Polyethyleneimine Addition for Control of Dissolved and Colloidal Substances: Effects on Wet-End Chemistry

Chun-jian Wang, Chen Chen, Hao Ren, Yi-qing Yang, and Hong-qi Dai *

Within the pulp and paper industry, the recycling of whitewater to reduce fresh water consumption and effluent volume leads to an accumulation of dissolved and colloidal substances (DCS) in the papermaking wet-end system. DCS interacts with certain electrolytes and polyelectrolytes to form non-ionic DCS interferents (pitch deposits and depositions), which adversely affect papermaking. Polyethyleneimine (PEI), a fixing agent with a low molecular weight and high cationic charge density, can control the DCS in the wet-end system. The fixation efficiency of DCS simulacra and the wet-end properties were explored under varying Ca^{2+} and PEI concentrations in pulp. The fixation and retention efficiency of DCS simulacra were improved, the zeta potential of pulp and drainage rate of pulp increased, and the cationic demand of pulp filtrate decreased with increasing PEI dosage. Ca^{2+} shielded the negatively charged ions on the surface of the fibers and DCS simulacra, influenced the fixation efficiency of PEI to DCS simulacra, and improved the drainage rate of pulp.

Keywords: Polyethylenimine; Dissolved and colloidal substances; Fixing agent; Wet-end properties; Interfering substances

*Contact information: Department of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing Jiangsu, 210037, P. R. China; *Corresponding author: hgdhq@njfu.edu.cn*

INTRODUCTION

In the papermaking process it is difficult to solve problems related to dissolved and colloidal substances (DCS) (Holmbom and Sundberg 2003; Zhang *et al.* 2007; Hubbe *et al.* 2012). The DCS can interact with inorganic electrolytes such as Ca^{2+} and soluble aluminum compounds in the wet-end system, leading to the formation of deposit-prone substances. For some time now, low molecular weight and high cationic charge density fixing agents (Zha *et al.* 2002; Xiao and Cezar 2005; Huang *et al.* 2006) have been widely used in the papermaking industry. Fixing agents cause anionic DCS to adhere onto fibers. The DCS can then be removed from the papermaking process water and be retained in the product (Miao *et al.* 2012; Wang *et al.* 2013b).

Polyethyleneimine (PEI) has the properties of high positive charge density and good solubility in water (Kobayashi *et al.*1990). Also, it is a relatively common retention and drainage aid and strengthening agent, and it can provide good fixation effects when used as an anionic trash fixing agent. It can also improve the papermaking wet-end performance to a certain extent (Jing *et al.* 2002; Fuente *et al.* 2005). Studies have showed that the PEI fixes DCS onto fiber through charge neutralization and charged patch mechanisms (Shetty *et al.* 1994). Charge neutralization is a process in which polyelectrolyte complexes will form by the mutual adsorption between DCS and fixing agents (Chen and He 2000). Furthermore, when PEI is added into the pulp, the partial anionic charge of DCS and fibers will be reversed locally to be cationic, forming a “charged patch”. Such a distribution of positive and negative areas on the solid surfaces can be expected to promote the agglomeration between DCS and fibers which is based on the charged patch mechanism (Pfau *et al.* 1999; Hubbe 2007).

In modern paper production processes, the process water is recirculated multiple times (Vidal *et al.* 2001; Wu *et al.* 2014), and the DCS is constantly enriched and presents a metastable state in the pulp system. DCS has intrinsically strong tendencies to aggregate and precipitate, and inorganic electrolytes accumulate in the system. DCS reacts with Ca^{2+} and other polyvalent metal ions, then loses its stability and combines to form neutralized complexes or "interferents", which have a tendency to form agglomerates and deposits within a paper machine system. In theory, once DCS has lost some of its negative charge by means of its interactions with multivalent metal ions, it becomes difficult for PEI to fix the DCS onto the fiber surfaces.

Thus, to prevent the DCS from becoming completely unstable, losing its negative charge character and becoming unfixable by highly cationic fixing agents, appropriate Ca^{2+} concentrations should be applied during the experiment. In an earlier study the mechanism of the aggregation process was studied for a DCS simulacra system, which included rosin acid sodium, sodium stearate, and sodium polyacrylate (Chen *et al.* 2015). When the concentration of Ca^{2+} in system reached 5 mmol/L, the DCS and Ca^{2+} interacted with each other to form complexes having substantially neutralized surface charge. Therefore, in order to prevent the loss of negative charge of the DCS (Li *et al.* 2002), the Ca^{2+} concentration in the system had to be kept under 5 mmol/L. The present study used the early stage results on whitewater components to simulate the actual water in the factory (Wang *et al*. 2013a; Chen *et al.* 2014). Rosin acid sodium and sodium stearate were selected to simulate sodium resinate or fatty acid sodium gel material in whitewater, and sodium polyacrylate was used to simulate the dissolved substances, which may come from a pigment dispersant. These substances were mixed at a 1:1:1 ratio. The fixation effect of a low-mass PEI product on DCS and its performance (Gill 1996) in papermaking wet-end chemistry were determined under different Ca^{2+} concentrations. The results will provide theoretical guidance for the control and elimination of DCS in the actual process of paper production.

EXPERIMENTAL

Materials

Natural rosin was supplied by the Fengkai chemical factory (Guangdong, China) with an acid value (in KOH) of 165.79 mg/g and a softening point of 80.50 °C. Stearic acid was supplied by the Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China) with an acid value (in KOH) of 196.09 mg/g and a melting point 69.60 °C. Pure polyacrylic acid, sodium salt was purchased from Shanghai National Medicine Group Chemical Reagent Co., Ltd. (Shanghai, China). The molecular mass of the polyacrylic acid (sodium salt) was 3000 Daltons. Branched PEI was supplied by Shanghai Aladdin Chemicals Co., Ltd. (Shanghai, China). The molecular mass of the PEI was 1800 Daltons. Hydrochloric acid and $CaCl_2$ was supplied by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China).

