

### NEW ANALYTICAL PARAMETERS AND BEHAVIORS OF FLOCCULATION AND DEFLOCCULATION OF THE FINES USING CONSTANT POLYETHYLENE OXIDE WITH VARIABLE COFACTOR IN WIDE RANGE CONCENTRATION USEFUL FOR RETENTION IN MILL

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#### ABSTRACT

In fines flocculation, our previous study showed the dependence of the cofactor (CF)- polyethylene oxide (PEO) retention aid performance on the cofactor concentration ( $C$ ) in wide range. Deflocculation occurred as a reverse process in all flocculation runs at different cofactor concentrations including PEO alone and flocculation and deflocculation parameters were found. In this work, we have analyzed the cofactor concentration effect and found the values of the significant parameters and concentrations that describe the CF-PEO retention aid behavior. We have determined the values of the flocculation, deflocculation, equilibrium, reverse

equilibrium rate constants; and floc size and flocculation dynamic magnifications. For more, significant important CF concentrations (points) such as asymmetric point, optimum cofactor concentration, critical cofactor concentration, the equal flocculation and deflocculation rate constant point, deflocculation acceleration point, and asymmetric dynamic point have been determined. These parameters and significant points are important to describe the CF-PEO retention aid behavior in research and in mill.

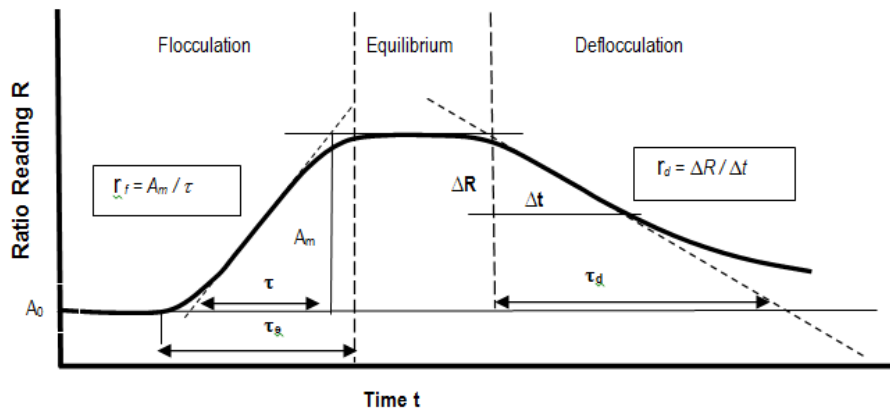
**KEYWORDS:** Polyethylene oxide, Cofactor, Retention aids, Flocculation, Deflocculation, Rate constant, equilibrium constant, reverse equilibrium constant.

## INTRODUCTION

The conventional cofactor (CF)-polyethylene oxide (PEO) retention aid is used in many industrial applications, one is retention of particles such as fillers, fines and fibers at high shear rates into a paper sheet in papermaking (Abdallah, Mohammad. R., 2002). The PEO alone can bridge some particles but becomes more effective when accompanied with a cofactor (Abdallah, Mohammad. R., 2002; Bjorkman., 2003). One feature of flocculation shown was deflocculation of the resulted flocs and departure of the deposited fines from fibers; this feature took the attention of the workers (Norman, B., 2008; Carignan, A. et al., 1998; van de Ven, T.G.M. 1994). In previous works, and in fines flocculation using CF-PEO system (the CF-PEO induced bridging mechanism) and flocculation using PEO alone (the asymmetric bridging mechanism), the deflocculation cause was ascribed to factors in PEO (Abdallah Qasaimeh, M.R. 2011). This ascription is in agreement with the results showing the instability of PEO entanglement with storage time, where the PEO coils entangle after PEO granules dissolution and then disentangle with time that affect the PEO coils capture efficiency to bridge particles (Abdallah, Mohammad. R., 2002). Some others worked on flocculation used polyelectrolyte retention aids and ascribed deflocculation to shear rate detachments and polymer breakages (Jacquelin, G., 1968; Healy, T. W. et al., 1964; Spicer, T. P. et al., 1996; Klomogorov, A. N., 1949; Higashitani, K., 1989). One problem in using cationic polyelectrolyte retention aids was the ion interactions and neutral PEO used as an alternative (Pelton, R.H. et al., 1980; Pelton, R.H. et al., 1981). Various types of CF used in literature to enhance PEO performance (van de Ven, T.G.M., 1997) have a phenol group (Pelton, R.H. et al., 1981; Noemi, Merayo et al., 2017; Tay, C.H. et al., 1982) and do not adsorb on most colloids (i.e latex particles as fillers), fines, and fibers as claimed by Lindstrom and coworkers (Lindström, T. et al., 1984 a; Lindström, T. et al., 1984 b) but adsorbed with PEO combination. The mechanism of retention of these particles was a matter of study, one was the network theory, which was fail as no evidence was shown for retention aids using the dynamic light scattering (Polverari, M. et al., 1996; Polverari, M. et al., 1994) and their flow through packed beds (Picaro, T. et al., 1995). The network mechanism was argued by van de Ven, T.G.M. and Alinec, B. (van de Ven, T.G.M. et al., 1996) who proposed the association-induced polymer bridging mechanism. In one way, the negative CF segments adsorb on PEO coils (of size  $\delta$ ), and expand and stiffen the coils by CF repulsion into the larger CF-PEO complexes of size  $\delta_x (> \delta)$ ,

