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FLOCCULATION AND DEFLOCCULATION BEHAVIOURS OF FINES IN THE COFACTOR-POLYETHYLENE OXIDE RETENTION AID SYSTEM: EFFECTS OF COFACTOR CONCENTRATION

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ABSTRACT

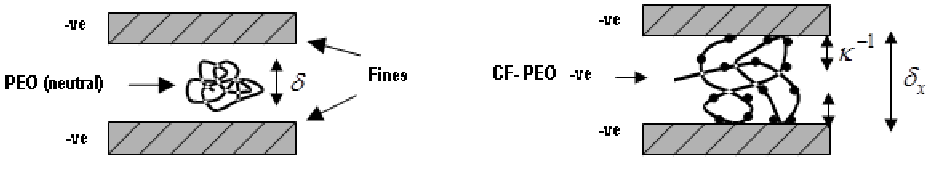
Flocculation and deflocculation of fines obtained from paper pulp were studied in the presence of polyethylene oxide (PEO) as a retention aid and different concentrations of a phenol-containing cofactor (CF). Depending on the CF concentration, significant enhancements of flocculation and deflocculation were observed. The relative floc size increased with CF addition at low concentrations, reached the maximum in the optimum zone, and then decreased to produce small flocs at high CF concentrations. The flocculation rate constant increased at first with CF concentration, plateaued in the optimum zone, and then significantly increased at higher CF concentrations. Deflocculation occurred in all experimental runs, and the reverse equilibrium constant (i.e., the ratio of deflocculation rate constant to flocculation rate constant) was about 0.408 when using PEO alone, decreased to 0.11 in the optimum zone of CF concentration, and then increased to 0.56 at high CF concentrations. These measured data on floc size and flocculation and deflocculation rate constants at different CF concentrations are useful for mills to produce paper with the desired characteristics.

KEYWORDS: Polyethylene oxide, Cofactor concentration, Flocculation, Deflocculation, Rate constants.

INTRODUCTION

Retention aids are used in papermaking to bridge fines (the fraction in pulp that could pass through a conical hole having a minimum diameter of 76 µm) with fibres and fines with fines, in order to retain fines in the paper sheet. These processes are performed at high shear rates to produce the required flocs to maintain uniform sheets. A previous work found that during fines flocculation using polyethylene oxide (PEO) with a cofactor (CF) at a high effective shear rate, a small portion of the fines was deposited on the fibres while the majority formed flocs (M. R. Abdallah, 2002). After reaching equilibrium, the flocs started to deflocculate, and the fines deposited on fibres began to leave the surfaces (B. Norman,2008; A. Carignan et al., 1998; T. G. M. van de Ven, 1994). For flocculation processes using polyelectrolyte retention aids, some researchers ascribed deflocculation to detachment by shearing and polymer breakage (R. J. Kerekes, 1995; U. Björkman, 2003; T. W. Healy, 1964; T. P. Spicer, 1996; A. N. Klomogorov, 1949; K. Higashitani et al., 1989). In fines flocculation with the CF-PEO system, deflocculation has been discussed in terms of factors related to PEO (M. R. Abdallah Qasaimeh, 2011). However, the amount of CF in the system should also play a role in fines flocculation-deflocculation. This is the focus of the present study.

Improving the flocculation of fines has been a main goal in papermaking and related research. In one study to improve the paper sheet, cellulose nanofibres (CNF) were treated with two different systems of polyvinylamine (PVA) and cationic starch (as reference). The addition of CNF improved the floc stability, minimized overdosing, increased the floc size for a given PVA dose, and improved the wet end in a paper machine (N. Merayo et al., 2017). The present author proposed using electrically neutral, high-molecular-weight PEO, instead of cationic retention aids that incorporate ions and thus have lower performances (R. H. Pelton et al., 1980; R. H. Pelton et al, 1981). Flocculation of some colloids and fines requires a sufficiently large coil size (δ) in the PEO chains to cancel the effect of electrostatic double layer thickness (κ^{-1}) and to bridge the surfaces (M. R. Abdallah, 2002), while a small δ does not induce bridging (Figure 1a). To further improve the performance of PEO, we added a CF containing phenol groups (R. H. Pelton et al., 1980; R. H. Pelton et al., 1981; C. H. Tay, T. 1982). A number of CF materials have been used in papermaking (T. G. M. van de Ven, 1997). Although these CFs and PEO alone do not adsorb on most colloids, fines, or fibres, when used in combination they adsorb on the fines and effectively bridge them (T. Lindström, 1984). One theory for particle-polymer bridging is the transient network mechanism (T. Lindström, 1984). This was argued by van de Ven and Alince (T. G. M. van de Ven, 1996) in the association-induced polymer bridging of fillers by CF-PEO, which occurs in two ways. In the first aspect, CF segments adsorbed on PEO (coil size δ) expand the PEO coils by forming a larger CF-PEO complex of size δ_x, which more effectively adsorbs on surfaces and bridges different particles. In this state, repulsion among the negatively (-ve) charged CF segments in the complex stiffens and expands the PEO coils to a size exceeding the thickness of the electrostatic double layer κ^{-1}. Thus, bridging occurs under the simultaneous conditions of $\delta_x > 2\kappa^{-1}$ and $\theta (= \Gamma/\Gamma_m) < 1$ (T. G. M. van de Ven, 1996). Here, θ is the fractional surface coverage by PEO, Γ is the PEO quantity covering the surfaces, and Γ_m is the quantity of PEO required to maintain full surface coverage (J. A. De Witt, 1992).



