of PC325-conditioned sludge. It is thus concluded that in sludge conditioning by polyelectrolytes, simultaneous use of surfactant must be carefully evaluated and the charge type of the surfactant is more crucial than the dosage.

## Acknowledgment

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