The pulp used in this study was fully bleached eucalyptus kraft pulp (Brazil) and refined to 42.8°SR beating degree, as tested with a JDJY 100 Schopper-Riegler beating degree tester (Shanxi University of Science & Technology, Xian China). Before the experiment, the pulp samples were converted to completely protonated form by soaking the pulp in HCl, then washing it with deionized water. The soaking and washing process were repeated four times until the metal ions had been substantially removed (Liu and Dai 2006).

Methods

Preparation of DCS simulacra objects

To prepare the sodium resinate solution, 0.400 g of rosin was accurately weighed, placed in a four neck round bottom flask, and 500 mL deionized water was added. The flask was put in a HH-S2 water-bath (Jinyi, Jintan, China). This was set at a constant 85 °C and 250 rpm stirring speed, until the rosin melted. Then 300 mL of 0.012 mol/L NaOH solution was added for saponification. After 4 h, 200 mL of deionized water was added to make the solution volume 1 L. This process resulted in a clear amber sodium resinate solution with a mass concentration of 0.4 g/L. The preparation of sodium stearate followed the same process as the preparation of sodium resinate, except with 0.400 g stearic acid and the saponification temperature at 75 °C. This resulted in a 0.4 g/L colorless sodium stearate solution. Deionized water was used to dilute the polyacrylic acid sodium solution to a mass concentration of 0.4 g/L. A 0.4 g/L mixture solution with deionized water, sodium resinate solution, and sodium stearate solution, at a ratio of 1:1:1, acted as the DCS simulacra solution.

Determination of charge neutralization point (V_{th})

Different mass concentration and volume $CaCl_2$ solutions were prepared with deionized water. For each test, 60 mL of the DCS simulacra solution was used. A certain amount of deionized water was added, and the solution pH value was adjusted to 7.5 using a PB-10 pH meter (Sartorius, Gottingen, Germany). An amount of $CaCl_2$ solution with a certain concentration was added to bring the volume of the solution to 120 mL. The mass concentration of DCS simulacra in the solution became 0.2 g/L. After mixing the above solution, cationic demand was measured with a PCD-03 type particle charge detector (Mütek, Aschaffenburg, Germany), and 0.001 N poly-diallyldimethylammonium chloride (PDADMAC) was used as the standard cationic polymer. A 1 g/L PEI solution was prepared with deionized water (Wang *et al.* 2013c). A specific amount of PEI solution was diluted with deionized water to produce a 0.01 g/L mass concentration, and the solution pH was adjusted to 7.5. The anionic demand was measured, and 0.001 N PES-Na was used as the standard anionic polymer (Wang *et al.* 2014). According to the principle of charge, the theoretical amount of PEI required to completely neutralize the negative charge of the DCS simulacra was calculated, and recorded as V_{th}.

Determination of properties of wall sticking of DCS interferents

For each test, 200 mL of the DCS simulacra solution was used. The solution pH was adjusted to 7.5, and the same volume of deionized water and $CaCl_2$ solution was added to make the total volume of the solution 400 mL. The mass concentration of the DCS simulacra solution was 0.2 g/L. Ten mL of the above prepared DCS simulacra solution was put into glass test tubes, and after 24 h of standing, each supernatant was drained. Pictures were taken to record the appearance of material adhering to the glass.

Application of fixing agents to the pulp

First, metal-free deionized pulp was weighed (the equivalent of 5 g of dry pulp) and put in a flask for defibering. The flask was kept at 45 °C and a 250 rpm stirring speed was used in the water bath. DCS simulacra solution was added to adjust the pH to 7.5, and then

$CaCl_2$ solution was added. The Ca^{2+} concentration in the pulp suspension was adjusted in the range from 0 to 2 mmol/L. Finally, a certain amount of 1 g/L PEI solution was added. The 1000 mL pulp consistency was 0.5%. The DCS simulacra mass concentration was 0.2 g/L, and the PEI content was 0, 1/8 V_{th}, 2/8 V_{th}, 3/8 V_{th}, 4/8 V_{th}, 5/8 V_{th}, 1 V_{th}, and 9/8 V_{th} in the paper stocks. The prepared paper stocks were stirred at 250 rpm, and the temperature was kept at 45 °C for 20 min by a SHA-C type constant temperature oscillation device (Guohua, Changzhou, China). The prepared paper stocks were put into the DFR-05 type dynamic retention tester (Mütek, Aschaffenburg, Germany), which was equipped with a 150-mesh sieve. The stirring speed was set at 800 rpm, and it was run for 20 s. The filter material and the filtrate were collected.

Measurement of fixation effect by PEI and filtrates properties

Filtrate turbidity was determined by using a 2100 N turbidity meter (Hach, Colorado, USA). A stock suspension containing fibers, cellulosic fines, and DCS was filtered using a 150-mesh screen. The mixture of fines and DCS that passed through the screen in the dynamic filtering experiments was called the 150-mesh filtrate. After the 150-mesh filtrate was separated from stock, it was allowed to stand in a 100 mL beaker for 5 min. The upper liquid was taken to be filtered using a 100 mL G3 fritted glass filter with 16 to 40 μm pore size to obtain a DCS-water mixture, which was called the DCS filtrate, and then its turbidity was measured. The 150-mesh filtrate mainly contained cellulosic fines and DCS, whereas the DCS filtrate mainly contained DCS. Therefore, the turbidity difference between the 150-mesh filtrate the DCS filtrate could be considered to be caused solely by cellulosic fines, and this turbidity difference could be used to obtain the concentration of cellulosic matter drained through the 150-screen. Furthermore, the concentrations and turbidities of these DCS filtrates and cellulosic fines suspensions were highly correlated. The turbidity of DCS and the fines can characterize the mass concentration of DCS and cellulosic fines in filtrates indirectly.