a-) No Bridging

b-) Bridging (Floc)

Figure 1: **Conditions and mechanism for the bridging of fines induced by CF-PEO.**

In the second way, CF segments adsorbed on PEO coils facilitate PEO adsorption on surfaces by reducing the heat of adsorption (T. G. M. van de Ven, 1996). This CF-PEO induced bridging (Figure 1b) is also active in fines flocculation (B. Norman,2008; T. G. M. van de Ven, 1997), where CF induces the PEO coils to adsorb onto fines and bridge them, even though both the CF and fines carry negative charges. One significant factor of bridging by CF-PEO is the microstate of PEO coils prior to flocculation (the entanglement size δ and the configuration), because bridging requires certain PEO dissolution conditions (M. R. Abdallah, 2002) to satisfy $\delta > 2\kappa^{-1}$ (M. R. Abdallah, 2002; J. A. De Witt, 1992). PEO entanglements usually form in the early phase when PEO granules dissolve to produce a clear aqueous solution (D. Kratochvil et al., 1999), and larger entanglements are more efficient for bridging particles (M. R. Abdallah, 2002; T. G. M. van de Ven et al., 2004). In contrast, without CF, PEO bridges particles through the asymmetric bridging mechanism. For example, PEO was found to adsorb on a class of fines in Kraft pulp, allowing the fines to adsorb onto other fines and thereby bridging the fines (A. Carignan et al., 1998; T. G. M. van de Ven, 1996). The present author and co-workers (M. R. Abdallah Qasaimeh et al., 2011) compared fines flocculation with PEO alone and with CF-PEO and found that the CF-PEO combination enhanced the flocculation efficiency and the floc size through several mechanisms. Similar results were reported in another work (M. R. Abdallah Qasaimeh, 2011).

From a kinetic point of view, fines flocculation using CF-PEO could be described by the Langmuir equation and Smoluchowski isotherm. The flocculation rate constant is assumed to be $k_0 (= \frac{4}{3} G_p \left(a_1 + a_2\right)^3)$, which is the collision rate between two spherical particles of radii a_1 and a_2 in a unit volume at a process shear rate G_p (M. R. Abdallah, 2002). When fines are deposited on fibres (heteroflocculation) using a polymeric retention aid, the deposition time in a unit volume with dominant attractive van der Waals forces is defined as $t_d (= \frac{1}{\eta\, k_o\, n_{fno}\, N_f})$. Here, n_{fno} is the initial number of fines in a unit volume of the suspension divided by the maximum number of fines that can be deposited on the fibres, N_f is the number of fibres per unit volume, and η is the deposition (flocculation) efficiency. Similarly, for the flocculation of fines of radius a among themselves (homoflocculation) under the same micro force conditions, the rate constant is $k_0 = \frac{16}{3} G_p a^3$ (M. R. Abdallah, 2002; J. Petlicki, 1992). For a given initial number of fines in a unit volume n and a flocculation efficiency η, the time needed to reduce their number at equilibrium by 1/2 is the half time $t_{1/2}$ $(= \frac{1}{\eta\, k_o\, n})$ based on the Smoluchowski theory (M. R. Abdallah, 2002; R. Gaudreault et al., 2009; B. Alince, 1999).

Because the negatively charged CF-PEO complex bridges the negatively charged fines through an induced mechanism, the bridging should have different characteristics from ionic bridging using polyelectrolytes. Here, we briefly discuss the literature to differentiate the two mechanisms and describe the PEO-induced bridging. The bridging of fines by adsorption of the CF-PEO complex depends on complex expansion, stiffness of chains, and enthalpy reduction in the adsorbent surface (T. G. M. van de Ven, 1996). CF-PEO-induced bridging is also affected by the shape and size of the complex with the necessary condition ($\delta_x > 2\kappa^{-1}$), while a higher salt content causes the PEO coils to shrink (M. R. Abdallah, 2002; T. G. M. van de Ven et al., 2007) and thus decreases δ_x; all of which affect flocculation efficiency, rate, and floc size. In contrast, ionic bridging depends on the charge difference and its magnitude, polymer coil configuration, chain charges, radius of gyration, and pH; all of which influence the flocculation rate, efficiency η, and floc size (Z. Yang et al., 2011; J. Nylund, 1994; B. Holmbom, 1995; A. Swerin et al, 1993; Z. Yang et al., 2012). Moreover, the flocculation efficiency η depends on the hydrodynamic shear rate G_p and colloidal forces. In general, η is the ratio of successful collision rate to the total collision rate k_o; $\eta = k_{att}/k_o$, where k_{att} is the attachment rate constant. When there is no ionic force, $\eta = \beta$, where β is the collision efficiency. In the case of attractive van der Waals forces, the collision rate is fast, and the collision efficiency is denoted as (β_{fast}), thus, we have $\eta = \beta_{fast}$. When the force is repulsive or attractive but not van der Waals type, the flocculation efficiency becomes a function of capture efficiency α; $\eta = \alpha\,\beta_{fast}$ (T. G. M. van de Ven, 1989). In case of CF-PEO-induced bridging satisfying $\delta_x > 2\kappa^{-1}$, the effects of electrostatic forces can be ignored, because the complex that bridges the particles is larger in size than the thickness of the zone for ionic effects. In this case, particles will be bridged and flocculation efficiency becomes equal to capture efficiency, which, as found in literature, applies $\eta = \alpha = 2\theta(1-\theta)$ (R. Hogg, 1984). In general, the attachment rate constant can be defined as $k_{att} = \eta\, k_o$, that can fit all force types and bridging mechanisms (T. G. M. van de Ven, 1989).

