Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 30 November 2001

To cite this Article Jean, D. S. , Chu, C. P. and Lee, D. J.(2001) 'FREEZE/THAW TREATMENT OF OILY SLUDGE FROM PETROLEUM REFINERY PLANT', Separation Science and Technology, 36: 12, 2733 — 2746
To link to this Article: DOI: 10.1081/SS-100107222
URL: http://dx.doi.org/10.1081/SS-100107222

SEPARATION SCIENCE AND TECHNOLOGY, 36(12), 2733–2746 (2001)

FREEZE/THAW TREATMENT OF OILY SLUDGE FROM PETROLEUM REFINERY PLANT

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ABSTRACT

A petroleum refinery plant in Taiwan generates approximately 2.8 $\times$ 10^4 tons of oily sludge, including the residual from storage tanks, and the scum sludge and waste-activated sludge from the wastewater treatment plant. Experimental results indicate that freezing and thawing can transform the flocs into large and compact aggregates and significantly enhance the sludge deliquorability for scum and waste-activated sludges. The results are attributed to the advance of an ice front during freezing that expels oil phases from the sludge body. Cationic polyelectrolyte conditioning only slightly influences sludge with a high oil content because the chemical conditioner largely binds to oily droplets on the sludge flocs. However, neither freeze/thaw treatment nor polyelectrolyte conditioning can satisfactorily condition the tank residual. Underlying mechanisms of oily sludge conditioning are discussed.

Key Words: Oily sludge; Freeze/thaw; Expression; Deliquoring; Polyelectrolyte

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INTRODUCTION

Petroleum refinery plants generate vast amounts of oily sludge that cannot be safely disposed unless its oil content is reduced below a certain limit (1). An average petroleum refinery plant in Taiwan annually generates approximately 2.8×10^4 tons of oily sludge. Currently, the plants employ the fluidized-bed incineration technique for treating oily sludges. However, complete incineration is energy intensive and cannot recover the valuable materials within sludge. Mechanical separation of liquor (oil and water) from the oily sludge, if feasible, would reduce the size of sludge and conserve resources. However, the original oily sludge is generally resistant to mechanical deliquoring (2,3).

Oily sludge contains a large amount of emulsified, negatively charged oil droplets. Chemical pretreatment is widely employed in the management of oily sludge. Related studies indicated that cationic polyelectrolytes can condition oily sludge by utilizing charge-neutralization mechanisms (2,4). Other investigators reported that the amount of polyelectrolyte required for sufficient sludge conditioning is proportional to the oily content in the sludge (2,3,5). Those investigators applied some skeleton builders, such as lime or fly ash, in oily sludge conditioning to increase sludge cake porosity and reduce compressibility. However, adding skeleton builders markedly increased the amount of waste sludge. In addition, the use of fly ash carries the risk of a heavy metal release (5–8).

The freeze/thaw technique is an efficient physical conditioning method for certain sludges (9,10). In previous work we noted that the freeze/thaw technique can physically separate the oily phase from the sludge body. which markedly enhances the sludge deliquorability (11). Such a finding provides an alternative means of handling oily waste in industries, particularly for those plants located in cool regions of the world, such as Northern America and Canada, where natural freezing is feasible. We (11) provided preliminary data of a sludge sample in which no comprehensive information regarding the underlying mechanisms is available. We examined 3 oily sludges from a petroleum refinery plant: 1 from oil storage tanks and the other 2 from a wastewater treatment plant. We demonstrated that freeze/thaw treatment could sufficiently condition the 2 wastewater sludges, but it failed to enhance the deliquorability for the tank residual. The floc size, zeta potential, and supernatant chemical oxygen demand (COD) data, together with microscopic observations, provide further insight into how the freeze/thaw treatment affects oily sludge conditioning. The efficiency of polyelectrolyte conditioning is also discussed through comparisons of the efficiencies of chemical and physical conditioning processes on oily sludges.