Based on the system described, the efficiency of DCS fixation by the addition of PEI can be calculated by the turbidity of the DCS filtrate when comparing treated and untreated stock. But the cellulosic fines matter retention cannot be calculated by turbidity directly, because the turbidity of 5 g/L pulp is hard to measure, and the linear equation between turbidity and concentration is not suitable at a high consistency of pulp. Therefore, a linear equation based on Fig. 4 was used to calculate the concentration of cellulosic matter that passed through the 150-screen by turbidity difference. Then the stock consistency was used to calculate the cellulosic matter retention ratio indirectly. The equations used for calculating the DCS fixation ratio and cellulosic fines matter retention ratio were as follows,

$$\text{DCS fixation ratio (\%)} = [1 - T_{DCS} / T_{(DCS,\ PEI=0)}] \times 100 \quad (1)$$

$$\text{Cellulosic fines retention ratio (\%)} = [1 - C_{Drained\ cellulosic\ fines} / C_{Stock}] \times 100 \quad (2)$$

$$C_{Drained\ cellulosic\ fines} = [(T_{150} - T_{DCS}) + \mathrm{B}] / \mathrm{K} \quad (3)$$

where T_{DCS} is the turbidity contribution of the colloidal fraction in the filtrate from the G3 fritted glass filter (NTU), $T_{(DCS,\ PEI=0)}$ is the corresponding turbidity of DCS before adding PEI to the stock (NTU), $C_{Drained\ cellulosic\ fines}$ can be calculated using Eq. 3, which is based on the linear equation (y=586.6x-47.19) in Fig. 4, B and K are constants having values of 586.6 and 47.19, T_{150} is the turbidity of 150-mesh filtrate (NTU), and C_{Stock} is the consistency of stock (g/L). The values of $T_{(DCS,\ PEI=0)}$ and C_{Stocks} were determined to be 60 NTU and 5 g/L.

In addition, the fixation of the DCS simulacra on the fibers was found to be uniform for the entire system. Thus, based on the above mentioned analyses, the calculation equation for the DCS simulacra retention ratio is as follows,

$$\text{Retention ratio of DCS simulacra} = \text{Cellulosic fines retention ratio} \times \text{DCS fixation ratio} \quad (4)$$

Furthermore, the status of DCS simulacra fixation on fibers was observed using a U-TV1X-2 type optical microscope (Olympus, Tokyo, Japan).

The drainage rate of stocks in the absence and presence of Ca^{2+} with different PEI dosages was measured. The experiment of drainage rate measured the water volume that passed through the 60-mesh filter screen with stirring at 800 rpm after 20 s of treatment in the dynamic retention tester, as follows,

$$\text{Filtering rate} = V_{Filtrate} \,/\, t_{Draining} \quad (5)$$

where $V_{Filtrate}$ is the volume which passed through a 60-mesh filter screen (mL) and $t_{Draining}$ is the filtrate time (s). The $t_{Draining}$ value was found to be constant at 20 s.

The cationic demand of the filtrate separated from stocks by 150-mesh screen was measured in the absence and presence of Ca^{2+} with different PEI dosages, and the zeta potential of the stocks with different PEI dosages was measured using a SZP06 Zeta potential meter (Mütek, Aschaffenburg, Germany).

RESULTS AND DISCUSSION

Study of Electric Charge Characteristics of DCS

V_{th}, the theoretical volume of PEI needed to react with DCS by charge neutralization mechanism, was determined according to the method used to determine the cationic demand. The charge neutralization point V_{th} of PEI for DCS simulacra was calculated based on the stoichiometric relation of the electric charges and was used as a reference standard for the amount of PEI added in subsequent experiments.

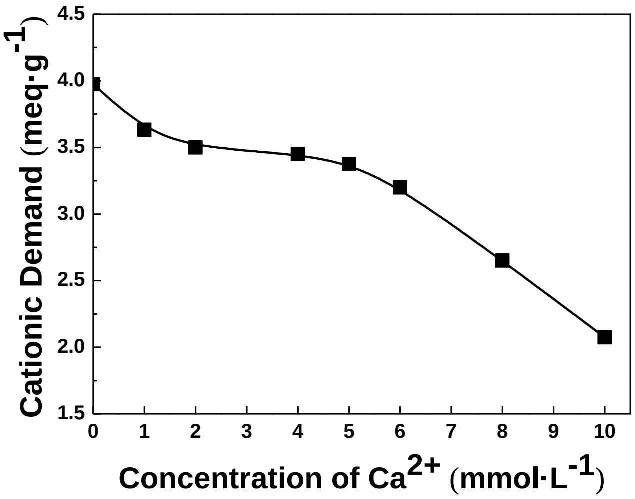


Fig. 1. Cationic demand of DCS simulacra at different concentrations of Ca^{2+}

Table. 1. Charge Neutralization Point of Cationic PEI to Anionic DCS Simulacra

Material	Cation Demand (meq/g)	V_{th} (Fixing agent/DCS)(g/g)
PEI (pH = 7.5)	-9.100	0.425
DCS (pH = 7.5)	3.867	

Figure 1 shows that increasing of the Ca^{2+} concentration in the system reduced the cationic demand of the solution after its chemical interaction with the DCS simulacra. This result is explained by the ion exchange between the DCS simulacra and Ca^{2+}, which reduced the amount of pedant carboxylic group with negative charge in the DCS simulacra and formed interferents; these were difficult to ionize. With the increase in Ca^{2+} concentration, more interferents were generated, and the negative charge character of the DCS simulacra and the cationic demand were reduced.

Adhering Characteristics of Interferents

In this paper, the precipitation and adsorption of the DCS interferents in the paper machine during papermaking was simulated by the interferents produced from the reaction between the DCS simulacra and Ca^{2+} adhering to the tube walls. Figure 2 shows the adhering characteristics of the DCS simulacra under different Ca^{2+} concentrations. With increasing Ca^{2+} concentration, greater precipitation was produced, and the amount of adhesive matter on the tube wall increased. This result indicated that during real production, the DCS interferents would tend to adhere to and form a deposit layer on equipment surfaces with a high surface energy, and some of the precipitants deposit in the tubes and headbox, which severely affects the normal operation of the paper machine.