When using CF-PEO as a retention aid, factors affecting η can be divided into preparation and process factors. Preparation factors are related to the dissolution of PEO granules, namely the stirring rate, stirring time, PEO concentration, solution storage time, and delivery such as shear rate after storage (M. R. Abdallah, 2002; T. G. M. van de Ven et al., 2004). Increasing these parameter values causes a decrease in η, which is ascribed to the dissociation of the entangled PEO coils into smaller free segments and changes in the PEO coil configurations (M. R. Abdallah, 2002). Among the process factors, there are six important ones. First is the size of particles (such as fines and fibres) that more readily form aggregates and flocs in water (R. B.

Wasser, 1978; R. J. Kerekes, 2006; H. Yan, 2006; H. Yan et al., 2006). Second is the particle concentration (the consistency C) which determines the free space between particles. When the fibre concentration exceeds the critical fibre concentration (CFC) (M. A. Hubbe, 2007), the fibres may rotate, collide, and flocculate. Third is the amount of PEO Γ (mg/g fines) added to flocculation, which adsorbs on the surfaces to maintain coverage. It is usually divided by the maximum value necessary for a full coverage and then expressed by the fractional coverage θ (M. R. Abdallah, 2002; R. Hogg, 1984), an important parameter to flocculation efficiency (D. Kratochvil et al., 1999). Fourth is the process shear rate G_p, which affects the rate constants of particle collisions, attachment, and detachment. One work reported on the G_p effect and showed the formation of fibre flocs after a reduction in G_p (R. J. Kerekes et al., 1985; U. Björkman, 2003). Another work claimed that increasing the stirring rate reduced the flocculation rate r_f, the flocculation amplitude (floc size A), and the characteristic time of flocculation (τ) (M. R. Abdallah Qasaimeh et al., 2014). Fifth is the concentration of the added CF (C_{CF}) with respect to the fines mass in the suspension. Sixth is the CF-to-PEO ratio, which indicates the negative charge density (r_{ch}) of CF segments on the PEO coils. The joint use of CF with PEO resulted in better flocculation and particle retention (R. H. Pelton et al., 1980; R. H. Pelton, 1981; C. H. Tay, T. 1982). An important common feature of particle flocculation with PEO alone and with CF-PEO is deflocculation of the resultant flocs (transient flocculation), a behaviour noted by the present author and other researchers (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011; M. R. Wu, 2009). The present author recorded the rate and the characteristic time of deflocculation (r_d and τ_d, respectively) when using PEO (asymmetric flocculation) or CF-PEO. In both cases, deflocculation was ascribed to PEO, and increasing C_{CF} caused r_f and r_d to increase (M. R. Abdallah Qasaimeh, 2011). In another work, when using a constant PEO concentration and increasing C_{CF} within a moderate range, A, r_f, and r_d increased while τ decreased, confirming that CF enhanced flocculation and deflocculation (M. R. Abdallah Qasaimeh et al., 2014). Based on the Langmuir equation ($r_f = r_{att} - r_{\det}$), where r_{att} is the rate of particle attachment and $r_{\det}$ is the rate of floc detachment, the amount of flocs increases with time during flocculation and plateaus at equilibrium ($r_{att} = r_{\det}$ and $r_f = 0$). However, deflocculation with rate r_d after equilibrium contradicts the Langmuir equation (M. R. Abdallah Qasaimeh, 2011; M. R. Wu, 2009).

In addition to the reported results of flocculation and deflocculation in literature, their major influencing factors and effects should be further studied. As an important extension of our previous work, the objective of this work is to investigate how CF in a wide concentration range (from low to very high) affects the flocculation and deflocculation of fines. The objective is also to explore the variations in the CF-PEO complex characteristics and behaviour to bridge and flocculate particles. Notably, this aspect of fine flocculation using CF-PEO has not been reported before. To exclude the effects of other variables, we fixed the type and quantity of the added PEO, the consistency of the fines C, process shear rate G_p, and room temperature (T), while varying C_{CF}. The flocculation parameters, namely the flocculation rate (r_f) and deflocculation rate (r_d), were experimentally measured at initial flocculation and initial deflocculation after reaching equilibrium. The results would help clarify the roles of CF in CF-PEO-induced bridging, which is useful for future studies of PEO entanglement instability as well as the effects of other process factors.

2. MATERIALS AND METHODS

2.1 Materials

The materials were the same as those used in our previous works (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011). The fines were obtained after disintegration and washing of different pulps collected from Masson Maclaren Mill (Canada). Neutral PEO ($M_w = 7 \times 10^6$; Flocc 999) and the negatively charged phenolic CF material (Interac 1323) were supplied by E.QU.I.P Inc., Canada (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011). In all runs, the fines were diluted by water to a consistency of $C = 0.1\%$, and then added with a fixed amount of PEO (0.08 mg/g fines) and different amounts of CF, denoted by C_{CF} (mg/g fines).