which effectively adsorb on surfaces and bridge the particles. In second way, the association-induced polymer bridging proposed that the adsorbed CF segments on PEO coils reduce the adsorption heat into adsorption zone that assists for PEO adsorption on the surfaces (van de Ven, T.G.M. et al., 1996). In either way the size  $\delta_x$  is larger than the electrostatic double layer thickness ( $\kappa^{-1}$ ) on the surfaces, thus eliminating the surfaces repulsion and bridging them. The bridging to be satisfied requires two conditions;  $\delta > 2\kappa^{-1}$  and  $\theta < 1$ , where  $\theta (= \Gamma/\Gamma_{\max})$  is PEO fractional coverage on surfaces (De Witt, J.A. et al., 1992), here ( $\Gamma$ ) is PEO quantity covering the surface and ( $\Gamma_{\max}$ ) is the PEO quantity at full monolayer coverage. In bridging using PEO alone, the asymmetric bridging occurred as a result of PEO adsorption on one class of particles that facilitate for flocculation with other particles the cases happened in flocculation of fines (Carignan, A. et al., 1998; van de Ven, T.G.M. et al., 1996; Abdallah/Qasaimeh, M.R. et al., 2011) and of fillers (Abdallah, Mohammad. R., 2002). In CF-PEO induced bridging, the CF makes PEO to adsorb on fines, and some particles with a larger complex ( $\delta_x > \delta$ ) that makes flocculation more efficient (Abdallah Qasaimeh, M.R. 2011; Pelton, R.H. et al., 1981; Tay, C.H. et al., 1982). The CF-PEO induced bridging and the asymmetric bridging are well described in previous work with the affecting factors (Mohammad Raji Abdallah Qasaimeh, 2022). The flocculation efficiency ( $\eta$ ) was claimed governed by the mainly two parameters  $\theta$  and  $\delta$  (or  $\delta_x$  with CF addition) and was well correlated by  $\eta = 2\theta(1-\theta)$  (Hogg, R., 1984). Number of factors affect flocculation efficiency  $\eta$ ; former factors ones prior to flocculation and process factors during flocculation (Abdallah Qasaimeh, M.R. 2011). The former factors usually occur during PEO granules dissolution (Abdallah, Mohammad. R., 2002) like stirring rate and time, the concentration and dilution of PEO, and PEO solution shearing during addition (Abdallah, Mohammad. R., 2002; van de Ven, T.G.M. et al., 2004). The former factors usually affect the PEO coils entanglement microstate; the coil configuration and the coil size  $\delta$ . In other hand, the mainly process factors are the particle type (Wasser, R.B., 1978; Kerekes, R. J., 2006; Yan, H. et al., 2006 a; Yan, H. et al., 2006 b), concentration (consistency) of fines (Hubbe, 2007), room temperature ( $T$ ), process shear rate ( $G_p$ ) (stirring rate  $N$ ) (Bjorkman, 2003; Jacquelin, G., 1968; Abdallah/Qasaimeh, M. R. 2014), the PEO addition  $\Gamma$  (Abdallah, Mohammad. R., 2002; Hogg, R., 1984; Meng R.Wu et al., 2009) and the CF concentration  $C$  (Pelton, R.H. et al., 1980; Tay, C.H. et al., 1982; Abdallah/Qasaimeh, M.R. et al., 2011). To study the effect of a definite parameter on flocculation, the flocculation runs will be performed at different values of the

definite parameter, while the all other parameters will be kept constants. The output signals of flocculation experiment, mainly are the flocculation intensity taken as a ratio reading ( $R$ ). This  $R$  reading is recorded and plotted (Fig.1) versus time ( $t$ ) to estimate after reaching equilibrium the floc size ( $A$ ), initial rates of flocculation ( $r_f$ ), characteristic time of flocculation ( $\tau$ ) and



**Figure 1: The flocculation and deflocculation intensity readings and parameters.**

Flocculation efficiency  $\eta$ . Deflocculation always appears after equilibrium at maximum floc size  $A (= A_m)$  and flocculation equilibrium time ( $\tau_e$ ). Deflocculation intensity is also shown (Fig.1) to estimate deflocculation rate ( $r_d$ ) and characteristic time of deflocculation ( $\tau_d$ ). In both induced and asymmetric flocculation bridging and after equilibrium, the deflocculation was recorded by number of workers (Abdallah Qasaimeh, Mohammad, et al., 2020) and by us (Abdallah Qasaimeh, M.R. 2011) with a deflocculation rate  $r_d$  and the characteristic time of deflocculation  $\tau_d$ . For more, increases in CF at low additions with constant PEO caused  $r_f$  and  $r_d$  to increase (Abdallah Qasaimeh, M.R. 2011), while higher CF additions at moderate values caused  $A$ ,  $r_f$  and  $r_d$  to increase and  $\tau$  to decrease resulting faster flocculation (Abdallah/Qasaimeh, M. R. 2014). Most of research work in literature concentrated on the PEO and CF mechanisms and concentrations. The CF concentration showed various characteristics in literature and in our works. In our previous work (Mohammad Raji Abdallah Qasaimeh, 2022), we studied the effect of CF concentration  $C$  and got number of results. All runs at different  $C$  values showed a transient flocculation process in equilibrium with deflocculation. Number of new parameters were found, mainly flocculation rate constant ( $k_f$ ), deflocculation rate constant ( $k_d$ ), equilibrium constant ( $K_{eq}$ ), reverse equilibrium constant ( $K_{-eq}$ ), and other parameters defined

and determined (Mohammad Raji Abdallah Qasaimeh, 2022). These parameters were expressed in a general form as  $(X)$  relative to optimum value  $(X_{opt})$  as  $X_r (= X/X_{opt})$ , and relative to initial value  $(X_o)$  like  $X = M_x X_o$  where  $(M_x)$  is the magnification of  $X_o$ .

Now based on the results of flocculation works in literature, results of our previous works, and results of our previous work (Mohammad Raji Abdallah Qasaimeh, 2022) that explored the CF role in a wide CF concentration range in fines flocculation using a constant addition of PEO, the objective of this work is to determine the kinetic behaviors of the transient flocculation-deflocculation processes in a wider concentration range of CF, and determine the characteristics of the resulting CF-PEO complexes and flocs.