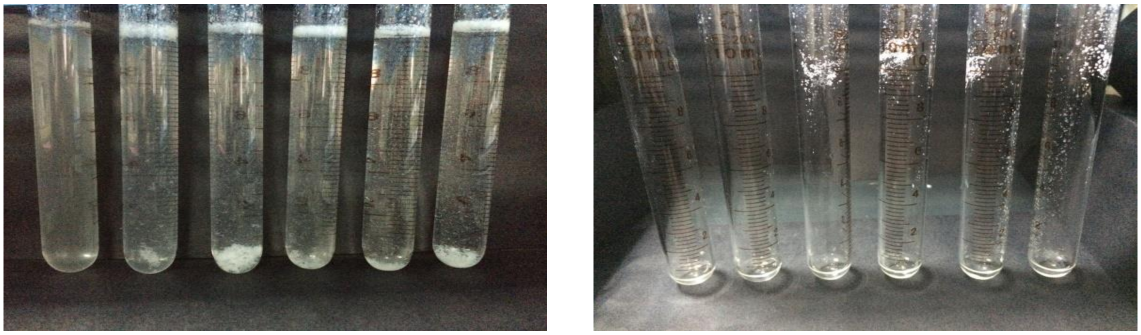


Fig. 2. Properties of wall sticking of DCS simulacra at different Ca^{2+} concentration. Ca^{2+} concentration of solutions from left to right is 0, 2, 4, 6, 8, and 10 mmol/L

Filtered PEI in DCS Simulacra

DCS simulacra suspensions and fiber suspensions with different concentrations were prepared, and the concentration and turbidity of these DCS simulacra suspension and fiber suspensions were highly correlated (Nylund *et al.* 2007), as shown in Figs. 3 and 4, the R^2 of the linear equation between concentration and turbidity of DCS was close to 1.

As PEI was added to the pulp system, the paper pulp was filtered through a 150-mesh screen in a dynamic drainage jar. During draining, the DCS simulacra and fines fixed on the fibers were retained on the screen, whereas the unfixed portion was drained into the filtrate separated from stocks by the 150-mesh screen. The turbidity of the 150-mesh filtrate indirectly represented its DCS simulacra and fines content, and thus indicated the fixation efficiency of the PEI (Ravnjak *et al.* 2003).

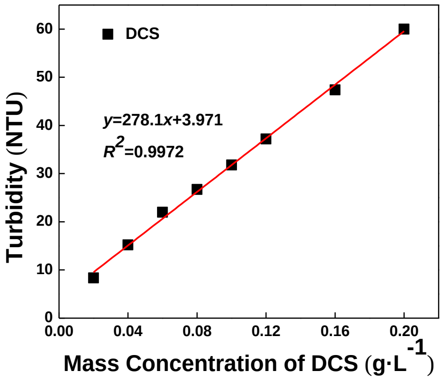


Fig. 3. The turbidity-concentration curve of DCS simulacra solution at pH 7.5

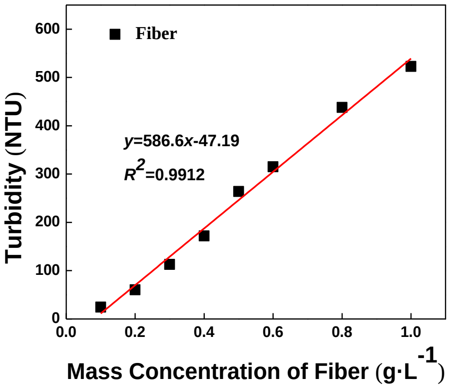


Fig. 4. The turbidity-concentration curve of fiber suspension at pH 7.5

The turbidity of the filtrate separated from stocks by 150-mesh screen was jointly caused by the fines and the drained DCS. As shown in Fig. 5, when the PEI fixing agent was added to the pulp system, dissociated or negatively charged DCS interferents were fixed by the PEI onto the fiber surface through a charge neutralization or charged patch mechanism (Holmbom and Sundberg 2003). As the amount of PEI was increased, more DCS interferents were fixed onto the fibers, and the amount of drained DCS in the filtrate decreased. The PEI also caused binding among the fines and between the fines and fibers, which increased the retention ratio of the fines and reduced the turbidity of the 150-mesh filtrate. With the same amount of fixing agent, the turbidity of the filtrate separated from stocks by 150-mesh screen was higher when Ca^{2+} was present in the pulp.

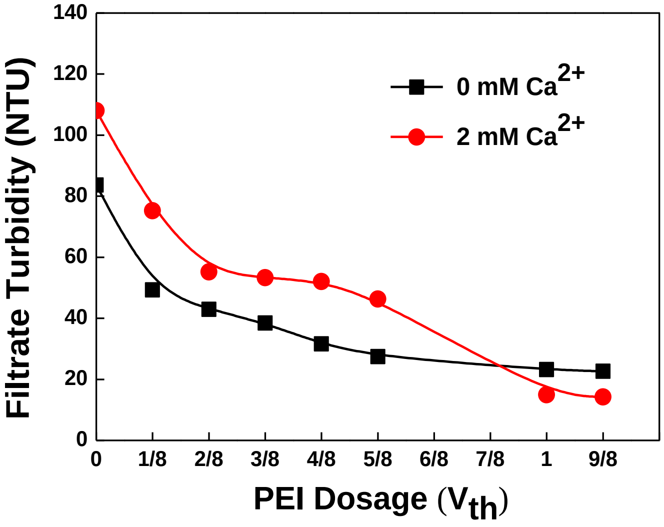


Fig. 5. Effect of PEI dosage on the turbidity of filtrate separated from stocks in the absence and presence of Ca^{2+}

Ca^{2+} greatly affected the repulsive force among DCS particles (Sundberg *et al.* 1993), which caused the aggregation of particles and the formation of stickies and precipitates that drained to the 150-mesh filtrate. This resulted in a higher filtrate turbidity.