2.2 Experimental setup

The experimental setup was also the same as that used in our previous works (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011; T. G. M. van de Ven et al., 2004; M. R. Abdallah Qasaimeh et al., 2011). The fines were added to the flocculation beaker, and flocculation runs were performed at different C_{CF} values. The following parameters were kept constant in all runs: amount of added PEO, C, Γ, G_p, N, T, and the tube shear rate (G_t). The first run was performed using PEO alone without CF (i.e, $C_{CF} = 0$, asymmetric flocculation). G_t was the shear rate on the fines stream from the beaker passing through the transparent tube into the photometric dispersion analyser (PDA) photo cell to measure the flocculation intensity (J. Gregory, 1984; Rank Brothers Ltd.). The flocculation amplitude A measured by the PDA was plotted versus time (t) as a curve to denote particle size. Flocculation amplitude A, flocculation rate r_f, characteristic time of flocculation τ, deflocculation rate r_d, and characteristic time of deflocculation τ_d were estimated in all runs.

2.3 Flocculation and deflocculation intensity readings

In each flocculation run, the ratio reading (R) was the main PDA output signal denoting the particle size A. The ratio reading R is the ratio of the alternating voltage (A_c) to the direct voltage (D_c) given by the PDA. The A_c occurs due to the voltage fluctuation resulting from flocculation, while D_c is the initial constant voltage before flocculation (J. Gregory, 1984; Rank Brothers Ltd.). The reading R was plotted versus time t by the recorder in the experiment similar to the curve drawn and shown in figure 2. After the fines in the beaker reached an initial steady state, CF was added followed by PEO. The R reading first increased with time, reaching a maximum R reading at equilibrium (having maximum amplitude A_m or maximum floc size), and then decreased due to deflocculation. The resultant curve (Figure 2) shows the maximum R reading (maximum floc size A_m) in arbitrary unit (A.U.), and the flocculation and defloccculation parameters can be measured or estimated experimentally. The initial rate of flocculation $r_f\ (= A_m / \tau)$ in A.U. is the slope of the curve at initial flocculation (M. R. Abdallah, 2002). The τ is characteristic time of flocculation, namely the time needed to reach amplitude A_m with the initial rate r_f (M. R. Abdallah, 2002). The time needed to reach equilibrium is

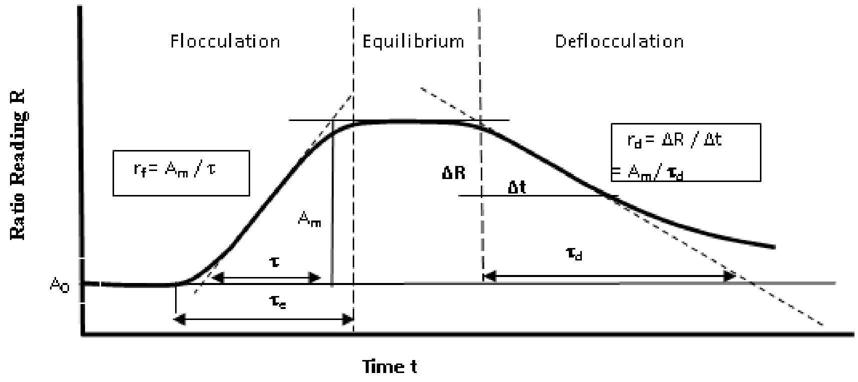


Figure 2: **Schematic illustration of flocculation and deflocculation intensity readings.**

defined as the equilibrium time (τ_e). Similarly, the slope of the curve at initial deflocculation is the initial rate of deflocculation $r_d\,(=\Delta R/\Delta t = A_m/\tau_d)$ (M. R. Abdallah Qasaimeh, 2011). The time needed after equilibrium of floc size A_m to drop to the initial particle size with an initial deflocculation rate r_d is the characteristic time of deflocculation (τ_d) (M. R. Abdallah Qasaimeh, 2011). The actual deflocculation time needed to reach the initial size of fines was recorded very long in all runs so deflocculation curve does not end with A_o. Since the raw data depend on the measurement devices used, we normalised flocculation and deflocculation parameters by the corresponding optimum values to facilitate comparison to other studies: if X is the measured value and X_{opt} is its optimum, then the normalised value is $X_r\,(=X/X_{opt})$.

3. RESULTS AND DISCUSSION

A number of factors affecting the flocculation of fines have been mentioned in the literature. Among them, this work focuses on the amount of added CF (the C_{CF}) and its effect on flocculation and deflocculation. Previous studies on PEO-based flocculation systems (including our own work) demonstrated the necessity of adding CF to PEO, the occurrence of deflocculation (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011; M. R. Abdallah Qasaimeh et al., 2014), and the production of small flocs at excess C_{CF} (M. R. Wu, 2009). To further clarify the role of CF, here we conducted fines flocculation at C_{CF} values in a wide range of 0–1.2. Upon increasing C_{CF}, the key parameters in fines flocculation and deflocculation displayed specific trends, which allowed us to divide the studied C_{CF} range into three subzones, namely Z_1 = 0–0.18, Z_2 = 0.18–0.55, and Z_3 = 0.55–1.2.