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EXPERIMENTAL

The Sludge Samples

After passing through several oil/water separators to recover most oils, the oil-containing wastewater of Chinese Petroleum Corp, Taoyuan, Taiwan, flows into a dissolved-air-flotation (DAF) unit. With floating air bubbles, the concentrated oil/water/solid mixture is removed from the top of the DAF unit. Then, the mixture is further concentrated using low-pressure steam. With a flow rate of 28 tons/day and a solid concentration of 3%, the concentrated scum sludge is termed the "original" scum sludge. The components of sludge extractable by *n*-hexane are referred to as the oil phase. According to the *n*-hexane extraction method, the weight fraction of the oily phase was estimated as 22.9% wt/wt. The above fractions are based on the total sludge weight. The 5 predominant substances of the oily phase appeared to be heptadecane (2.1% wt/wt), dodecane (1.9% wt/wt), eicosane (1.7% wt/wt), tridecane (0.93% wt/wt), and pentadecane (0.9% wt/wt). Pycnometer (AccuPyc 1130, Micromeritics, Atlanta, GA, USA) tests revealed that the densities of the supernatant and of the dried solid were 960 and 1813 kg/m^3, respectively. A particle sizer (Sedigraph 5100C, Micromeritics, USA) was used to determine the particle mean size. After mixing and prior to settling, the zeta potentials of aggregates were measured by a zeta meter (Zeter-Meter System 3.0, Zeter-Meter Inc, USA).

The effluent water from the DAF unit was fed into the secondary treatment stage that consisted of the conventional activated-sludge process. The excess sludge was 0.63% (wt/wt). The densities of the supernatant and the solid were 1001 and 1540 kg/m^3, respectively. From an *n*-hexane extraction method, the weight fraction of the oily phase in the excess sludge was determined as 0.16% wt/wt.

The third kind of sludge was the tank residual, which was taken from the storage tank and was a black semisolid of a very high viscosity. The tank residual could be almost completely dissolved in *n*-hexane, indicating that the organic content was rather high. The 5 predominant substances of the tank residuals appeared to be pentadecane (16.6% wt/wt), tetradecane (8.1% wt/wt), heptadecane (7.5% wt/wt), dodecane (6.9% wt/wt), and trimethyl dodecane (6.6% wt/wt), respectively. The weight fractions are based on the whole sludge.

Freezing Apparatus and Test

For freezing and thawing tests, sludge samples in containers of radius 2.3 cm and height 4 cm were placed in a $-16.5°C$ room for 24 hours. Preliminary studies demonstrated that a sludge sample could be completely frozen within 2 hours. The time of exposure to subfreezing temperatures was the same for all samples, which accounts for why the curing effect proposed by Parker, Collins, and Dempsey (12) was not considered. The frozen samples were then thawed at room temperature for 12 hours.

A cationic polyelectrolyte floccule producer, polymer T-3052 obtained from Kai-Guan Inc, Taiwan, was employed for demonstrating how polyelectrolyte flocculation affects sludge deliquorability. The polymer T-3052 is composed of polyacrylamide and has an average molecular weight of 10^7. After a series of acid treatments, the molecules were modified to carry a charge density of 20%. The weighed sludge sample was first put into a baffled mixing chamber that housed a stirrer. The polyelectrolyte solution was then gradually poured into the mixing vessel and was stirred at 200 rpm for 5 minutes and then by 50 rpm for another 20 minutes.

A constant head piston press (Type 147, Triton Electronics Ltd, UK) was employed to identify the expression deliquoring characteristics. Chang et al. (13) schematically depicted the experiential setup. A hydraulic pressure of 3000 psi was exerted through a port onto the free piston, which pressed directly upon the sludge to force the liquor out. Cake from the 2 wastewater treatment sludges were weighed and dried at 105°C to determine the residual liquor content.

RESULTS AND DISCUSSION

Expression Deliquoring

Figure 1 depicts the results of consolidation ratio (U_c) versus consolidation time (θ_c) for DAF scum sludge at 3000 psi. U_c is defined as $(L - L_f)/(L_i - L_f)$, where L_i, L, and L_f are the initial cake thickness, the thickness at consolidation time θ_c, and the final cake thickness, respectively, (14). The original sludge strongly resists mechanical deliquoring. At a pressure as high as 3000 psi, the expression is accomplished at rates up to 4000 seconds. However, the freeze/thaw treatment markedly enhanced the deliquoring rate. For example, the time required for deliquoring the original sludge reduced from 3000 seconds to less than 200 seconds after freezing and thawing, which was a marked improvement.

In contrast, the presence of polyelectrolyte molecules had a relatively mild (but still finite) effect on the deliquoring rate. An optimal dose of 100 ppm was noted for the original scum sludge that yielded the greatest consolidation rate. Nevertheless, for the frozen/thawed sludge, the deliquoring efficiency increased with increasing polyelectrolyte doses up to 500 ppm. In fact, because the deliquoring rate for the frozen/thawed sludge was so good, the benefit obtained by adding more polyelectrolyte was marginal.