## Experimentation

### Materials

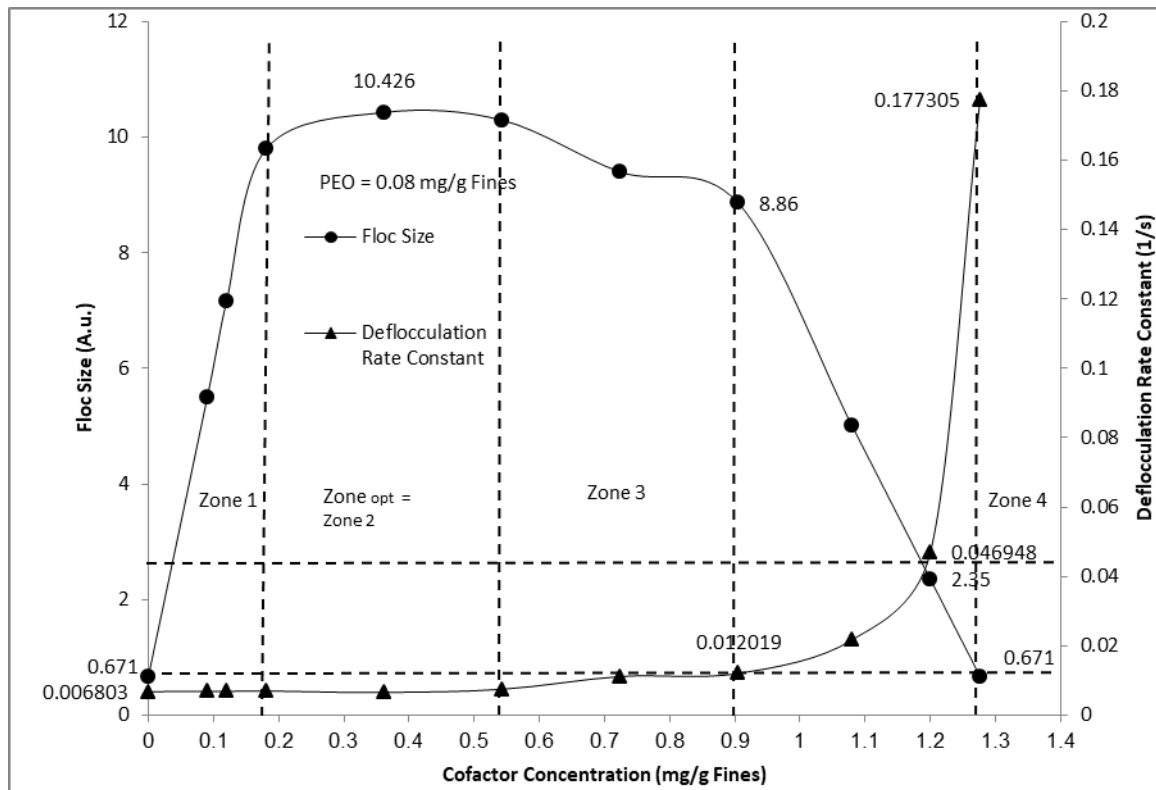
In flocculation experiments in this work, the materials used are the same used in previous works. Mainly this work is an extension of our previous work (Mohammad Raji Abdallah Qasaimeh, 2022). Neutral PEO (Flocc 999) of 7 million molecular weight and a cofactor (Interac 1323) of a negative phenol were supplied by I.Q.U.I.P Inc, Canada (Abdallah, Mohammad. R., 2002; Mohammad Raji Abdallah Qasaimeh, 2022) are used in this work. The fines were obtained from different pulps of Masson Maclaren Mill - Canada, disintegrated and washed before use.

### Experimental Setup

The experimental setup used is the same used in previous works (Abdallah Qasaimeh, M.R., 2011; Mohammad Raji Abdallah Qasaimeh, 2022; Gregory, J., 1984). Flocculation runs were performed in a beaker at different CF concentration  $C$  values and fixed PEO, while the other parameters were kept constants. In each run, the CF was added after the fines addition to the beaker at consistency of  $C_{fn}$  ( $=0.1\%$ ), followed with 0.08 mg/gm-fines PEO addition as used in a mill. Process shear rate  $G_p$  was at  $N = 118$  (*r.p.m*) and room temperature  $T$  was constant. The fines stream was pumped at a constant tube shear rate  $G_t$  ( $=287 s^{-1}$ ) from the beaker via a transparent tube to pass the cell of the Photometric Dispersion Analyzer (PDA) to measure flocculation intensity (Rank Brothers Ltd., PDA 2000; R. G. Kerekes, 1983). The  $G_t$  was low enough not to break the flocs rather than the extensional effect occurred at the tube entrance (R. G. Kerekes., 1983), the tube diameter was to fit PDA cell.