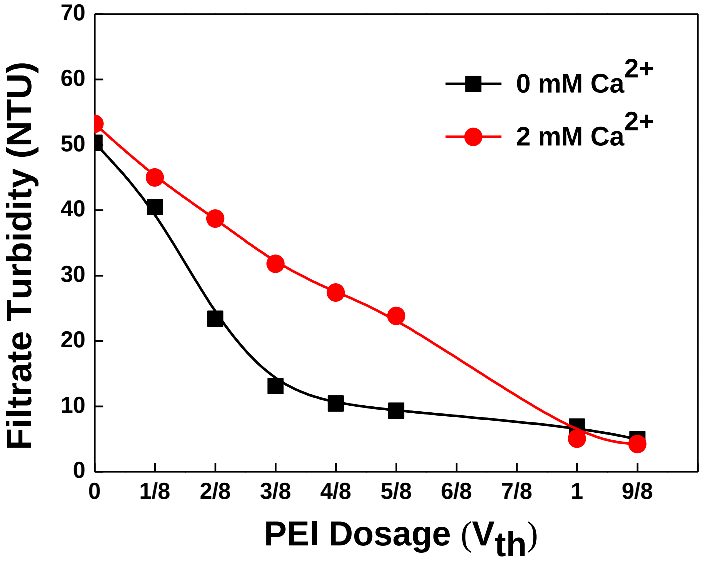


Fig. 6. Effect of PEI dosage on the turbidity of DCS filtrate (passing through the G3 fritted glass filter) in the absence and presence of Ca^{2+}

The filtrate separated from stocks by 150-mesh screen was filtered using a G3 fritted glass filter. The turbidity of the obtained filtrate was mainly caused by the drained DCS, which indirectly represented the PEI fixation efficiency on DCS. As shown in Fig. 6, as the amount of PEI was increased, the turbidity of the DCS filtrate decreased.

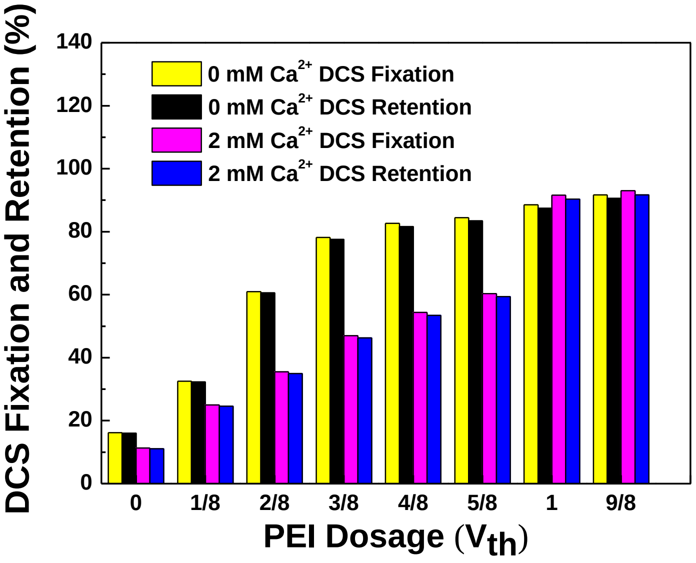
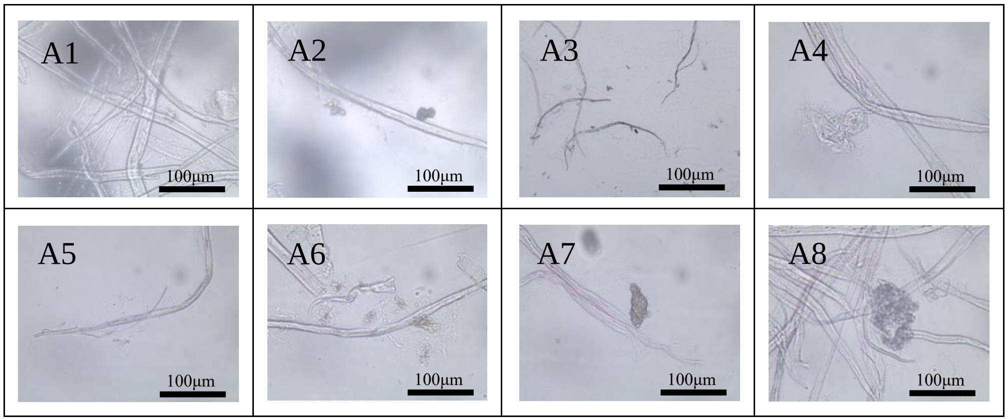
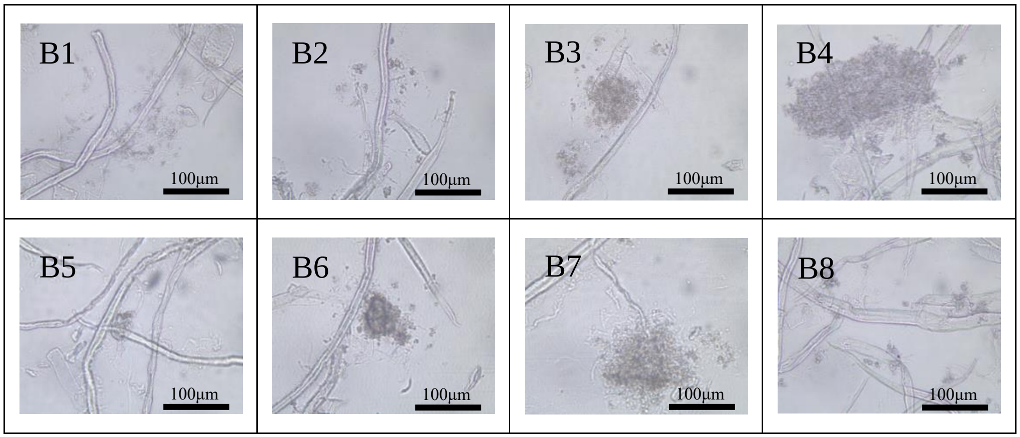


Fig. 7. Effect of PEI dosage on the fixation efficiency of DCS simulacra in the absence and presence of Ca^{2+}

With Ca^{2+} present in the pulp, the turbidity of DCS filtrate was relatively high. This was because the Ca^{2+} bonded with the carboxyl groups on the DCS simulacra and formed interferents that tended to precipitate and reduce the negative charge level of the DCS. Furthermore, the “charge screening” effect of the Ca^{2+} reduced the negative charges on the surface of fiber, and the effective contact point on the fiber where the PEI can fix DCS to fiber was reduced. Thus, the PEI fixation efficiency decreased, and the amount of residual DCS interferents in the pulp increased. Then the DCS interferents passed into the filtrate and increased the turbidity of the DCS filtrate. This indicated that the presence of Ca^{2+} in the pulp reduced the fixation efficiency of PEI on DCS.