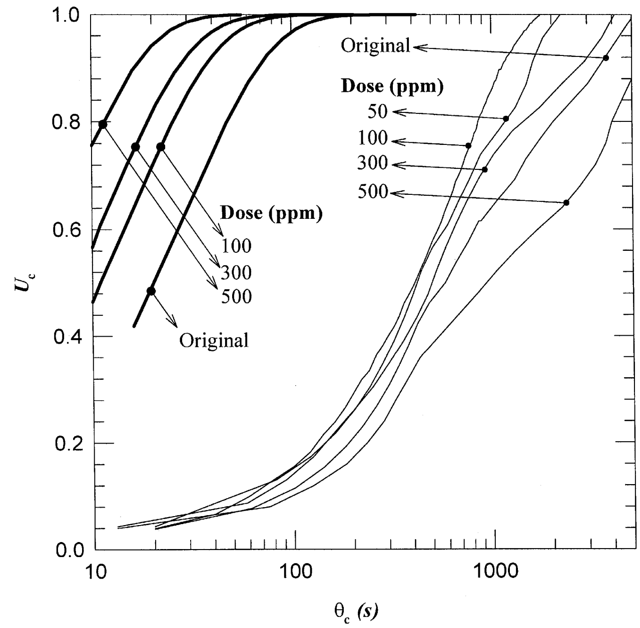

Figure 1. U_c vs. θ_c plot for scum sludge. 3000 psi. Bold and normal curves denote the sludge after and prior to freezing and thawing treatment. Numerical values are the floccule-producing polymer dosages.

Figure 2 depicts the expression deliquoring characteristics of excess activated sludge. The original sludge resists mechanical deliquoring; however deliquoring the activated sludge is much easier than deliquoring the scum sludge. At 3000 psi the expression is accomplished at 700 seconds. The freeze/thaw treatment markedly enhanced the deliquoring rate by reducing the deliquoring time to less than 50 seconds.

In contrast to the scum sludge, the presence of polyelectrolyte molecules could provide a marked improvement on the deliquorability of activated sludge. An optimal dose could be identified for both the original and the frozen/thawed activated sludges that yielded the greatest consolidation rate. In deliquoring practice, a polyelectrolyte dosage exceeding 300 ppm to the original activated sludge and a direct freeze/thaw treatment without the addition of polyelectrolyte provided similar sludge-expression performances.

The tank residual was of very high viscosity. Expression under 3000 psi of 300 g of sludge for 4 hours could yield only 5 g of filtrate. The filtrate rate was too low for the construction of consolidation curves. Freezing and thawing had no detectable effects on the appearance and expression efficiency. The inability of the

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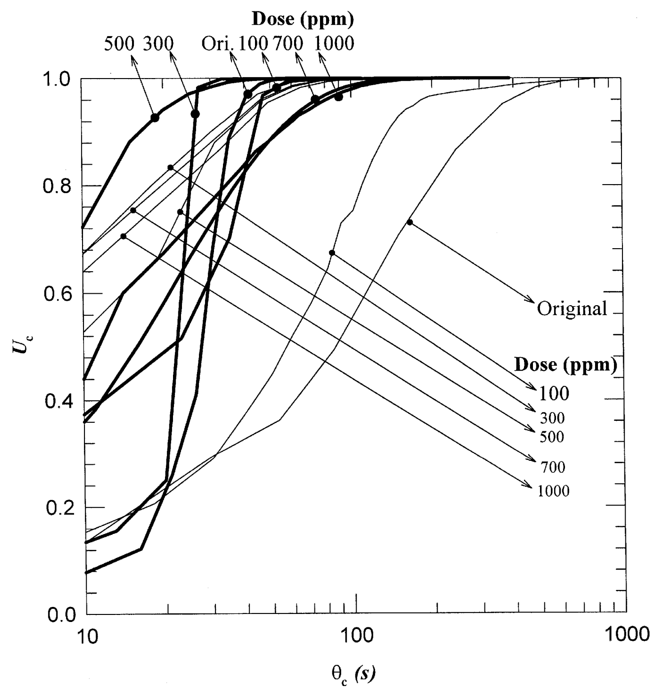


Figure 2. U_c vs. θ_c plot for excess activated sludge. 3000 psi. Bold and normal curves denote the sludge after and prior to freezing and thawing treatment. Numerical values are the floccule-producing polymer dosages.

freeze/thaw treatment to affect tank sludge can be attributed to the heavy hydrocarbons in the residual. The water and the solid phase occupy a small proportion of the whole sludge ($< 2\%$ wt/wt). As a result, one cannot physically separate the oil from the other phases (no other phases exist from which the oil can be separated).