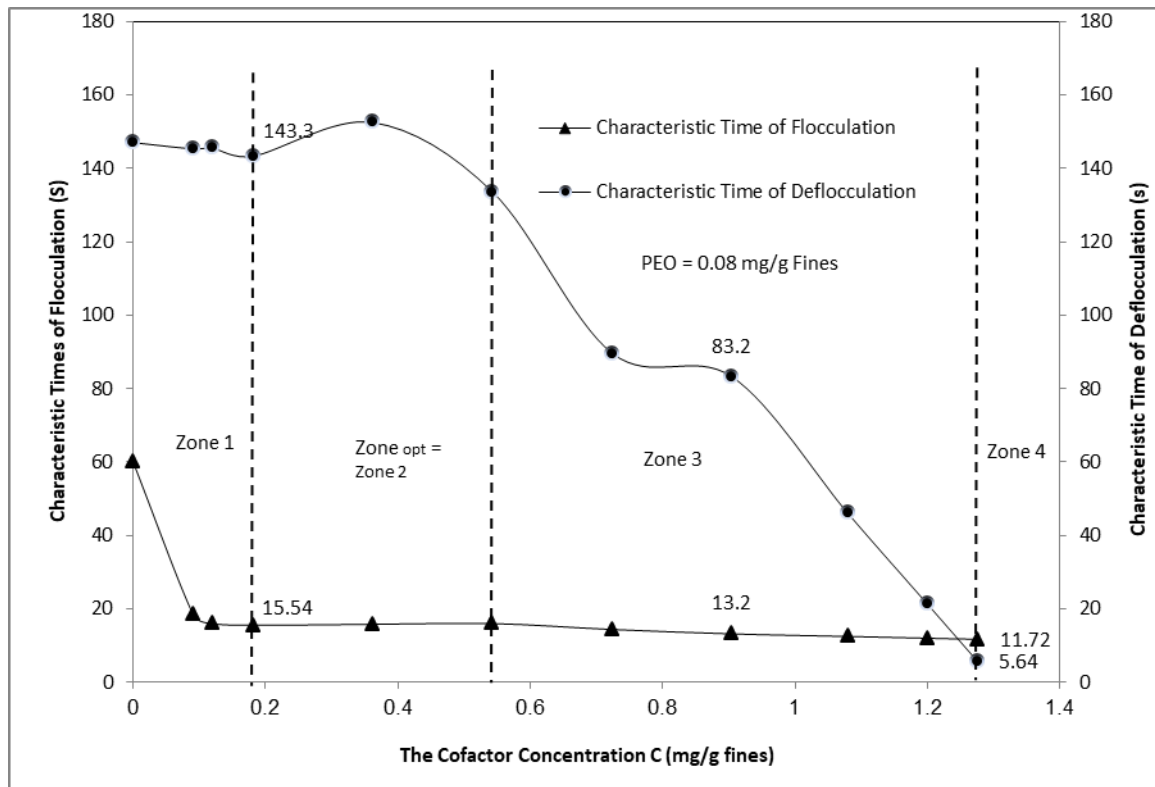
## RESULTS AND DISCUSSION

This work is a continuation of our previous work (Mohammad Raji Abdallah Qasaimeh, 2022), using same experimental set up, materials, procedure and settings. The objective of the previous work (Mohammad Raji Abdallah Qasaimeh, 2022) was to study the effect of cofactor concentration  $C$  on fines flocculation in the wide CF range  $TR(0 \leq C \leq 1.2)$ . The objective in this work was to find out new parameters by analyzing the kinetic behaviors of fines flocculation with changes in  $C$ . We took the results of the runs in (Mohammad Raji Abdallah Qasaimeh, 2022) and added some complementary work to get sufficient results to kinetic analysis and all flocculation process parameters were fixed constants except the  $C$  was a variable. The CF was not added  $C_o (= C = 0)$  in the first run, while PEO was added at 0.08 mg/g fines as used in papermaking mills maintaining asymmetric bridging (van de Ven, T.G.M. et al., 1996) with a floc size (denoted by  $A_o$ ) in arbitrary unit (A.U.). In all other runs, different values of CF addition  $C$  (mg CF/g fines) were added first, followed with constant (0.08 mg/g fines) PEO addition to imply the CF-PEO induced bridging (van de Ven, T.G.M. et al., 1996) flocculation. The flocculation runs were performed in the wide range of CF concentrations  $TR(0 \leq C \leq 1.276)$  comprising both asymmetric and CF-PEO induced bridging. The floc size in previous work (Abdallah Qasaimeh, M.R, 2011; Mohammad Raji Abdallah Qasaimeh, 2022) and by others (Abdallah Qasaimeh, Mohammad, et al., 2020) was reported to increase to get large at low CF concentration  $C$  values and then got smaller as  $C$  increases to higher. We have extended the  $TR$  to end at  $C=1.276$ , where the floc size was found equal to the initial asymmetric size  $A_o (=0.671)$ , and called  $C=1.276$  the critical cofactor concentration ( $C_c$ ) at which the floc size is critical  $A_c (= A_o)$ . The  $C_c$  was about seven times the normal CF addition (0.18 mg/g fines) in papermaking and as recommended. Deflocculation occurred in all flocculation runs and as the resulted parameters varied with  $C$  in  $TR$ . The range of  $TR$  was divided into ( $Z$ ) zones to study precise variable parameter behaviors.



**Figure 2: The effect of cofactor concentration on floc size and on deflocculation rate constant in the wide range of cofactor concentration.**

These zones (Fig. 2) are  $Z_1$  ( $0 < C < 0.18$ ), the optimum zone  $Z_{opt}$  ( $=Z_2=0.18 \leq C \leq 0.55$ ) as in previous work (Mohammad Raji Abdallah Qasaimeh, 2022), while  $Z_3$  ( $0.55 < C \leq 1.276$ ) and  $Z_4$  ( $C > 1.276$ ) are modified in this work. The resulted values of  $A$  (Fig.2) show the floc size variations with  $C$  for all runs. The smallest floc size is the initial ( $A=A_o$ ) at no CF addition, while after CF addition the floc size  $A$  started to increase with increases in  $C$  and becomes maximum ( $A_{opt}$ ) at optimum concentration ( $C_{opt}$ ). More increase in  $C$  ( $>C_{opt}$ ), the floc size started to decrease reaching the minimum  $A_c$  ( $=A_o$ ) at high  $C_c$ , a result in agreement to literature (Abdallah Qasaimeh, M.R, 2011; Mohammad Raji Abdallah Qasaimeh, 2022; Abdallah Qasaimeh, Mohammad, et al., 2020). In addition to floc size increase with  $C$ , the magnitudes of these increases vary along  $TR$  zone (Fig.2) and can be measured in term of magnification  $M_A$  ( $=A/A_o$ ) as shown Fig.6). The magnification of floc size  $M_A$  ( $=1$ ) at  $C_o$  or initial floc size and then varies with changes in  $C$  to  $M_A=15.54$  at  $C_{opt}$  in  $Z_{opt}$ , decreases to  $M_A=13.2$  at