(a) 0mM Ca^{2+}



(b) 2mM Ca^{2+}

Fig. 8. Fixation of DCS simulacra on the fiber with varying condition of PEI (400x magnification). The dosage of PEI in Fig. A1/B1~A8/B8 is 0 V_{th}, 1/8 V_{th}, 2/8 V_{th}, 3/8 V_{th}, 4/8 V_{th}, 5/8 V_{th}, 1V_{th} and 9/8 V_{th}, respectively.

The DCS fixation ratio and retention ratio was applied to carry out a suitable assessment of the PEI chemical fixation efficiency. As shown in Fig. 7, under different Ca^{2+} concentrations, the DCS fixation ratio and retention ratio increased with the amount of PEI added. Without Ca^{2+} in the system, the fixation efficiency and retention efficiency of the PEI on the DCS simulacra were better overall than those of the pulp system that contained Ca^{2+}. This was because interferents formed from the reaction between the Ca^{2+} and DCS reduced the negative surface charge. And the “charge screening” effect of the Ca^{2+} reduced the negative charges on the surface of fiber, and the effective contact area on the fiber where the PEI can fix DCS to fiber reduced. Thus, the PEI fixation efficiency was reduced, as well as the DCS retention ratio and fixation ratio. These results are consistent with the variation pattern for the turbidity of the DCS filtrate shown in Fig. 6.

When PEI was employed to fix the DCS simulacra, the DCS in the solution existed in the form of a dissociated colloid or dissolved matter in the pulp system with no Ca^{2+}, and the fibers were arranged in a cluttered way under the microscope. The DCS particles in the samples had relatively small sizes and were present on fiber surfaces and in the sample in a relatively scattered way (Figs. 8A1 through A4). As the amount of PEI added increased, the DCS fixation efficiency increasingly improved, dissociated particles aggregated to the fiber surface, the particle size increased, and the fixation efficiency improved (Figs. 8A5 through A8).

With Ca^{2+} present in the pulp and no PEI added, the DCS simulacra reacted with the Ca^{2+} to form insoluble interferents, which were dispersed in the pulp system in a relatively even pattern (Fig. 8B1). With an increase in the amount of PEI added to the pulp system, the size of the interferents formed from the reaction between the DCS simulacra and Ca^{2+} increased. One possibility is that this was caused by the charged patch mechanism, where the PEI acted as a patch to make the DCS particles aggregate, while simultaneously being fixed on the fiber surface (Figs. 8B2 through B4). The stickies in the formed interferents had a certain tackiness and were able to continue binding with other colloidal substances, which caused the size of the particles fixed to the fiber surface to increase (Figs. 8B5 through B8).

Effect of PEI on Wet-end Properties in Pulp

As a result of the charge neutralization and because PEI is a fixing agent with a high cationic charge density, the total charge amount of the DCS changed with an increase in cations. As shown in Fig. 9, the cationic demand of the filtrate separated from stocks decreased with increasing PEI.

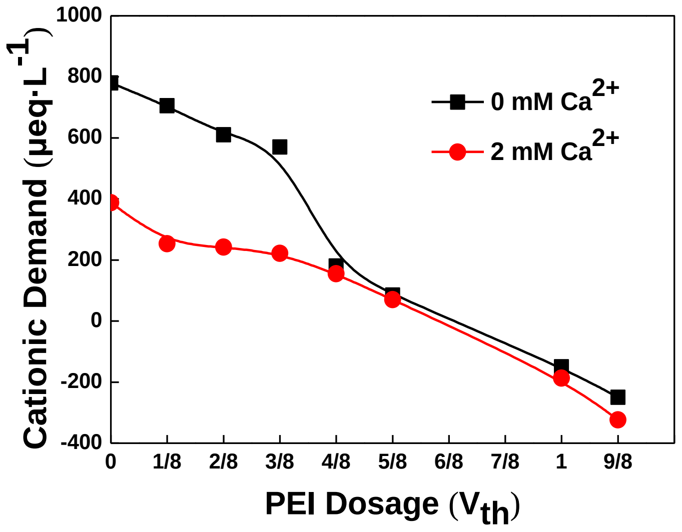


Fig. 9. Effect of PEI dosage on the cationic demand of filtrate separated from stocks by 150-mesh screen in the absence and presence of Ca^{2+}

When the amount of PEI added was approximately 5/8 V_{th}, the cationic demand of the filtrate separated from stocks was 0, and the charge of the 150-mesh filtrate became reversed to a positive sign. The change in the charge property of the 150-mesh filtrate did not occur at the theoretical charge neutralization point. This was because the PEI fixed the

DCS through both charge neutralization and the charged patch mechanism. When the charged patch mechanism took effect, the local charges of the DCS adsorption were not only neutralized, but reversed in a patch-wise pattern. This generated cationic patching and mutual attraction with other particles' anions through electrostatic attraction, during which the amount of anions in the system decreased and caused a decrease in the actual cationic demand as well.

The fixing agent added to the pulp not only neutralized the negative charge carried by the DCS, but was also adsorbed onto the fiber surface, which affected the electric potential of the pulp. Thus, the zeta potential change in the pulp was used to indirectly explore the adsorption of PEI on fibers. As shown in Fig. 10, with no Ca^{2+} present in the pulp, the zeta potential change in the pulp increased as the amount of PEI increased, and the absolute value of the zeta potential under such a condition was much greater than in the pulp system with Ca^{2+}. This was because with no Ca^{2+} present in the pulp, there were some anions on the fiber surface, which resulted in a relatively high negative charge strength on the surface of the pulp. With the Ca^{2+} present in the pulp, the "charge screening" effect of the Ca^{2+} on the charges of the fiber surface caused a relatively small absolute value for the zeta potential.

