Polymer Dose Effects on Filtration Followed by Expression of Clay Slurries

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Filtration followed by expression characteristics of cationic polymer conditioned clay slurries are reported for the first time in this work. As the polymer dosage increases, the resistance to filtration greatly decreases until a specific dose has been reached, where the zeta potential is close to zero. And further increase in polymer dose conversely raises the resistance. The expression data are interpreted by the Terzaghi–Voigt combined model, from which the model parameters are evaluated. The polymer conditioning has only a mild effect on the primary consolidation process but has, however, a considerable influence on secondary consolidation characteristics. When zeta potential changes from negative to positive, both the easiness of creeping of constituent particles within the sludge cake and the fraction of moisture removal by the secondary consolidation attain a maximum. The optimal polymer dose criterion considering the filtration and expression stages separately, or in combination, is   © 1997 Academic Press

Key Words: expression; filtration; polymer conditioning; creep effect; zeta potential.

INTRODUCTION

Polymer conditioning has been employed for quite some time to pretreat slurry to increase its settleability and the corresponding filterability. Charge neutralization and interparticle bridging are the two major mechanisms for flocculating constituent particles into larger flocs (1). When the former dominates, a strong correlation exists between the polymer dose at which the particle surface charge neutralizes and the maximum settling velocity and/or minimum resistance to filtration (2). A rational criterion for the optimal polymer dose is thereby setting at such a specific polymer dose where charge neutralized, which can be easily determined by the zeta potential measurement or the streaming current device (3). However, the requirement of floc characteristics for the two separation processes is not identical (4).

Owing to the relatively low energy consumption rate required by compression compared with thermal dewatering methods, it is widely employed in industries to separate liquid from cake by mechanical pressure (5). A major application relates to water and wastewater sludge treatments. Yeh (6) and Tong (7) have provided a brief literature review. Heij *et al.* (8) report the application of expression to sludges.

Over the past three decades, most of the research on constant-pressure expression has been accomplished by the Japanese investigators, Shirato and Murase (9–14), and by Tiller of Houston University (5). Investigations of constant pressure provide basic understanding of the detailed mechanisms involved and of the implications for sludge characteristics.

In water and wastewater sludge dewatering operations, filtration followed by an expression process is frequently employed. Examples are the belt filter press or the screw press, and in these processes polymer conditioning almost always occurs. However, a comprehensive study of the filtration followed by expression characteristics of polymer conditioned slurry is still lacking in the literature. This paper presents an experimental study of the effects of polymer dose on the filtration followed by expression operations of cationic polymer conditioned clay slurries. The role of particle surface charge on resistance to filtration, and the parameters in expression stage are examined. We also address the so-called ''optimal polymer dose'' for these clay slurries.

EXPERIMENTAL

The test material was clay powders. The particle size distribution, determined by a Sedigraph 5100C (Micromeritics), was as a monodispersed distribution with a mean diameter of approximately 4.6 μm. The true solid density was measured by a Accupyc Pycometer 1330 (Micrometritics), giving 2584 kg/m^3 with a relative deviation of less than 0.5%. The slurry was prepared by mixing clay particles and 10^{-1} M NaClO$_4$ in the distilled water. (Note: the addition

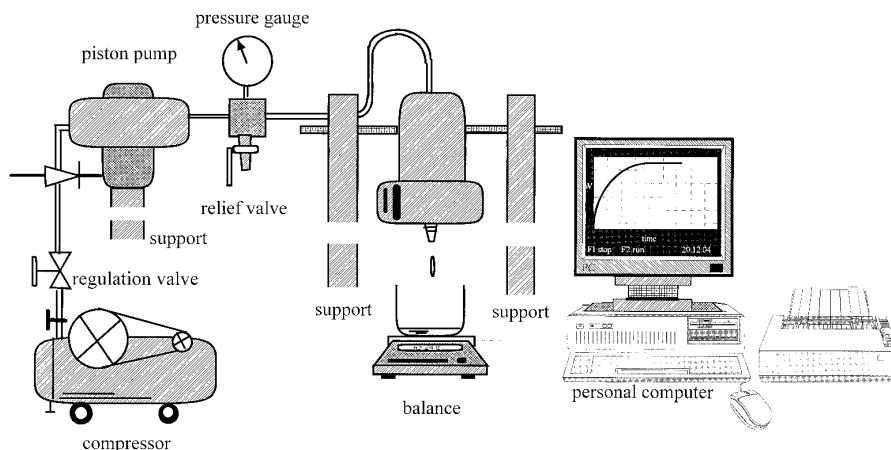[1] To whom correspondence should be addressed. E-mail: djlee@ccms.ntu.edu.tw.