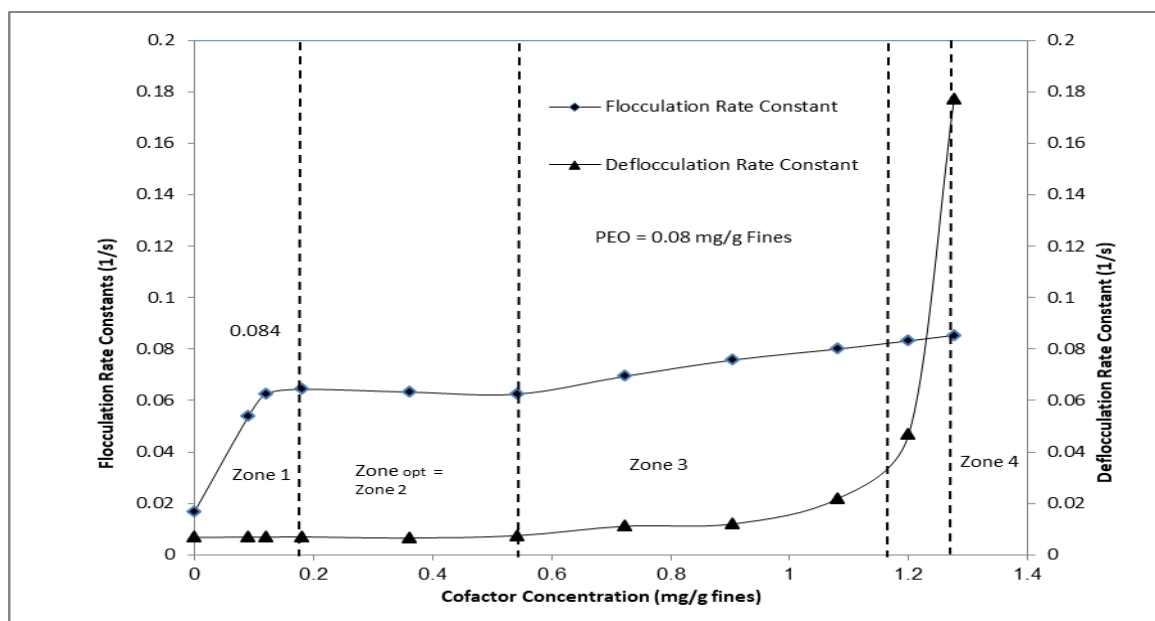


**Figure 3: The effect of cofactor concentration on the characteristic times of flocculation and deflocculation, the PEO addition was 0.08 mg/g fines for all runs.**

$C = 0.9$  and then to  $M_A = 1$  at  $C_c = 1.276$  in  $Z_3$ . At higher values of  $C (> C_c)$  in  $Z_4$  and from curve extension (Fig.2), the floc size values are to decrease to values lower than the initial floc size ( $A < A_o$ ) and CF addition can be supposed as a dispersion agent. Accompanied to flocculation is deflocculation occurring in all runs in  $TR$ , and in each run the characteristic times of flocculation  $\tau$  and of deflocculation  $\tau_d$  were varied with  $C$  and measured. Flocculation rate constant  $k_f (=1/\tau)$  and deflocculation rate constant  $k_d (=1/\tau_d)$  were estimated since they are important parameters in flocculation rate  $r_f = f(k_f)$  and deflocculation rate  $r_d = f(k_d)$ . To find out the effect of  $C$ , we have plotted  $A$  and  $k_d$  (Fig. 2);  $\tau$  and  $\tau_d$  (Fig.3); and  $k_f$  and  $k_d$  (Fig.4) versus  $C$ . The larger the  $A$  value is the larger the floc size, and the lower the  $\tau$  or  $\tau_d$  values is the faster the flocculation or delocculution respectively. Results (Fig.3) show that  $\tau$  decreased drastically with the increase in  $C$  and becoming  $\tau = \tau_{opt} (=15.5 s)$  at  $C_{opt}$  in  $Z_{opt}$ , showing faster flocculation. At higher  $C$ , the  $\tau$  shows more slight decrease and ends to the lowest value at  $C_c (=1.276)$ , the fastest flocculation. In other hand, the decrease in  $\tau_d$  (Fig.3) is shown slight at low  $C$  values in  $Z_1$  up to  $Z_{opt}$  and then starts to decrease in  $Z_3$  with the increase