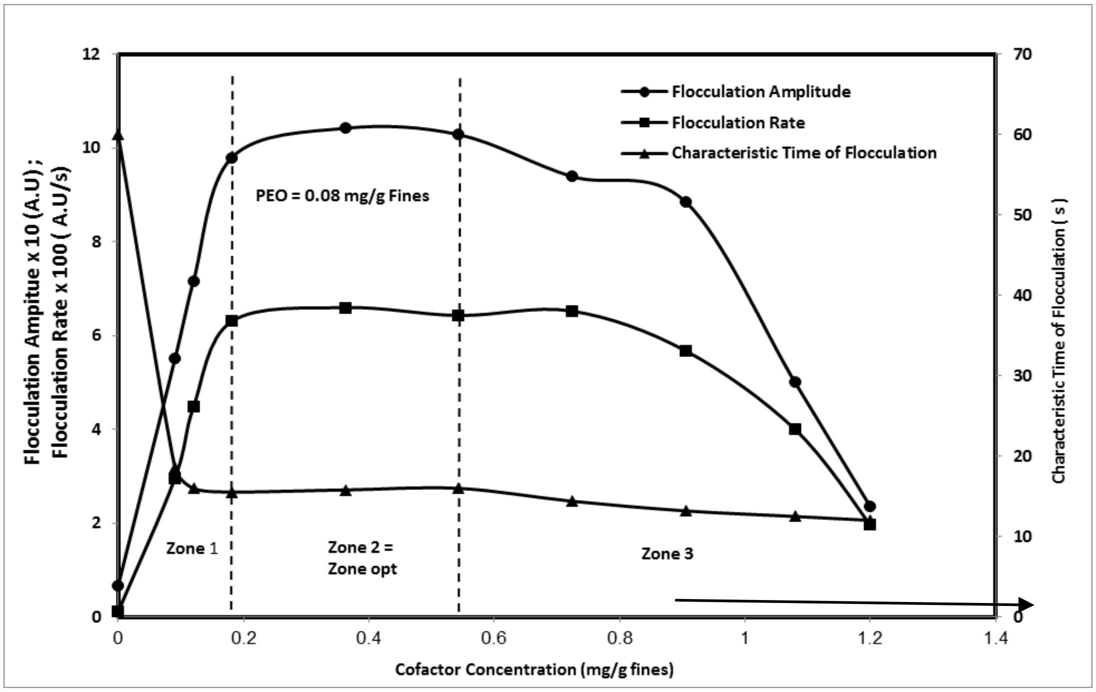


Figure 3: **Division of the cofactor concentration C_{CF} into three zones according to the measured flocculation parameters.**

According to Figure 3, parameters A, r_f, and τ show the following trends with increasing C_{CF} in the entire range. The floc size A and flocculation rate r_f increase significantly in Z_1 (acceleration zone) and reach the maximum at C_{CF} = 0.18. Meanwhile, the characteristic time τ drops drastically (fast flocculation) at first and reaches the minimum at C_{CF} = 0.18. Z_2 is called the optimum zone (Z_{opt}) because the parameters have optimum values of $A(=A_{opt})$, $r_f\,(=r_{f\,opt})$, and $\tau\,(=\tau_{opt})$ (Figure 3). In Z_3 (excess CF), A, r_f, and τ start to decrease, while the system displays small flocs and faster flocculation. These results agree with those reported by Wu and van de Ven (M. R. Wu, 2009). In our first run at $C_{CF}=0$ (asymmetric bridging), smaller flocs and lower r_f values were obtained compared with all runs with CF-PEO-induced bridging. Deflocculation was also characterized by measuring r_d and τ_d in all runs, in agreement with previous works (M. R. Abdallah, 2002; M. R. Abdallah Qasaimeh, 2011; M. R. Abdallah Qasaimeh et al., 2014). As mentioned earlier, the flocculation parameters in all runs were reported as relative values. We defined flocculation rate in terms of the flocculation rate constant $k\,(=1/\tau)$, where τ was measured experimentally as shown in Figure 2. In the optimum zone Z_{opt}, k = $k_{opt}\,(=1/\tau_{opt})$. We also defined the relative flocculation rate constant $k_r = (k/k_{opt})$, which gives $k_{r\,opt}(=1)$ in Z_{opt}.

For a flocculation run conducted at a given C_{CF} value and fixed parameters (C, Γ, G_p, N, T, and G_t), k_r can be expressed as

$$k_r = \frac{k}{k_{opt}} = \frac{\tau_{opt}}{\tau} = \frac{t_{1/2\,opt}}{t_{1/2}} = \frac{(1/\eta\, k_o\, n)_{opt}}{(1/\eta\, k_o\, n)} = \frac{\eta\, n}{\eta_{opt}\, n_{opt}} = \eta_r\, n_r \qquad (1)$$

where η_r is the relative flocculation efficiency, and n_r is the relative number of particles.

Similarly, at a given C_{CF} the relative floc size is

$$A_r = (A/A_{opt}) \qquad (2)$$

where $A_{r\,opt}(=1)$ since $C_{CF} \in Z_{opt}$.

Figure 4 plots the measured A_r and k_r values as functions of C_{CF}. For the first run conducted at $C_{CF} = 0$, we have $A_r = A_{r0} = 0.064$. Further, $A_r < 1$ in Z_1 and Z_3, $A_r = A_{r\,opt} = 1$ in Z_{opt}, and at $C_{CF} = 1.2$ we have $A_r = 0.225$.