Microscopic Observation

Microscopic observation cannot be performed on the tank residual. However, essential information on the oil distributions in sludge could be extracted from the observation of the 2 wastewater sludges.

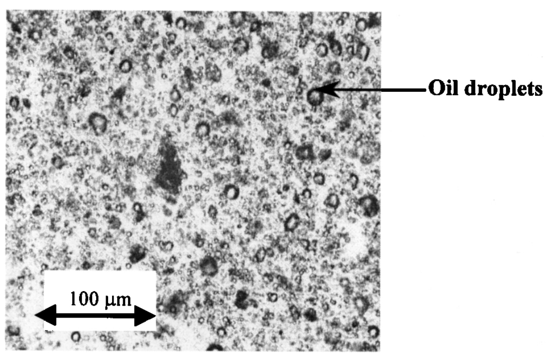
Figure 3a illustrates a photomicrograph ($\times$ 200) of the original scum-sludge flocs. Tiny oil droplets exist among the flocs. Figure 3b illustrates the photomicrograph ($\times$ 200) of the frozen/thawed sludge. Two results are noteworthy. First, the flocs became more compact and much larger after treatment. Second, tiny oil droplets were not as prevalent in the microphotographs of the frozen/thawed samples as they were in the original sludge. The oil droplets were pushed together to form an oily layer in the thawed sludge. Also, some oil droplets may have been trapped inside the flocs.

Figure 4a illustrates a photomicrograph (× 200) of the original activated sludge. A few tiny oil droplets are still noticeable in the photograph; however, fewer are seen than in the scum sludge micrograph (Fig. 3a). Figure 4b illustrates the photomicrograph (× 200) of the frozen/thawed sludge. As with the scum sludge, the flocs became more compact and much larger after freezing and thawing. The tiny oil droplets were less prevalent in the solution after the sample was frozen and thawed.

Characteristics of Scum Sludge

Figure 5 depicts the zeta potential and the particle size of the scum sludge as a function of polyelectrolyte dose. Three results deserve mention. First, the zeta potentials for both original and frozen/thawed scum sludges vary only mildly with the polyelectrolyte dose, indicating the insignificance of the charge neutralization

(a)



(b)

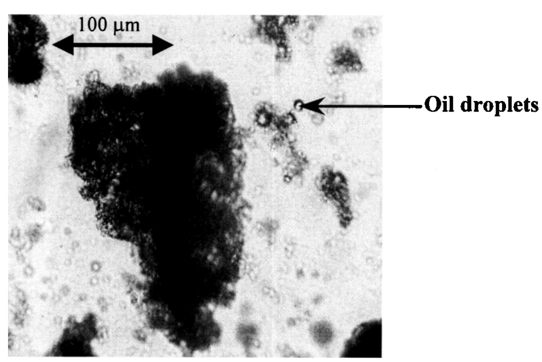


Figure 3. Microphotographs of the scum sludge (× 200). (a) Original sludge. (b) Frozen/thawed sludge.

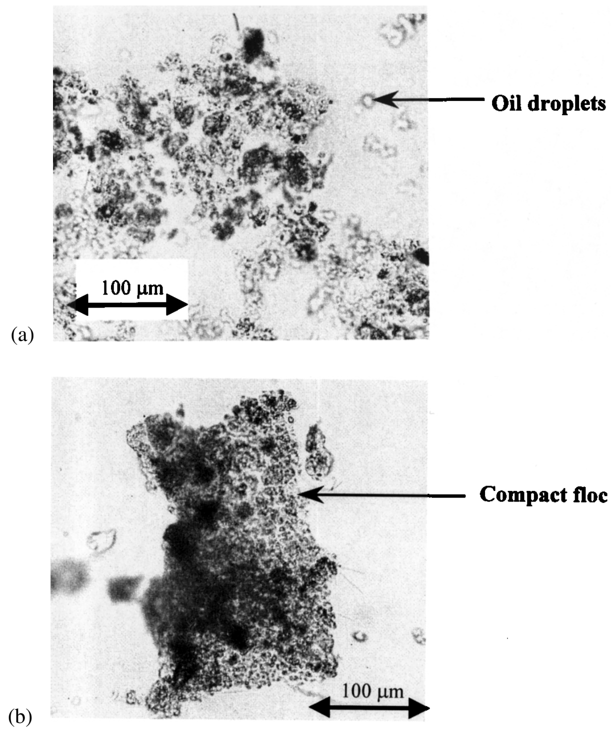


Figure 4. Microphotographs of the activated sludge (× 200). (a) Original sludge. (b) Frozen/thawed sludge.