FIG. 1. Experimental setup.

of $NaClO_4$ provides a sufficient ionic strength to prevent interference from other ions that the clay particle surfaces might release.) The pH values are fixed at three levels: 3, 7, and 10.

Cationic polyelectrolyte, designated as polymer T-3052, was obtained from Kai-Guan, Inc., Taiwan. This polymer is a polyacrylamide with an average molecular weight of 10^7 and a charge density of 20%. The mixing unit was a baffled mixing chamber with a stirrer. The weighed powder was first suspended in distilled water. Polymer solution was then gradually poured into the mixing vessel, stirred at 200 rpm for 5 min, followed by 50 rpm for 20 min. Following mixing and prior to settling, a small quantity of the clay-polymer aggregates in the vessel was carefully transferred to a fresh electrolyte of the same pH and electrolyte concentration as the original electrolyte. The zeta potentials of the clay-polymer aggregates were then measured by a zeta meter (Zeter-Meter System 3.0, Zeter-Meter Inc., USA).

A constant head piston press (Triton Electronics Ltd., type 147) was employed in all the tests. Figure 1 is a schematical drawing of the experimental setup. The sludge was placed in a stainless steel cylinder, 7.62 cm in diameter and 20 cm high. A hydraulic pressure of 1000 psi was exerted on the piston to force out the moisture. The time evolution of the filtrate weight was then automatically recorded by an electronic balance connected to a personal computer. Given these data and the true solid density, the time evolution of cake porosity was subsequently obtained.

Under each experimental condition, three independent tests were conducted to check the reproducibility. Owing to the rather high solid content (20% w/w) and the wide range of polymer dosage (0–1000 ppm, based on the weight of slurry) under investigation, the mixing becomes an essential step in determining the subsequent sludge dewatering characteristics. Extreme care should be exercised to ensure that reproducible experimental results are obtained.

RESULTS AND DISCUSSION

General

Typical experimental data for compression are summarized in Fig. 2. The complete test illustrated in Fig. 2 includes the filtration and expression stages (5). The porosity term used as the ordinate represents the average value of the slurry and cake in the filtration stage, and the average value for the consolidated cake in the expression stage that follows. In all the tests involving the three pH values, as the polymer dose increased, the cake porosity versus time curve clearly shifted to the left till the polymer dose reached a critical amount. Above the critical dosage for pH 3 and 7, the curves return to the right. Such a reversal phenomenon, however, has not been observed for pH 10. Notably, the critical polymer dose determined from Fig. 2 depends strongly on the pH of the slurries: a lower critical dose corresponds to a lower pH. The critical dose is approximately 500 ppm and 600 ppm for pH 3 and 7 tests, respectively.

The filtration and the expression stages in Fig. 2 are separately discussed in the later sections. Shirato *et al.* (9) proposed a simple, graphical method for locating the transition point between these two stages. Yeh (6) used an alternative method: a certain amount of gas retained in the expression chamber was quickly expelled once the piston touched the cake, thereby signaling the transition. We here adopt Shirato's method, since the transition point of the clay slurries can easily be determined graphically. Typical examples are given in Fig. 3. In Fig. 2, the obtained transition points are also indicated as arrows, separating each experimental curve into two regions labeled *F* and *E*.