Similar trends were observed for k_r, n_r, and η_r. Specifically, k_{r0} = 0.262 when $C_{CF} = 0$, $k_r = \eta_r\, n_r$ in zones Z_1 and Z_3, and $k_{r\,opt} = \eta_{r\,opt} = n_{r\,opt} = 1$ in Z_{opt}. Moreover, we used magnification (M) to describe the ratio of the same parameter between two different runs or cases. Considering the role of CF in expanding PEO entanglement to induce bridging and the effect of very high C_{CF} on the floc size, the trends in Figure 4 may also originate from the size of

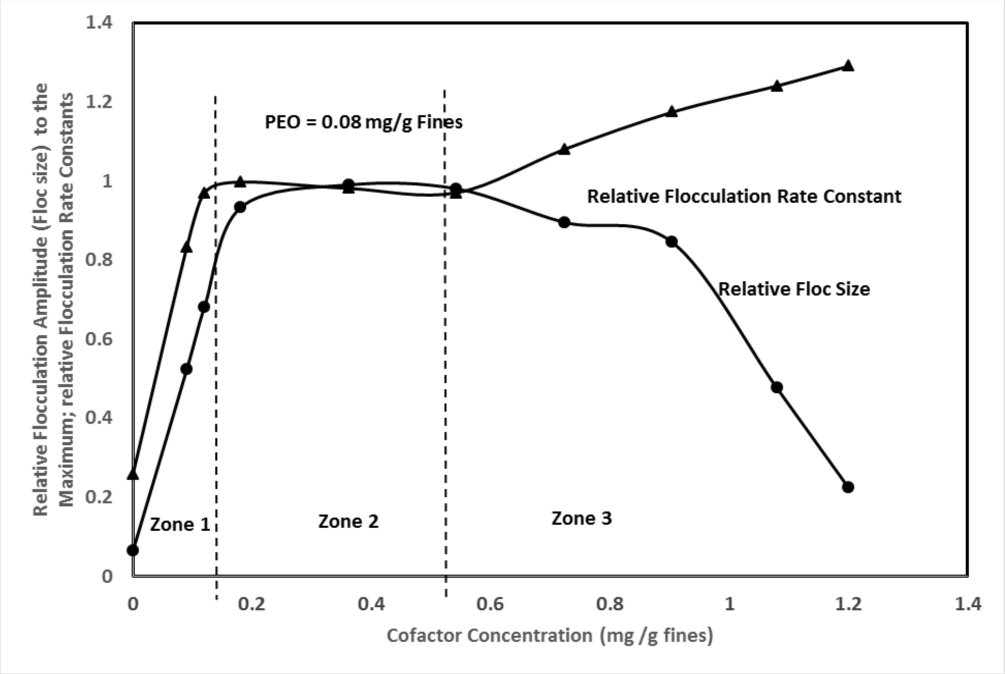


Figure 4: **Effect of C_{CF} on the relative floc size and relative flocculation rate constant.**

the CF- PEO complex. The maximum floc size in Z_{opt} also corresponds to the maximum size of the CF-PEO complex. The size change can also be described in terms of *M*, usually relative to the first run without CF ($C_{CF}=0$). One important case is the floc size magnification. When using CF-PEO within Z_{opt} (Figure 4), there is a largest magnification of $M_{Aopt}=A_{ropt}/A_{r0}=15.63$ all over the wide range. This largest magnification is mostly likely due to the largest size of the CF-PEO complex compared with that of other complexes in other zones and with initial PEO entanglement size at $C_{CF}=0$. One important feature of zone Z_3 is the relative floc size at $C_{CF}=1.2$ ($A_r=0.225$), which is larger than that at $C_{CF}=0$ ($A_{r0}=0.064$, with $M_A=0.225/0.064=3.52$). This indicates that flocculation continues at $C_{CF}>1.2$ but with smaller flocs. In general, the floc size magnification is $M_{Aopt}=15.63$ in Z_{opt} and $1<M_A<15.63$ in Z_1 and Z_3. The magnifications at even higher CF concentrations $(C_{CF}>1.2)$ could be studied in future work.

We also calculated the magnification of the flocculation rate constant $M_k\ (=k_r/k_{r0})$ using the data from Figure 4. In Z_{opt} with the optimum C_{CF}, M_k reached a maximum value of 1/0.262 =

3.82. Within Z_3, the flocculation rate constant increased significantly upon increasing C_{CF}, reaching $M_k = 1.31/0.262 = 5$ at $C_{CF} = 1.2$.

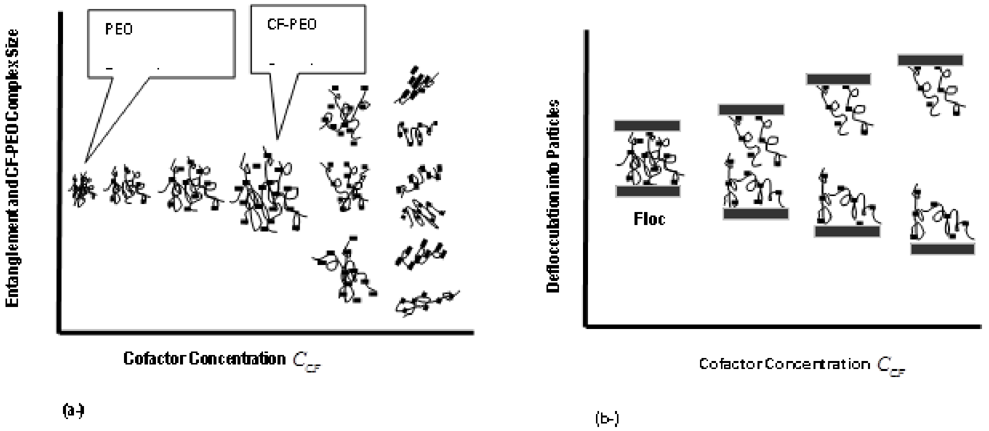


Figure 5: **Schematic effect of C_{CF} on (a) size of the CF-PEO complex and (b) deflocculation.**