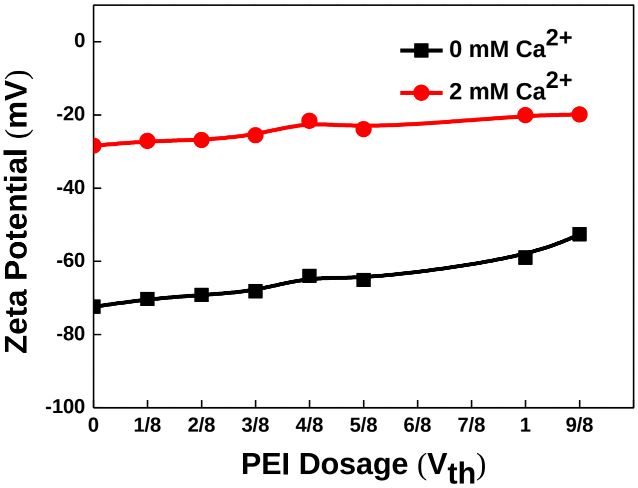


Fig. 10. Effect of PEI dosage on the Zeta potential of stocks in the absence and presence of Ca^{2+}

PEI can improve the drainage performance of stocks through fines aggregation. However, the polyelectrolyte complex formed by the DCS and fixing agent decreases the drainage performance of pulp (Dunhan *et al.* 2002). Thus, the competitive relation between the two previously mentioned effects needs to be comprehensively considered when studying the drainage rate of pulp under PEI chemical control. The influence of PEI on the pulp drainage performance is shown in Fig. 11. With an increase in PEI usage, the drainage rate slightly increased. This result indicates that fines formed dense aggregates after the PEI acted on the pulp, which reduced the specific surface area of the fibers, as well as the water-holding capacity of the solid content in the pulp. However, the drainage rate was to some extent inhibited by the polyelectrolyte complex formed by the DCS and fixing agent (Chen and Wang 2010). As shown by the comparison between the two effects in Fig. 11, the fines aggregation was slightly greater. With the Ca^{2+} present in the pulp, the drainage rate of pulp noticeably increased. This was because the increase in the Ca^{2+} concentration compressed the electric double-layer of the suspended particles in the pulp (Yuan *et al.*

2011), which decreased the zeta potential of pulp, and decreased the water-holding capacity. This was favorable for pulp dewatering. Studying the drainage rate of pulp under PEI chemical control demonstrated that PEI had a certain filter aiding effect on the pulp.

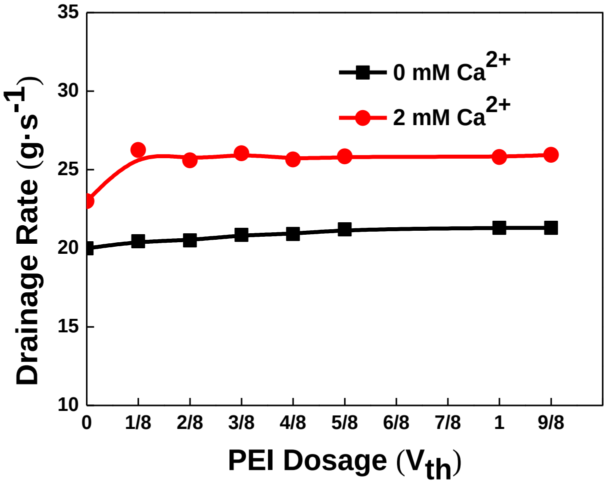


Fig.11. Effect of PEI dosage on the drainage rate of stocks in the absence and presence of Ca^{2+}

CONCLUSIONS

1. When PEI was used to chemically control the DCS simulacra, at higher PEI dosages the fixation ratio and retention ratio of the DCS simulacra both increased, the absolute value of the zeta potential of pulp and the cationic demand of the stock filtrate passing through a 150-mesh screen both decreased, and the drainage rate of pulp increased slightly.
2. With Ca^{2+} present in the pulp, both the retention ratio and fixation ratio of the DCS decreased. The Ca^{2+} screened the surface negative charges of the fibers and DCS simulacra, which made the absolute value of the zeta potential of pulp and the cationic demand of the filtrate through a 150-mesh screen lower than in a pulp system without Ca^{2+}. In addition, the drainage rate of pulp increased.
3. To achieve whitewater closure in papermaking, under the current neutral/alkaline papermaking environment, the key to "controlling and eliminating DCS accumulation in whitewater system" technology is to avoid excessively high concentration of calcium ions, which will allow better outcomes to be achieved in the DCS chemical control.

ACKNOWLEDGMENTS

The authors are grateful for the support from the National Natural Science Foundation of China (project number: 31270614) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

REFERENCES CITED

Chen, C., Xu, H., Su, W., and Dai, H. (2014). "Separation and characterization of dissolved and colloidal substances from white water and study on their stability," *Transactions of China Pulp and Paper* 29(4), 23-29. DOI: 10.11981/j.issn.1000-6842.2014.04.23

Chen, C., Su, W., and Dai, H. (2015). "Aggregation process and mechanism of pitch trouble in papermaking wet-end system," *China Pulp & Paper Industry* 36(16), 22-29. DOI: 10.3969/j.issn.1007-9211.2015.16.003

Chen, F. S., and Wang, S. L. (2010). "Effect of highly cationic polymers on the retention and drainage properties of high yield pulp," *China Pulp & Paper* 29(4), 36-39. DOI: 10.3969/j.issn.0254-508X.2010.04.008

Chen, Y., and He, B. (2000). "Colloid titration ratio and its novel progress," *Paper Chemicals* 12(1), 13-16.

Dunhan, A. J., Sheman, L. M., and Alfano, J. C. (2002). "Effect of dissolved and colloidal substances on drainage properties of mechanical pulp suspensions," *Journal of Pulp and Paper Science* 28(9), 298-304.

Fuente, E., Blanco, A., Negro, C., Pelach, M. A., Mutje, P., and Tijero, J. (2005). "Study of filler flocculation mechanisms and floc properties induced by polyethylenimine," *Industrial & Engineering Chemistry Research* 44(15), 5616-5621. DOI: 10.1021/ie0503491

Gill, R. I. S. (1996). "Chemical control of deposit-scopes and limitations," *Paper Technology* 37(6), 23.

Holmbom, B. R., and Sunberg, A. (2003). "Dissolved and colloidal substances accumulating in papermaking process waters," *Wochenblatt Für Papierfabrikation* 131(21), 1305-1311.