The zeta potential data are summarized in Fig. 4. At pH 3 and 7, the zeta potentials increase from negative to positive as the polymer dose increases. In both cases the specific dose producing a surface neutralization situation are identified in
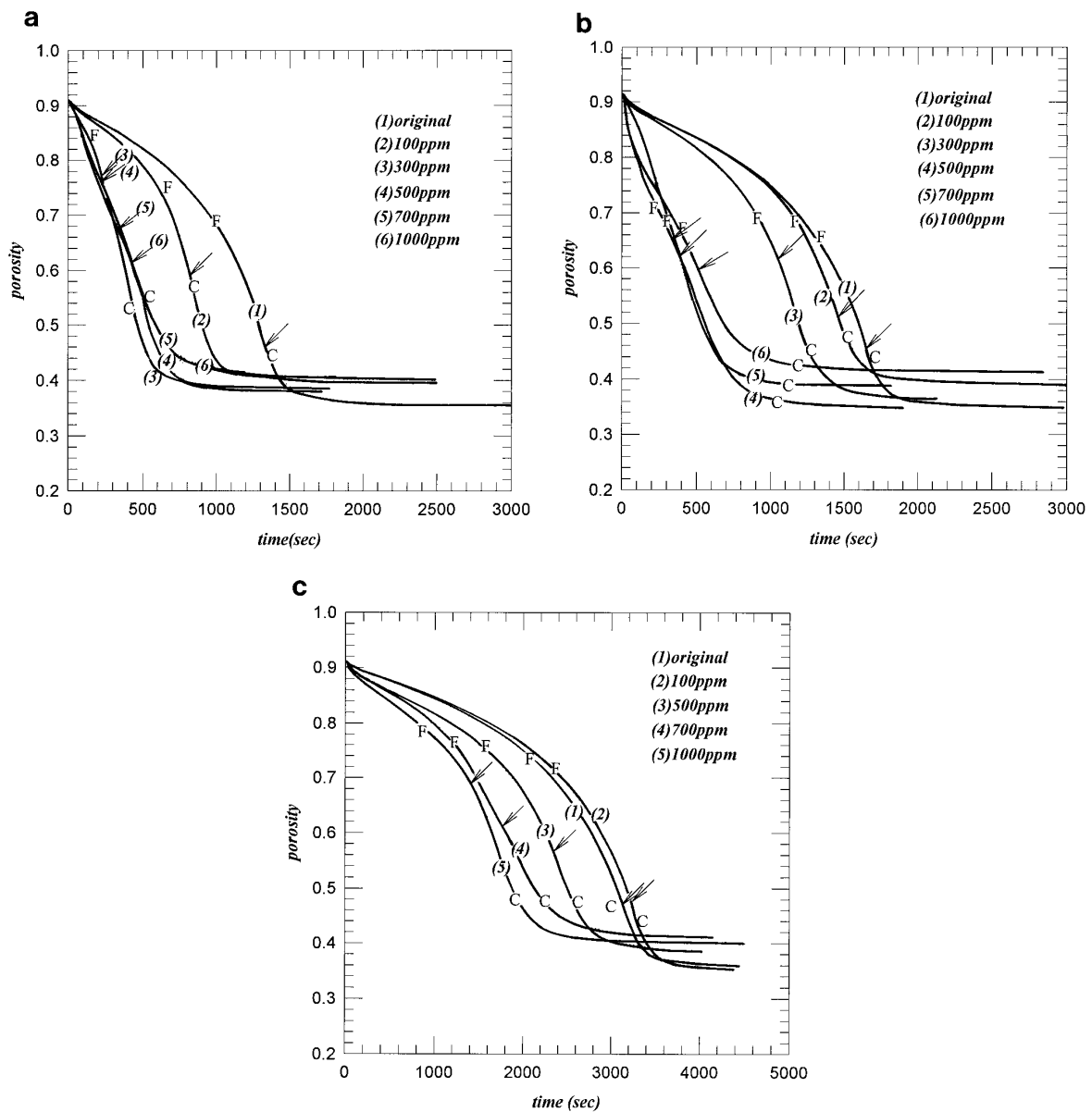
FIG. 2. Time evolution of cake porosity. 1000 psi. Clay slurry, 20% w/w. 10^{-1} M. Arrows indicate the transition points. Symbol F denotes the filtration stage; symbol E, the expression stage. (a) pH 3, (b) pH 7, (c) pH 10.

Fig. 4, and the results read, respectively, 480 and 520 ppm at pH 3 and 7. It is not surprising that these dosages are close to the critical doses found in Figs. 2a and 2b. We refer to these values hereafter in this paper as the critical polymer dose. (Note: the zeta potentials close to the charge neutralization region are rather difficult to determine accurately, since there are particles with positive or negative charges present in the slurry. The polymer doses thus determined reflect an element of uncertainty.) For pH 10, the dewatering efficiency did not markedly improve once the polymer dosage exceeded 700 ppm (Fig. 2). The zeta potential measured

at high polymer dose exhibits greater uncertainty since the resulting flocs settle quickly in the measurement cell.

The coincidence of the zeta potential measurements and the efficiency of the dewatering process reflects the important role of surface charge characteristics on particle packing and the associated dynamic response of the cake structure under loading. The zeta potentials of aggregates are strongly affected by pH. The zeta potential of polymer-clay aggregate at higher pH is lower than at lower pH. Actually, the pH value of solution affects the surfaces both of clay and polymer. At acidic condition, negatively charged
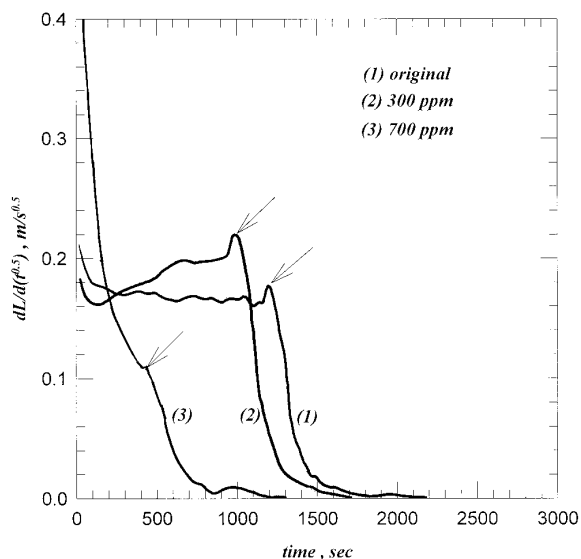
FIG. 3. Transition between filtration and expression stages. Arrows indicate the transition points. pH 7.