The calculated changes in floc size as a function of C_{CF} (as indicated by A_r and M_A) are in agreement with those of the floc and complex sizes reported by Meng et al (M. R. Wu, 2009). Additionally, the formation of flocs and their growth in size are ascribed to the expansion of PEO entanglement due to the stronger repulsive forces induced by the CF segments adsorbed on the PEO coils (T. G. M. van de Ven, 1996). In this work, we found smaller flocs at excess $C_{CF} \in Z_3$, and reference (M. R. Wu, 2009) also reported smaller complexes formed at high C_{CF}. These two sets of results (Figure 5a) indicate that dissociation of PEO entanglement in the suspension can be related to reduced transient interactions among PEO coils (M. R. Abdallah Qasaimeh, 2011), and it is enhanced by the stronger repulsive forces induced by CF segments

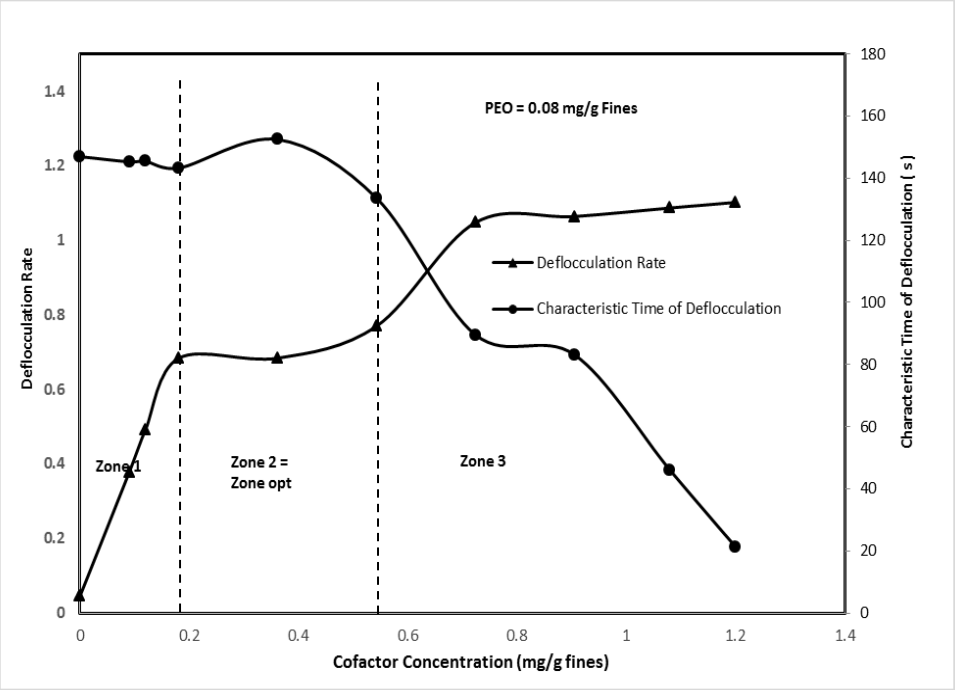


***Figure 6:* Effect of C_{CF} on deflocculation dynamics in fines flocculation.**

adsorbed on PEO coils. The resultant small complexes contain abundant CF adsorbed on PEO coils, and therefore they can bridge small fines to produce small flocs.

In addition to flocculation, we studied deflocculation as a function of C_{CF}. Both flocculation and deflocculation occurred in the same run having the same maximum amplitude A_m at equilibrium. The floc size in flocculation rises to A_m at equilibrium and then starts deflocculation with a decrease in size from A_m. As shown in Figure 6, r_d initially increased significantly and τ_d decreased slightly as C_{CF} increased within Z_1, both parameters plateaued in zone Z_{opt}, and then r_d increased significantly and τ_d decreased drastically in zone Z_3. These results agree with previous reports including those by Meng et al. (M. R. Wu, 2009) and the current author (M. R. Abdallah Qasaimeh, 2011). Deflocculation is seemingly occurring (Figure 5b) in a manner similar to the dissociation of the CF-PEO complex in suspension at high C_{CF}, but with some additional repulsive forces from the negatively charged fines in the floc. It has been proposed that deflocculated fines become separated, with some CF-PEO complexes flattened on their surfaces (T. G. M. van de Ven, 1994; T. G. M. van de Ven, 1996; A. Carignan, 1996; K. R. Stack et al., 1991). Results in this work confirm that deflocculation is caused by a decrease in the transient interactions of PEO entanglement in flocs as time progresses. The CF adsorbed on PEO coils acts in several stages. First, it induces repulsive forces among the PEO coils to expand the entanglement. Next, it induces bridging between fines to produce flocs. In a floc, the induced repulsive forces, the decreasing interaction among PEO coils, and the repulsion among fines all contribute to deflocculation. Similarly, we define the following three deflocculation parameters at a given C_{CF}: (1) the dynamic rate of deflocculation by the deflocculation rate constant $k_d\ (=\frac{1}{\tau_d})$, (2) the corresponding relative deflocculation rate constant $k_{d\,r}\ (=\frac{k_d}{k_{d\,opt}}=\frac{\tau_{d\,opt}}{\tau_d})$ against the optimum value, and (3) the reverse equilibrium rate constant (K_{-equ}) defined as the ratio of the deflocculation rate constant to the flocculation rate constant. Using $k\,(=\frac{1}{\tau})$, K_{-equ} can be rewritten as