mechanism for the sludge system. Second, the freezing and thawing process led to a small but finite increase (i.e., less negative values) in zeta potential over the non-treated sludge. The decrease in the amount of emulsified oil in the solution, which carries a negative charge, may account for the increase. Third, the size of the original scum sludge is little affected by the polyelectrolyte; the polyelectrolyte is inefficient in conditioning the original scum sludge. However, the particle size of frozen/thawed scum sludge was markedly higher when the polyelectrolyte dose exceeded approximately 300 ppm than it was for frozen/thawed scum sludge without floccule-inducing polymer additions.

The inefficiency of polyelectrolyte in conditioning the original scum sludge is highly unfavorable in practice and might be attributable to 1 of the following 2 mechanisms: a) The polyelectrolyte molecules could not bind with the sludge flocs and remained in the aqueous supernatant (15,16), or b) the polyelectrolyte molecules combine mainly with the oil droplets rather than the sludge flocs because of hydrophobic interactions or electrostatic forces (the oily droplet usually carries a negative charge). The consequence of mechanism (a) would be a marked

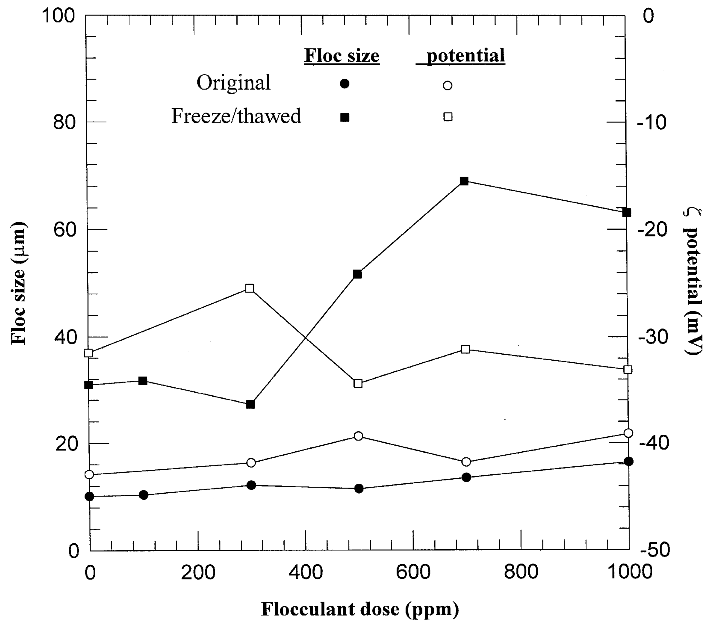


Figure 5. Zeta potentials and the floc size of scum sludge.

increase in viscosity and charge density of the supernatant. Mechanism (b) could either increase supernatant viscosity and COD if the oil-polyelectrolyte compounds had been released to the bulk solution, or it could hinder the relative mobility of adjacent particles in a filter cake if the oil-polyelectrolyte compounds had been kept together with the sludge flocs.

Table 1 lists the supernatant viscosity, charge density, and the COD of the scum sludge and the activated sludge. Neither the polyelectrolyte conditioning nor

Table 1. The Viscosity, Charge Density, and COD Values of the Scum Sludge Supernatant

	Original				Frozen/thawed			
Floccule-producing dose (ppm)	0	100	300	500	0	100	300	500
Viscosity (Pa·s)	0.0025	0.0021	0.0029	0.0026	0.0031	0.0021	0.0028	0.0022
Charge density (mEq/g)	0.01	ND	ND	0.01	ND	ND	0.01	ND
COD (mg/L)	2922	3121	3087	3128	3504	2936	2311	1928

ND, Not detectable.