FIG. 5. α_{av} versus polymer dose amount. Arrows indicate the corresponding critical polymer doses.

clay or clay-polymer aggregate causes a less charge than at higher pH conditions. As to polymer, it is also considered that the proton concentration affects its charge density through the hydrolysis reaction. Hence, the acidic condition favors clay-polymer aggregation due to decreased repulsion between clay particles and to increased repulsion between polymer segments.

In the following sections, based on the transition points identified in Fig. 3, it will be more informative to discuss the filtration and expression stages separately. To avoid confusion, in the following discussion the clay-polymer aggre-
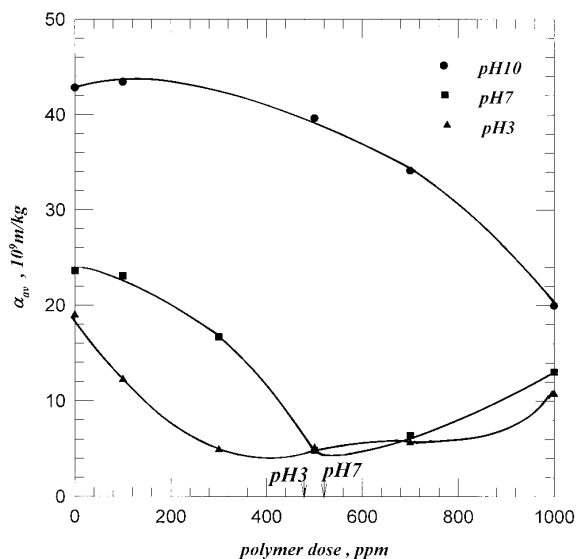
gates constituting the sludge or the filtration cake are termed as aggregates, while the clay particles constituting the aggregates are termed as the particles.

Filtration Stage

Considering the filtration stage data (stage *F* in Fig. 2), the corresponding average specific resistance are obtained according to procedures proposed by Leu (15). The average specific resistances under 1000 psi constant-pressure filtration are shown in Fig. 5.

At pH 3 and 7, the lowest average specific resistance of cake occurs at a dose close to the critical polymer dose identified by zeta potential measurements. This result corresponds to the well-known fact that constituent aggregates with neutralized charges can form a loosely structured cake with a loose structure, thereby permitting a high filtration rate. A low specific resistance is advantageous from dewatering considerations.

The separation points shown in Fig. 3 can be employed in the manner described later to calculate the residual moisture ratio, the moisture not removable during the filtration stage (moisture remaining in the cake at the end of filtration divided by the total moisture content). First, read out the initial porosity of the sludge (ϵ_0) and then at separation point (ϵ). Calculate the corresponding void ratio e_0 and e. The fraction of liquid remaining in the cake is e/e_0. The results are shown in Fig. 6. A maximum is noted at the corresponding critical polymer dose. This arises naturally owing to a loose, nearly neutralized cake trapping more moisture during filtration. However, the higher residual moisture in cake after filtration is not favorable to final sludge disposal.
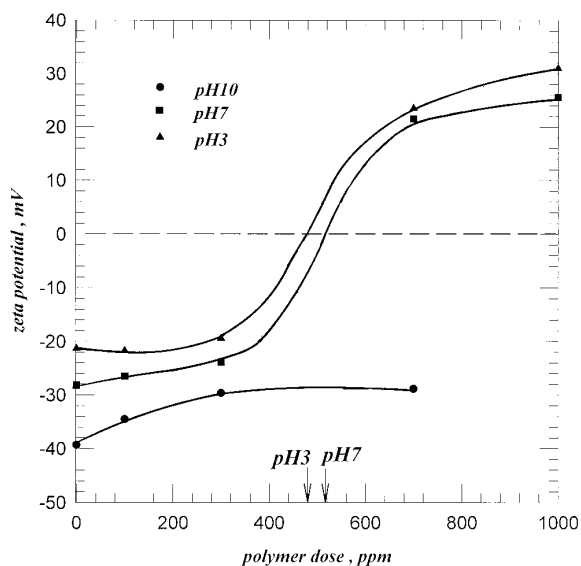