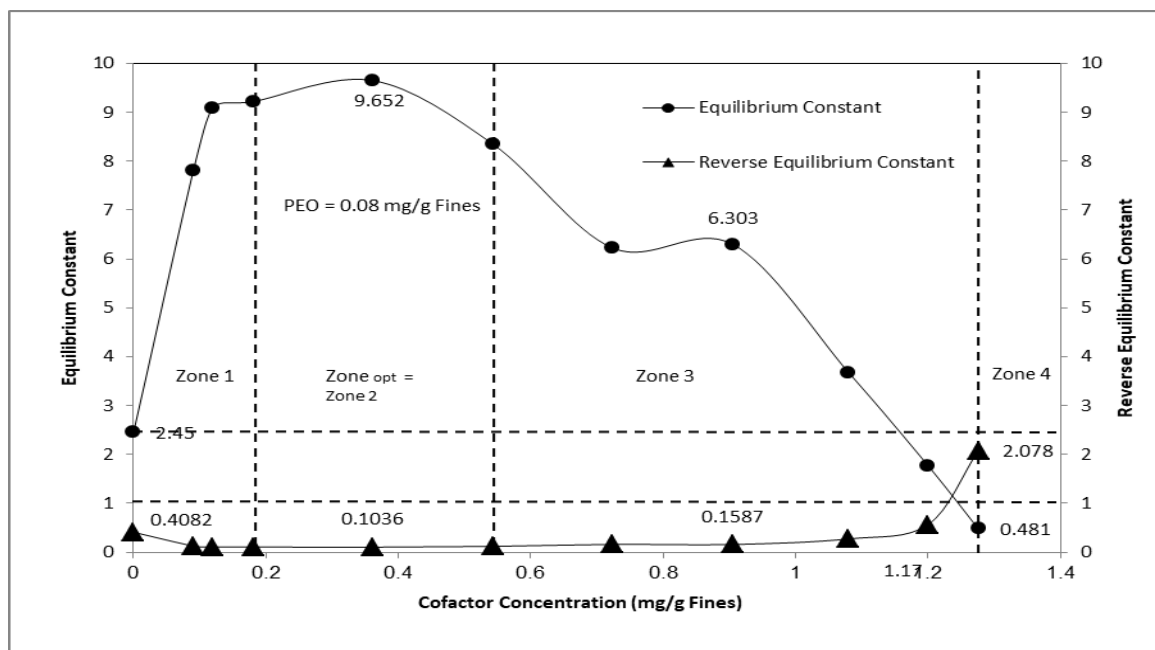
in  $C$ . This decrease in  $\tau_d$  in  $Z_3$  starts to accelerate the  $k_d$  (Fig.4) at a concentration we called the deflocculation acceleration point  $C_a$  ( $=C=0.9$ ) and shown in table 2. Higher than  $C_a$ , the  $\tau_d$  decreases and  $k_d$  increases drastically and end at  $C_c$  showing fastest deflocculation. Another important concentration is the  $C_e$  ( $=1.246 < C_c$ ), where flocculation and deflocculation have equal speeds ( $\tau = \tau_d$ ) and the two curves intersect (Fig.3) in  $Z_3$ , but flocculation still occurring first ( $A_e > A_o$ ) followed with deflocculation. Finally, at  $C$  ( $=C_c=1.276$ ), the  $A=A_o$  and  $\tau_d < \tau$  that means flocculation occurs instantly and hardly noticed followed with faster deflocculation. Taking the extensions of the curves for  $C(>C_c)$  in  $Z_4$ , we get  $A < A_c = 0.671$  (Fig.2) and ( $\tau_d = 5.64$ )  $<$  ( $\tau = 11.72$ ) (Fig.3), indicating that the CF-PEO system is seemingly functioning as a fast dispersion agent. Based on these results, the designers in the mill can suggest the proper value of  $C$  and the particle retention time ( $\tau_r$ ) in flocculation unit and units after.



**Figure 4: The effect of cofactor concentration on flocculation and deflocculation rate constants, the PEO addition was 0.08 mg/g fines for all runs.**

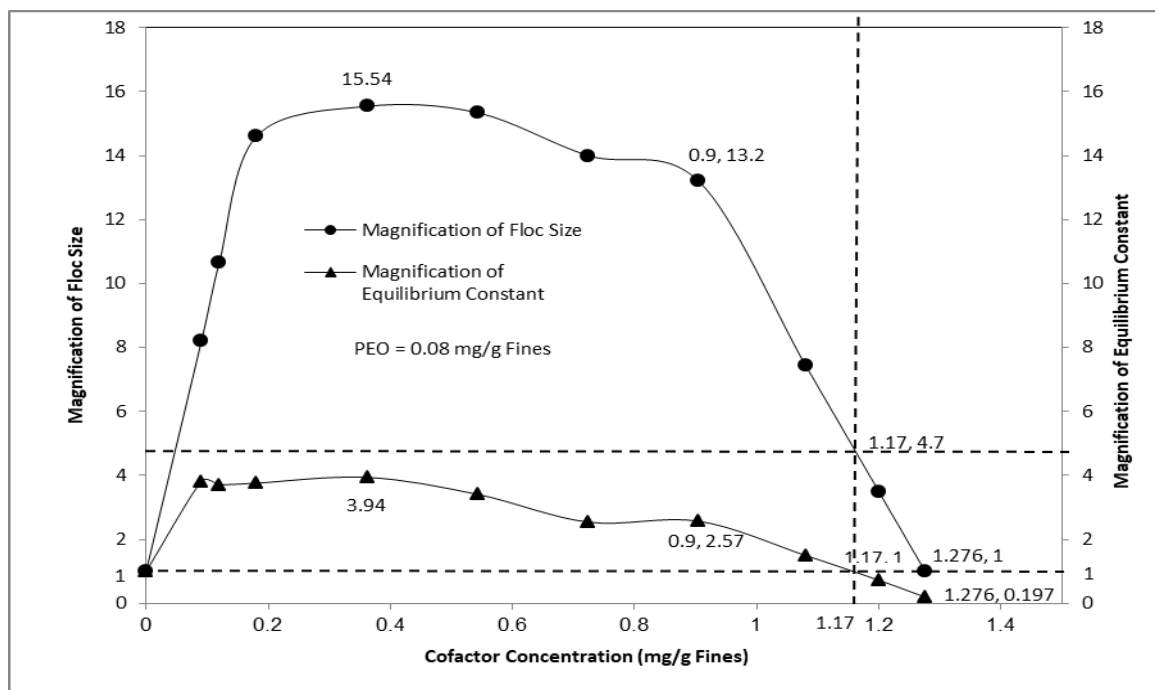
Further analytical results discussed are flocculation rate constant  $k_f$  ( $=1/\tau$ ) and deflocculation rate constant  $k_d$  ( $=1/\tau_d$ ), since the flocculation rate  $r_f$  is accompanied with deflocculation rate  $r_d$  and are in forward and reverse states having equilibrium constants as well. Both  $k_f$  and  $k_d$  are important to determine the kinetics of the transient flocculation-deflocculation process, where the higher the constant is the faster. Both  $k_f$  and  $k_d$  (Fig.4) are shown increasing with increases