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the freeze/thaw treatment affected the supernatant viscosity. Furthermore, the charge densities of supernatant were all close to zero. These results preclude the role of mechanism (a). Although the COD seems to increase with polyelectrolyte dose for the original scum sludge, a hypothesis test revealed that the COD had no significant relationship with floccule-producing polymer dose at a confidence interval of 95% (17). SSR = 13 215; the conditional estimate of the COD values yields ($s^2_{Y|X}$) = 7411; hence SSR/$s^2_{X|Y}$ = 1.78 < $F_{1,2,0.05}$ = 18.5. The polyelectrolyte molecules had not changed the supernatant viscosity.

Freeze/thaw treatment affects the COD in scum-sludge supernatant. Hung et al. (9) demonstrated that freeze/thaw treatment could release some extracellular polymers (ECPs) from their original waste-activated sludge into the bulk solution. As noted in Table 1, the COD for the scum sludge differed: 2922 mg/L for the untreated sludge and 3504 mg/L after freezing and thawing the sludge. This result correlates with the findings of Hung et al. (9), but it is presumed to be due to the release of interparticle oils instead of ECPs from the sludge.

In addition, the COD of frozen/thawed scum sludge decreased with the addition of floccule-producing polymer dose. The hypothesis test revealed that the COD strongly correlates with floccule-producing polymer dose at a confidence interval of 95%. The corresponding SSR = 1 384 345; $S^2_{Y|X}$ = 30 705; SSR/$s^2_{X|Y}$ = 45.1, which is greater than $F_{1,2,0.05}$ = 18.5. Although no direct experimental proof supports the speculation, the decrease in COD with polyelectrolyte addition may be attributable to the binding between polyelectrolyte molecules and the released oils. In addition, the floc size data for frozen/thawed sludge (Fig. 5) reveal that the polyelectrolyte can effectively flocculate particles if the dosage exceeds 300 ppm. Such a result indicates that the surfaces of frozen/thawed particles have been modified such that the adsorption of polyelectrolyte molecules is favored.

We adopted the same unidirectional freezing apparatus employed by Hung et al. (18) for investigating the role of the freezing speed. Figure 6 depicts the mean floc size and the capillary suction time (CST) of sludge. As Fig. 6 reveals, at a low freezing speed, the flocs became larger while the CST was reduced; this result correlates with the tests completed with the activated sludge of negligible oily content (18). The possible mechanisms proposed in the literature (e.g., 10) for the freeze/thaw treatment of normal sludges, such as interfacial dehydration or initiation of interface instability, might also be applicable to an oily sludge.

Characteristics of Waste Activated Sludge

Figure 7 depicts the zeta potential and the particle size of the original activated sludge as a function of polyelectrolyte dose. The zeta potential increased from −58 mV to approximately −40 mV with a dose up to 300 ppm. Beyond a

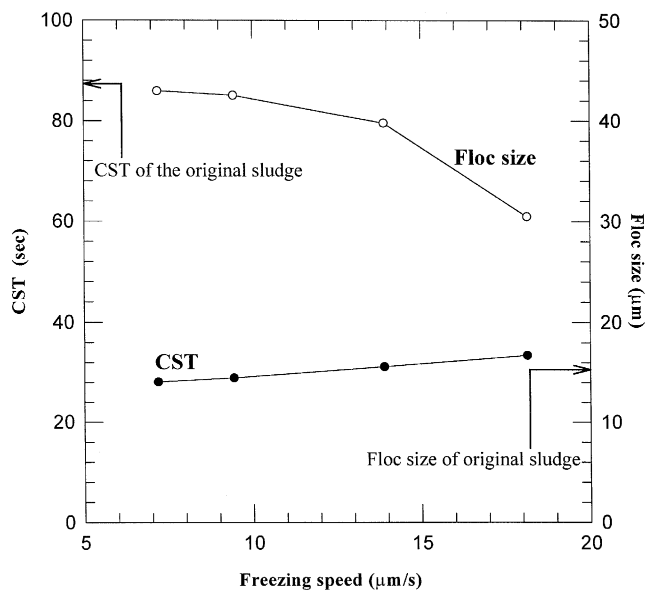

Figure 6. Floc size and CST vs. freezing speed of scum sludge.