FIG. 4. Zeta potential versus polymer dose amount. Arrows indicate the estimated critical polymer doses.
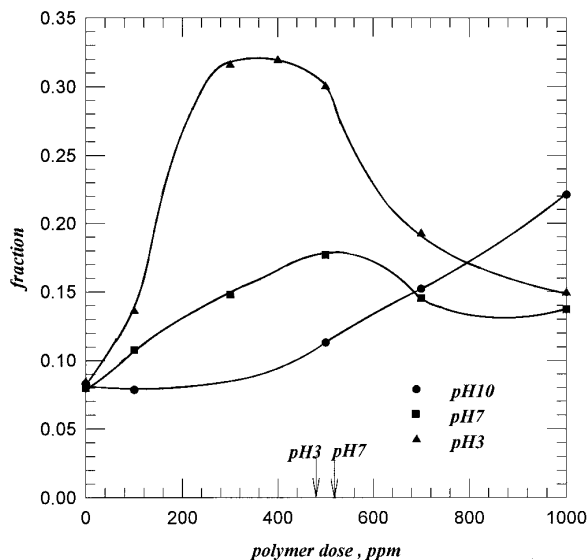
FIG. 6. Fraction of moisture removed in filtration stage versus polymer dose amount. Arrows indicate the corresponding critical polymer doses.

At pH 10, as the polymer dose increases, the average specific resistance decreases (Fig. 5), while the residual moisture amount increases monotonically (Fig. 6). Both results indicate a looser cake structure associated with a higher polymer dose. The optimal polymer dose was, therefore, not achieved, although the conditioned, unfiltered slurry and the filtrate both became very viscous.

Expression Stage

The expression stage (stage *E* in Fig. 2) can be differentiated from the filtration stage and is redrawn in Fig. 7. The first phase of expression usually exhibits only a weak dependence on the amount of polymer dosing. The subsequent expression stage, however, is strongly influenced by the polymer addition. At pH 3 and 7, as the polymer dose increases, the expression curves first shift to the left, and then, after passing the corresponding critical polymer dose, they return. At pH 10, nevertheless, the curve becomes insensitive to polymer dosage amount once the concentration exceeds 700 ppm. The comparisons between Figs. 7a to 7c indicate that the expression dewatering efficiency approximately follows the sequence: pH 3 > pH 7 > pH 10.

By employing the Terzaghi–Voigt combined model to relate the cake local void ratio with the local compressive pressure, Shirato *et al.* (10) arrived at a tedious solution to account for the time evolution of cake thickness under constant-pressure consolidation. The Terzaghi–Voigt combined model is illustrated in Fig. 8. (Note: this model is a phenomenological model that lacks theoretical basis. The spring element in the Terzaghi model accounts for the elastic behavior of cake, the action of which under loading is referred to

as the ''primary consolidation.'' The dashpot and spring elements of the Voigt model account for viscous behavior, whose action under loading is referred to as ''secondary consolidation.'' It is clear from Fig. 8 that both the Terzaghi and the Voigt elements respond simultaneously when a loading is exerted onto the cake surface. If it is assumed that the rate of primary consolidation is much higher than that of the secondary consolidation, which is usually the case in practice, a reduced form of a solution can be stated as follows:

$$
\begin{aligned}
U_c &= \frac{L_1 - L}{L_1 - L_f} \\
&= (1 - B)\left\{ 1 - \exp\left(-\frac{\pi^2 Ce}{4\omega_0^2}\, \theta_c \right) \right\} \\
&\quad + B\{ 1 - \exp(-\eta\theta_c) \}. \quad [1]
\end{aligned}
$$

In Eq. [1], U_c is the consolidation ratio, L the cake thickness, L_1 and L_f, respectively, the initial and final cake thickness, η the creep factor, demonstrating the easiness of the relative mobility of constituent aggregates, ω_0 the cake volume on unit area of the filter, Ce the consolidation coefficient (a measure of the ratio of the spring rigidity of the Terzaghi model to the consolidated cake average specific resistance), and θ_c the consolidation time. The first and the second term on the right-hand side of Eq. [1] are attributed to the primary and secondary consolidations, respectively. The parameter B is defined as $E_1/(E_1 + E_2)$, that is, the ratio of moisture removal by the secondary consolidation to that by the overall consolidation. As $\theta_c \to \infty$, Eq. [1] reduces to the form

$$
U_c = 1 - B \exp(-\eta\theta_c), \quad [2]
$$

from which the parameters B and η can be estimated via a regression analysis of the experimental data (11–13).