in  $C$  indicating faster flocculation since  $k_f > k_d$  up to  $C_e (=1.246)$ . The deflocculation increase starts to accelerate at  $C_a = 0.9$  while flocculation continues increasing but remains faster. At  $C_e$  (Fig.3, Fig.4), the two curves intersect ( $k_f = k_d$ ) indicating equal speeds of flocculation and deflocculation. To relate floc size with deflocculation dynamics, plots of  $A$  and  $k_d$  versus  $C$  are shown (Fig.2). In flocculation-deflocculation process, with increases in  $C$ , the floc size started to increase at low values of  $C$ , becoming the largest at  $C_{opt}$  in  $Z_{opt}$  and then started to decrease and accelerate decreasing at  $C_a = 0.9$ . In other hand, the increase in deflocculation speed  $k_d$  is low at low  $C$  values, getting larger at  $C_{opt}$  and then started to accelerate increasing at  $C_a = 0.9$ . These results show deflocculation becoming faster with the increase in  $C$  and more significant at  $C > C_a$ , and in contrary the floc size shows a significant decrease. Since flocculation process using the CF-PEO retention aid is transient and having flocculation rate  $r_f$  (the forward rate) and deflocculation rate  $r_d$  (the reverse rate), the equilibrium constant  $K_{eq} (=k_f/k_d)$  and the reverse equilibrium constant  $K_{-eq} (=1/K_{eq})$  (Mohammad Raji Abdallah Qasaimeh, 2022) are defined and determined. For more analysis, we have plotted  $K_{eq}$  and  $K_{-eq}$  versus  $C$  (Fig.5) and got additional results to figure 4. The  $K_{eq}$  and  $K_{-eq}$  curves show the flocculation and deflocculation



**Figure 5: The effect of cofactor concentration on equilibrium and reverse equilibrium constants, the PEO addition was 0.08 mg/g fines for all runs.**

dynamic speeds, and when intersect ( $K_{eq} = K_{-eq}$ ) at  $C_e = 1.246$  the two processes have equal speeds. As a result of  $C$  effect, flocculation is faster than deflocculation when  $C < C_e$  and have equal speeds at  $C = C_e$ . In other hand, when  $C > C_e$  deflocculation becomes significant and faster than flocculation. Also at  $C > C_c$ , deflocculation keeps faster than flocculation ( $K_{-eq} > K_{eq}$ ), while floc size becomes smaller than the initial asymmetric size ( $A < A_o$ ); the process is seemingly to be dispersion. For more results, as CF addition with PEO induced flocculation and the increase in  $C$  affect both floc size  $A$  and flocculation dynamics  $K_{eq}$ , we have plotted (Fig.6) the magnification of floc size  $M_A (=A/A_o)$  and the magnification of flocculation dynamics  $M_{K_{eq}} (=K_{eq}/K_{eqo})$  versus  $C$ . This plot (Fig.6) shows the CF-PEO induced flocculation



**Figure 6: The magnifications of equilibrium and reverse equilibrium constants with the increase, the PEO addition was 0.08 mg/g fines for all runs.**

magnifications at different values of  $C$  relative to the initial asymmetric flocculation at  $C_o$ , and gave the following results: at  $C_o$  the  $M_A = M_{K_{eq}} = 1$ ; at  $C_{opt}$  the  $M_A = 15.54$  and  $M_{K_{eq}} = 3.94$ ; at  $C_a$  the  $M_A = 13.2$  and  $M_{K_{eq}} = 2.57$ ; and at  $C_c$  the  $M_A = 1$  and  $M_{K_{eq}} = 0.197$ . For more, a new point, we call it the dynamic point  $C_{dyn} (=1.17)$  is found, at which the dynamics magnification is equal to dynamics magnification at asymmetric flocculation ( $M_{K_{eq}} = 1$ ), but the floc size

magnification ( $M_A=4.7$ ) is not equal to floc size magnification at asymmetric flocculation ( $M_A=1$ ). It means that due to fast deflocculation at high  $C$ , the asymmetric dynamic at  $C_{dyn}=1.17$  is reached before the asymmetric size at critical  $C_c=1.276$ .

We have determined the effect of cofactor concentration  $C$  on flocculation floc size and flocculation dynamics in the wide cofactor concentration range  $TR(0 \leq C \leq 1.276)$ . For more, the

**Table 1: The flocculation parameters values and magnifications of floc size and equilibrium constant as functions of cofactor concentration. For all runs, the PEO was 0.08 mg/g fines, the CF was  $C$  (mg CF/gm Fines) was variable, and the fines consistency was  $C_{fn} (=0.1\%)$ .**

	$C_0=0$	$0 < C \leq 0.18 Z_1$	$0.18 \leq C < 0.55$ $Z_{opt}$	$0.55 \leq C \leq 1.276 Z_3$	$C_c=1.276$	$C > 1.276$ $Z_4$
$A$	$A=A_0$ $=0.671$	$0.671 < A \leq 10.4$ $A_0 < A < 15.5 A_0$	$A=A_{opt}=10.4$ $=15.5 A_0$	$10.4 > A \geq 0.671$ $15.5 A_0 > A > A_0$	$A=A_c$ $=0.671$ $=A_0$	$A < 0.671$ $A < A_0$
$M_A$	$M_A=M_{A_0}$ $=1$	$M_{A_0} < M_A < 15.5 M_{A_0}$	$M_A=15.5 M_{A_0}$	$15.5 A_0 > M_A \geq M_{A_0}$	$M_A=M_{A_c}$ $=M_{A_0}$	$M_A < M_{A_0}$
$k_f$	$k_{f_0}$ $=0.0166$	$0.0166 < k_f < 0.064$ $k_{f_0} < k_f < 3.855 k_{f_0}$	$k_f=k_{f_{opt}}=0.064$ $=3.855 k_{f_0}$	$0.064 < k_f \leq 0.085$ $3.855 k_{f_0} < k_f < 5.12 k_{f_0}$	$k_{f_c}=0.085$ $=5.12 k_{f_0}$	$k_f > 0.085$ $k_f > 5.12 k_{f_0}$
$k_d$	$k_{d_0}$ $=0.0068$	$0.0068 < k_d < 0.007$ $k_{d_0} < k_d < 1.03 k_{d_0}$	$k_d=k_{d_{opt}}=0.007$ $k_d=1.03 k_{d_0}$	$0.007 < k_d \leq 0.177$ $1.03 k_{d_0} < k_d \leq 26 k_{d_0}$	$k_{d_c}=0.177$ $=26 k_{d_0}$	$k_d > 0.177$ $k_d > 26 k_{d_0}$
$K_{eq}$	$K_{eq}=K_{eq_0}$ $=2.44$	$2.44 < K_{eq} \leq 9.14$ $K_{eq_0} < K_{eq} \leq 3.746 K_{eq_0}$	$K_{eq}=K_{eq_{opt}}=9.14$ $=3.746 K_{eq_0}$	$9.14 > K_{eq} \geq 0.48$ $3.746 K_{eq_0} > K_{eq} \geq 0.197 K_{eq_0}$	$K_{eq}=K_{eq_c}$ $=0.48$ $=0.197 K_{eq_0}$	$K_{eq} > 0.48$ $> 0.197 K_{eq_0}$
$M_{K_{eq}}$	$M_{K_{eq_0}}=1$	$1 < M_{K_{eq}} \leq 3.75$	$M_{eq}=M_{K_{eq_{opt}}}$ $=3.75$	$3.75 < M_{K_{eq}} \leq 0.197$	$M_{K_{eq_c}}=0.197$	$M_{K_{eq}} > 0.197$