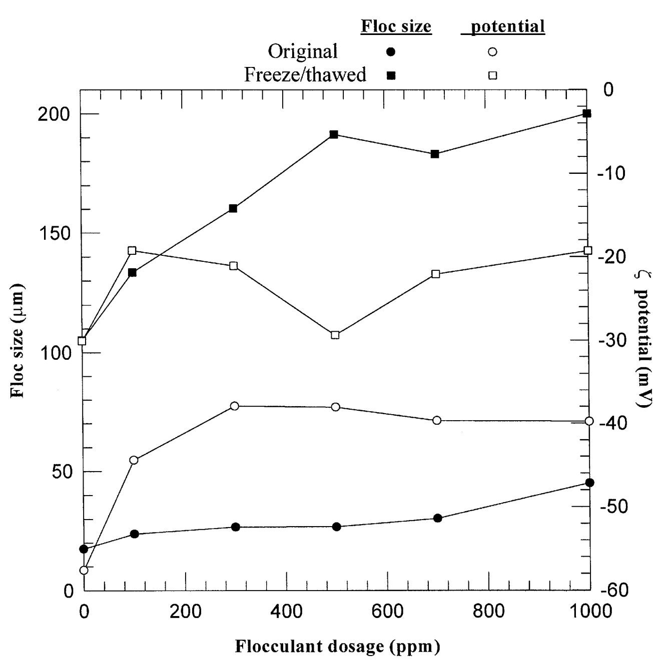

Figure 7. Zeta potentials and the floc size of original excess-activated sludge.

Table 2. The COD Values of Excess-Activated Sludge Supernatant

	Original				Frozen/thawed			
Floccule-producing polymer dose (ppm)	0	100	500	1000	0	100	500	1000
COD (mg/L)	13	7	28	25	37	36	30	22

dose of 300 ppm the zeta potential remained nearly constant. The particle size increased from 18 μm to around 50 μm at a dose of 1000 ppm. Interparticle bridging therefore dominates the flocculation processes in excess activated sludge (19). Table 2 lists the COD values of the supernatant of the excess activated sludge. The measured COD values are all rather low, indicating a negligible amount of unflocculated polyelectrolyte or oil-polyelectrolyte compounds in the bulk solution.

The particle size for the original activated sludge is approximately 18 μm, a size generally smaller than those observed in normal activated-sludge samples and corresponding to a relatively inferior bacterial aggregation capability. The small size could be attributable to the appearance of toxic substances in the influent, the reduction of dissolved oxygen in the aeration pool, or too high a biological oxygen demand (BOD) load. The oil phase in wastewater could be responsible for all the size-inhibiting factors. However, the particle size of frozen/thawed sludge increased up to 160 μm, an 8-fold increase over that of the original sludge. Such a large change in floc size correlates with the results reported in the literature (20,21). As a result, the excess activated sludge with a small amount of oily components (0.16% wt/wt) behaves similarly to the biosludge noted in a common wastewater treatment plant.

Oily Sludge Conditioning

The above-mentioned experimental results clearly reveal that although polyelectrolyte addition (chemical conditioning) failed in conditioning the present scum sludge, freeze/thaw treatment (physical conditioning) could successfully condition both the scum sludge and the activated sludge (Figs. 1 and 2). Such a difference is not attributed to the change in surface charge (zeta potential data in Fig. 5), but is strongly correlated with the oil content in the sludge (photographs in Figs. 3 and 4). (We had not excluded the possibility that polyelectrolytes that exhibit different surface characteristics might efficiently condition the oily sludge.)

Chemical conditioning enhances sludge deliquorability by building new chemical bonds. When a high fraction of oil phase exists in the sludge, polyelectrolyte molecules appear to bind mainly with the oil droplets but not the sludge flocs (Table 1 for scum sludge), thereby leading to the failure in conditioning.

The freeze/thaw treatment could sufficiently expel out the oil phase from the sludge body by physical forces usually associated with the motion of the ice front. The data depicted in Fig. 6 also reveal that the effects of freezing become more predominant when the freezing speed goes down (11). Because physical force separates the oil molecules from the sludge body, oil content only mildly affects the efficiency of freeze/thaw treatment on scum sludge and activated sludge. The depletion of oil phases from the sludge also largely enhances the efficiency of polyelectrolyte conditioning. However, because the tank residual contains over 98% wt/wt oily compounds, freezing only transforms the oily sludge into a solid state. No physical separations between phases could be achieved by freeze/thaw treatment.

ACKNOWLEDGMENT

The authors are grateful to Chinese Petroleum Co, Taoyuan, Taiwan for providing sludge samples. National Science Council, ROC, financially supports this project.

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Received June 2000
Revised October 2000