As indicated in Fig. 7, for all the sludge tests, a linear $\ln(1 - U_c) - \theta_c$ region follows the initial decreasing in U_c. This confirms the validity of employing Eq. [2] to describe the expression characteristics for these conditioned clay slurries. Figures 8 and 9 represent the best fitting B and η. Interestingly, at pH 3 and 7, a maximum is also detected for both figures that is close to the corresponding critical polymer dose. That is, the easiness of the creeping of the constituent aggregates (or particles) in the cake, and the fraction of moisture removal by the secondary consolidation, both increase greatly when the aggregate surface charge is around neutral.

At pH 10, since the critical polymer dose was not achieved in experiments, the B value increases in line with an increase in polymer dose as occurs in the lower polymer dosage range
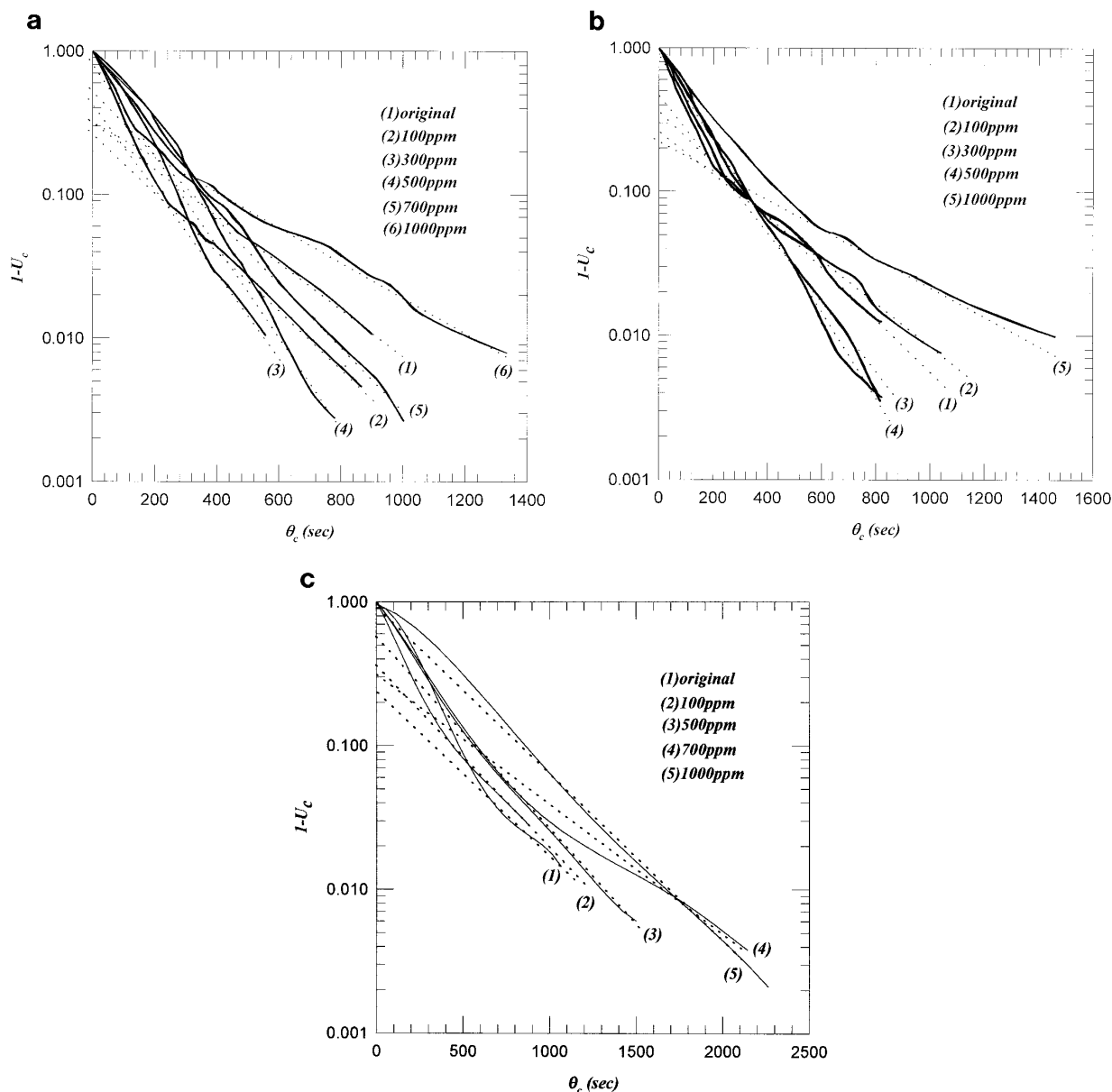
a

b

c

FIG. 7. 1-U_c versus θ_c. (a) pH 3, (b) pH 7, (c) pH 10.