Huang, L., Xiao, H., and Ni, Y. (2006). "Cationic-modified microporous zeolites/anionic polymer system for simultaneous removal of dissolved and colloidal substances from wastewater," *Separation & Purification Technology* 49(3), 264-270. DOI: 10.1016/j.seppur.2005.10.009

Hubbe, M. A., Sundberg, A., Mocchiutti, P., Ni, Y., and Pelton, R. (2012). "Dissolved and colloidal substances (DCS) and the charge demand of papermaking process waters and suspensions: A review," *BioResources* 7(4), 6109-6193. DOI: 10.15376/biores.7.4.6109-6193

Hubbe, M. A. (2007). "Flocculation and redispersion of cellulosic fiber suspensions: a review of effects of hydrodynamic shear and polyelectrolytes," *BioResources* 2(2), 296-331. DOI: 10.15376/biores.2.2.296-331.

Jing, Y., Zhou, H., Hu, X., and Dai, H. (2002). "Research on the application of anionic catchers in waste news pulp," *Journal of Nanjing Forestry University (Natural Sciences Edition)* 26(4), 75-77. DOI: 10.3969/j.jssn.1000-2006.2002.04.019

Kobayashi, S., Shirasaka, H., Suh, K. D., and Uyama, H. (1990). "Viscosity behaviors and gel properties of linear and branched polyethylenimines: Effects of micro-structures," *Polymer Journal* 22(5), 442-446.

Li, H., Ni, Y., and Sain, M. (2002). "The presence of dissolved and colloidal substances in BCTMP and their effect on sizing," *Journal of Pulp & Paper Science* 8(2), 45-49.

Liu, L., and Dai, H. (2006). "The surface chemical characteristics of fines," 3rd Emerging Technologies of Pulping and Papermaking, Guangzhou, China, pp. 93-96.

Miao, Q., Huang L., and Chen, L. (2012). "Advances in the control of dissolved and colloidal substances present in papermaking processes: A brief review," *BioResources* 8(1), 1431-1455. DOI: 10.15376/biores.8.1.1431-1455

Nylund, J., Sundberg, A., and Sundberg, K. (2007). "Dissolved and colloidal substances from a mechanical pulp suspension—Interactions influencing the sterical stability," *Colloid Surfaces A* 301(1-3), 335-340. DOI: 10.1016/j.colsurfa.2006.12.068

Pfau, A., W. Schrepp, A., and Horn, D. (1999). "Detection of a single molecule adsorption structure of poly(ethylenimine) macromolecules by AFM," *Langmuir* 15(9), 3219-3225.

Ravnjak, D., Zule, J., and Moze, A. (2003). "Removal of detrimental substances from papermaking process water by the use of fixing agent," *Acta Chimica Slovenica* 50, 149-158.

Shetty, C. S., Greer, C. S., and Laubach, G. D. (1994). "A likely mechanism for pitch deposition control," *Tappi Journal* 77(10), 91-96.

Sundberg, A., Ekman, R., Holmbom, B., Sundberg, K., and Thornton, J. (1993). "Interactions between dissolved and colloidal substances and a cationic fixing agent in mechanical pulp suspensions," *Nordic Pulp and Paper Research Journal* 8(1), 226-231.

Vidal, G., Videla, S., and Diez, M. C. (2001). "Molecular weight distribution of *Pinus radiata*, kraft mill wastewater treated by anaerobic digestion," *Bioresource Technology* 77(2), 183-91. DOI: 10.1016/S0960-8524(00)00141-3

Wang, J., Mao, S., Su, W., Chen, C., and Dai, H. (2013a). "The origin and analysis methods of DCS in papermaking wet-end system," *Transaction of China Pulp and Paper* 28(3), 59-62. DOI: 10.11981/j.issn.1000-6842.2013.03.59

Wang, L., Li, G., Zhang Y., and Xiao, H. (2013b). "Synthesis and evaluation of P(AM-b-DADMAC) as fixative for dissolved and colloidal substances," *Journal of Applied Polymer Science* 130(6), 4040-4046. DOI: 10.1002/app.39679

Wang, L., Zhang, Y., and Li, G. (2013c). "Behavior of polyamine fixing agents on agglomeration of dissolved and colloidal substances in papermaking," *BioResources* 9(1), 472-481. DOI: 10.15376/biores.9.1.472-481

Wang, L., Zhang, Y., Chen, H., Xia, X., Liu, Z., and Hu, Z. (2014). "Effect of fixing agent dosage on the mechanism of colloidal substances retention onto pulp," *BioResources* 9(2), 3225-3235. DOI: 10.15376/biores.9.2.3225-3235

Wu, R., He, B., Zhao, G., and Li, X. (2014). "Immobilization of pectinase on polyethyleneimine-coated pulp fiber for treatment of whitewater from papermaking," *Journal of Molecular Catalysis B Enzymatic* 99(99), 163–168. DOI: 10.1016/j.molcatb.2013.11.007

Xiao, H., and Cezar, N. (2005). "Cationic-modified cyclodextrin nanosphere/anionic polymer as flocculation/sorption systems," *Journal of Colloid & Interface Science* 283(2), 406-413. DOI: 10.1016/j.jcis.2004.09.008

Yuan, G., Dai, H., Ye, C., Zhang, Y., and Wang, Z. (2011). "Adsorption of Ca (II) from aqueous solution onto cellulosic fibers and its impact on the papermaking process," *BioResources* 6(3), 2790-2804. DOI: 10.15376/biores.6.3.2790-2804

Zhang, H., He, Z., Ni, Y., Hu, H., and Zhou, Y. (2007). "Characteristics of dissolved and colloidal substances in high yield pulp and their impact on filler retention," *Appita Journal* 60(5), 390-395.

Zha, L., Hu, J., Wang, C., Fu, S., and Luo, M. (2002). "The effect of electrolyte on the colloidal properties of poly(N-isopropylacrylamide-*co*-dimethylaminoethyl-methacrylate) microgel latexes," *Colloid & Polymer Science* 280(12), 1116-1121. DOI: 10.1007/s00396-002-0734-8

Article submitted: July 13, 2016; Peer review completed: August 28, 2016; Revised version received and accepted: September 4, 2016; Published: September 29, 2016.
DOI: 10.15376/biores.11.4.9756-9770