$$K_{-equ}\ (=\frac{k_d}{k})=\frac{\tau}{\tau_d}=\frac{r_d}{r_f} \qquad (3)$$

Figure 7 plots r_f, r_d, and K_{-equ} versus C_{CF}. In all runs at different C_{CF} values, the parameters can be analysed by K_{-equ}, since it is the ratio between r_d and r_f. From Figure 7, when there is only PEO (C_{CF} = 0), K_{-equ} has a higher value (0.408) than that in zone Z_1. K_{-equ} decreases when C_{CF} exceeds 0, indicating a faster deflocculation during asymmetric flocculation. Within Z_{opt}, K_{-equ} has a constant minimum value $(K_{-equ\,opt}=0.11)$ regardless of C_{CF}, corresponding to the slowest deflocculation. Within Z_3, K_{-equ} increases drastically upon increasing C_{CF} and reaches a maximum value of 0.562 at $C_{CF}=1.2$, indicating the fastest deflocculation in the studied C_{CF} range.

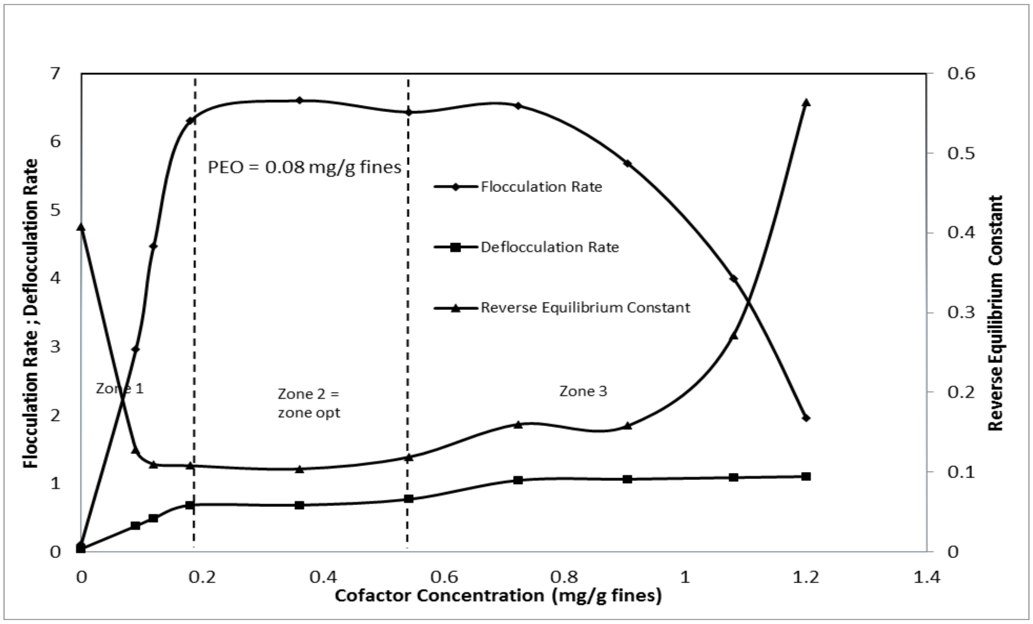


Figure 7: **Effect of C_{CF} on the flocculation rate, deflocculation rate, and the reverse equilibrium constant (i.e., deflocculation rate constant/flocculation rate constant).**

According to Figures 6 and 7, increasing C_{CF} enhances deflocculation, and the cause is ascribed to the transient state of PEO coils that confirms the results in Reference (M. R. Abdallah Qasaimeh, 2011). Paper mills that aim to enhance flocculation and minimize deflocculation should select a suitable C_{CF} value, and the equilibrium time τ_e, the maximum floc size A_m, and the operation cost should also be considered when characterizing the flocculation process. One such characterization method was proposed in our previous work (M. R. Abdallah Qasaimeh, 2012), and mill operators could adopt an appropriate method to optimize the process performance. Another important contribution of this work is measuring the key parameter values (mainly the floc size, the flocculation and deflocculation rate constants, and the reverse equilibrium constant) in a wide range of CF concentration. These data provide additional guidance for choosing the amount of CF addition to satisfy the requirements in practical operations.

4. CONCLUSIONS

We measured key parameters describing the flocculation and deflocculation of fines in the CF-PEO system at a fixed PEO concentration and a wide range of CF concentrations (C_{CF}). The studied C_{CF} range was divided into three zones according to the trends of the measured parameters. We proposed the relative floc size as a useful parameter and investigated the rate constants of dynamic flocculation and deflocculation at different C_{CF} values. The results confirmed previously reported mechanisms of CF in bridging fines and enhancing fines flocculation (namely, by expanding the PEO entanglement to produce larger CF-PEO complexes). These experimental data shall also aid mill operators in choosing the suitable conditions to achieve the desired performance and avoid unwanted effects.

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