at pH 3 and 7. However, the rate of increase rate in B becomes faster and approaches unity when the polymer dose exceeds approximately 700 ppm (Fig. 9). That is, the secondary consolidation contribution becomes more important (larger B) in the basic condition. Since the dewatering in secondary consolidation is usually slower than that in the primary consolidation, a greater B is not favorable to sludge dewatering. The corresponding parameter η remains almost constant with the addition of polymer (Fig. 10), reflecting no marked improvement of aggregates/particles creep. Consequently, as depicted in Fig. 7c, the dewatering efficiency of the expression deteriorates as polymer is added. It is therefore clear that the improvement of

dewatering rate at pH 10 in Fig. 2c is mainly achieved by reducing filtration resistance. The addition of polymer, actually, retards the expression and is unfavorable to sludge expression dewatering.

Surface Charges and Sludge Dewaterability

Experimental results reflect the important role of the aggregate surface charges on the sludge dewatering efficiency. As stated in the literature and found in this work, the filtration cake structure with nearly neutral constituent aggregates is loose, giving a low resistance to filtration and substantial
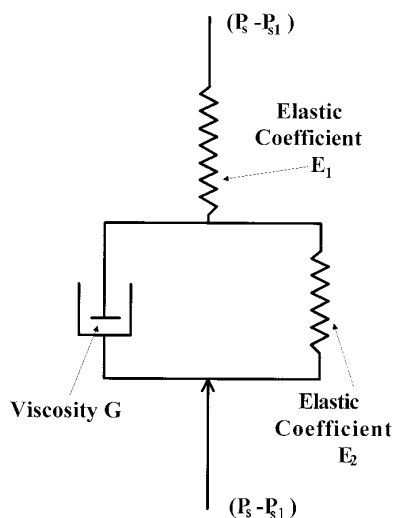
FIG. 8. Schematics of the Terzaghi–Voigt combined rheological model.

residual moisture. Meanwhile, the consolidated cake at a critical polymer dose exhibits higher η (faster particle creeping) and B values (a greater secondary consolidation contribution). This effect has not been well documented in the literature and, therefore, warrants some discussion.

Primary consolidation had been defined as the escape of pore liquid and the collapse of cake structure; and secondary consolidation, as the disturbance of the structural bonding of aggregates or the creeping of the constituent particles (16). The corresponding maximum B value at the critical polymer dose for pH 3 and 7 indicates relatively smaller properties of moisture being removed at the primary consolidation stage. That is, although the porosity is greater for the
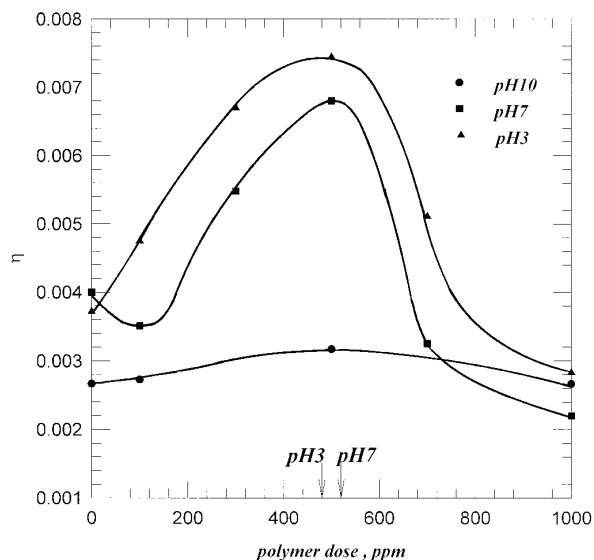

FIG. 9. Parameter B versus polymer dose amount. Arrows indicate the corresponding critical polymer doses.

FIG. 10. Parameter η versus polymer dose amount. Arrows indicate the corresponding critical polymer doses.

resulting cake at the end of the filtration stage, the resistance to global structure collapse during the first phase of expression is even stronger. This is especially true at pH 10. One possible explanation is that for a nearly neutralized consolidated cake, the aggregate sizes are larger and the *intraaggregate* strength greater. With the former, large pores can exist in the cake, resulting in considerable filtration cake volume (Fig. 6). With the latter, once pressure is exerted on the cake, there is increased resistance to the global structure collapsing. Further moisture removal is mainly accomplished by rearranging the positions of the aggregates within the cake, a process which is attributed to the secondary consolidation stage. We have found from an independent test that the resulting flocs under ultrasonic field are stronger when at critical polymer dose or with raised pH.