values of all determined flocculation and deflocculation parameters versus  $C$  in  $TR$  and their values related to their values at  $C_0$  in form of correlations are shown in Table 1. Each correlation is written in the form  $X=M X_0$ , where  $X$  is the parameter at  $C$ ,  $X_0$  is the initial parameter value at  $C_0$ , and  $M$  is the number that the parameter is magnified. For more, the values of the critical points, the points at which the parameter behavior is changed into a new value, are found (Table 2) and related to their initial values at  $C_0$ . Critical points are important for the changes in parameters.

**Table 2: important critical cofactor concentrations (points) in flocculation of fines using the CF-PEO retention aid at variable CF concentration  $C$  (mg CF/gm Fines), the PEO concentration is constant (0.08 mg CF/gm Fines), and constant fines consistency  $C_{fn}$  ( $=0.1\%$ ). The concentrations of CF are the initial  $C_o$ ; the optimum  $C_{opt}$ ; the accelerating deflocculation  $C_a$ ; the equal dynamic point  $C_{dyn}$ , at which the equilibrium constant equals to that at  $C_o$ ; the equal flocculation and deflocculation constants (equal dynamic speeds)  $C_e$ ; and the critical concentration  $C_c$  at which the floc size is reduced to the initial size due to deflocculation.**

	$C_o=0$	$C_{opt}=0.18$	$C_a=0.9$	$C_{dyn}=1.17$	$C_e=1.246$	$C_c=1.276$
$A$	$A_o=0.671$	$A_{opt}=10.4$ $=15.5 A_o$	$A_a=8.86$ $=13.2 A_o$	$A_{dyn}=3.1$ $=4.62 A_o$	$A_e=1.4$ $=2.086 A_o$	$A_c=0.671$ $=A_o$
$M_A$	$M_{A_o}=1.0$	$M_A=15.5$	$M_A=13.2$	$M_A=4.62$	$M_A=2.086$	$M_A=1.0$
$k_f$	$k_{f_o}=0.0166$	$k_{f_{opt}}=0.064$ $=3.86 k_{f_o}$	$k_{f_a}=0.0757$ $=4.56 k_{f_o}$	$k_{f_{dyn}}=0.082$ $=4.94 k_{f_o}$	$k_{f_e}=0.084$ $=5.06 k_{f_o}$	$k_{f_c}=0.085$ $=5.12 k_{f_o}$
$k_d$	$k_{d_o}=0.0068$	$k_{d_{opt}}=0.007$ $=1.03 k_{d_o}$	$k_{d_a}=0.012$ $=1.76 k_{d_o}$	$k_{d_{dyn}}=0.0336$ $=4.94 k_{d_o}$	$k_{d_e}=0.084$ $=12.35 k_{d_o}$	$k_{d_c}=0.177$ $=26.03 k_{d_o}$
$K_{eq}$	$K_{eq_o}=2.44$	$K_{eq_{opt}}=9.14$ $=3.746 K_{eq_o}$	$K_{eq_a}=6.308$ $=2.585 K_{eq_o}$	$K_{eq_{dyn}}=2.44$ $=1.0 K_{eq_o}$	$K_{eq_{dyn}}=1.0$ $=0.41 K_{eq_o}$	$K_{eq_c}=0.48$ $=0.197 K_{eq_o}$
$M_{K_{eq}}$	$M_{K_{eq_o}}=1.0$	$M_{K_{eq_{opt}}}=3.746$	$M_{K_{eq_a}}=2.585$	$M_{K_{eq_{dyn}}}=1.0$	$M_{K_{eq_e}}=0.41$	$M_{K_{eq_c}}=0.197$

## CONCLUSION

In this work, we have performed an analytical study on the effect of cofactor concentration (in a wide range) on the behaviors of fines flocculation and deflocculation using the CF-PEO retention aid system. We have taken this work as an extension to our previous work to get more results that enrich the literature. We have found number of the flocculation and deflocculation parameters and constants with their values, their correlations, and magnification of their initial values at no cofactor addition (asymmetric flocculation). The resulted analytical values of the parameters are plotted in figures and shown in tables with the critical points as well. As flocculation process, the floc size and the rate constant are found increasing at low cofactor concentration, the effect of deflocculation is found low at low cofactor concentrations, but becoming increasing at high concentrations resulting small flocs until reaching the critical point. The floc size becomes equal

to the initial size at the critical concentration, and shows more decrease in floc size at higher CF concentration with faster deflocculation. The action of CF-PEO retention aid system is the expected to be fast dispersion at concentrations higher than the critical point.

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