The easiness of particle creep is controlled by the forces acting resistively on neighboring particles, including at least an external mechanical force, the drag force exerted by the highly viscous surface water layers, and electrostatic repulsion forces. We can picture in imagination the fricative passage (creeping) of one aggregate over the other with the same sign of charge owing to the electrostatic repulsion force. This phenomenon can explain qualitatively the larger creep coefficient observed near the critical polymer dose for pH 3 and 7, which is favorable to dewatering since a greater expression rate can be obtained. At pH 10, as evidenced by the zeta potential measurements in Fig. 4, the surface charge does not approach closer to zero as polymer dose is higher than 300 ppm. The creeping factor η therefore remains unchanged accordingly. When the surface charge is neutralized, the higher (or near constant) η values reflect a weaker
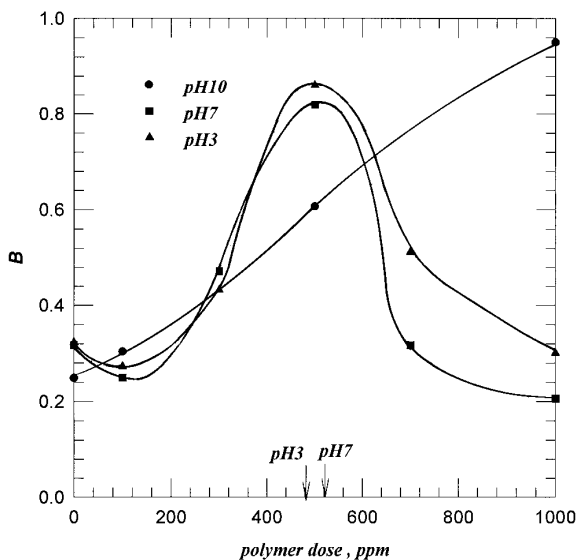
interaggregate interaction. These results reveal that the parameters B and η might be controlled by different factors.

Optimal Polymer Dose

This study demonstrates a need for re-evaluating the optimal polymer dose criterion by considering the filtration followed by expression process as a whole. As suggested by Moudgil and Shah (4), an optimal polymer dose actually depends on what the specific requirement for the sludge treatment is. For example, if the clarifier and/or the filter area is the major concern, the critical polymer dose identified by a zeta potential measurement may be the ideal optimal polymer dose, since it provides the most satisfactory settleability and filterability. However, if the reduction of filtration cake volume is the focus of interest, the critical polymer dose becomes the worst choice, since it leaves the largest residual moisture content in the filtration cake. The trend is also observed at pH 10 although the critical polymer dose was not achieved within the experimental range.

Considering the expression stage separately, if it is relatively slow (which is especially true for biological sludges dewatering) and if the required residual moisture content is within the range that the initial phase of the expression stage can achieve, no specific polymer dose is strongly recommended, since the dependence on polymer amount is weak (Fig. 7). If a still dryer cake is a prerequisite for final sludge disposal, a subsequent expression stage is required, at which point secondary consolidation begins. The critical polymer dose is still the best choice for the slurry at pH 3 or 7 at our study, since the effect of an increase in η is not been completely compensated by the increase in B. However, at pH 10, owing to the marked increase in B and a near constant η, the expression performance deteriorates with the addition of polymer. No polymer should be added thereafter.

The combined filtration and expression process may result in a more complicated situation. The optimal polymer dose would depend on what design parameter is the critical one. For example, in some of the cases discussed previously, no specific polymer dosing amount is recommended. This is somewhat surprising since the charge neutralization mechanism still plays a major role in present-day slurry system. The experimental results in this work, therefore, support the arguments in Moudgil and Shah (4) that different aggregate characteristics are required for various intended applications.

CONCLUSIONS

The filtration followed by expression characteristics of cationic polymer conditioned clay slurries were evaluated

experimentally. For slurries conditioned too close to the critical polymer dose at which the zeta potential changes from negative to positive, the average specific resistance of the filtration stage reaches a minimum owing to the loose cake structure formed thereby. However, the corresponding residual moisture content is also the largest. During the expression stage, the polymer dose has a substantial influence on the secondary consolidation. According to the combined Terzaghi-Voigt rheological model, the slurries containing a close to a critical polymer dose will exhibit the highest particle creeping mobility and the largest secondary consolidation contribution. However, the creep is not been enhanced greatly in the basic condition, which cause expression performance to deteriorate when polymer is added. The optimal polymer dose with regard to the filtration/expression process is not necessarily definitely at critical polymer dose even if the particle surface charge is the dominating mechanism.

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