ADSORPTION OF Ca(II) FROM AQUEOUS SOLUTION ONTO CELLULOSIC FIBERS AND ITS IMPACT ON THE PAPERMAKING PROCESS

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Calcium(II) is one of the most common metal ions in papermaking systems. However, the effect of Ca^{2+} on papermaking processes has not drawn much attention. The adsorption of Ca^{2+} from aqueous solutions onto bleached *Eucalyptus globulus* kraft pulp fibers was investigated. Thermodynamic results indicate that the adsorption of Ca^{2+} onto bleached *E. globulus* kraft pulp fibers was exothermic, reversible, and spontaneous. The equilibrium data followed Langmuir isotherms. The adsorption basically agrees with the ionic reaction model between carboxyl groups of fibers and Ca^{2+} in which the molar ratio of carboxyl to Ca^{2+} is close to 2:1. The binding capacity with carboxyl groups is so strong that the anionic charge of the adsorption sites in fibers can be screened, leading to decreased performance of cationic polyacrylamide for retention and drainage, Alkyl Ketene Dimer (AKD) for sizing, and cationic starch for dry strength. The precipitation effect of Ca^{2+} with three kinds of dissolved and colloidal substances (sodium rosinate, sodium stearate, sodium oxalate) also was investigated. The results showed that deposits formed by Ca^{2+} and dissolved and colloidal substances, which could adsorb to the surfaces of fibers, would affect drainage and retention abilities of cationic polyacrylamide.

Keywords: Ca^{2+}; Adsorption; Bleached Eucalyptus globulus kraft pulp; Charge screening effect; Drainage and retention abilities; Paper sheets properties

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INTRODUCTION

Closing the water circuit in pulp and paper mills is becoming an inevitable trend (Bygrave and Englezos 1998). However, the wet-end operations and properties of paper sheets are affected by many complex factors. Numerous studies have shown that as the amount of non-process elements (NPE) is increased along with closing water circuits, the effects of wet-end addition agents are affected, pitch problems become more serious, drainage and retention properties of pulp decreased; therefore, the closing of water circuits has been limited because of these problems. Past studies have focused on the characteristics of dissolved and colloidal substances (DCS) in papermaking systems, with emphasis on substances having negative charge (Chow et al. 2003; Donat et al. 2003; Li et al. 2002; Miranda et al. 2009; Nylund et al. 2007; Zhang et al. 2007). There has been less attention paid to effects of metal ions on the wet-end operations and the effect of interactions between metal ions and DCS.

When closing white water circuits, metal ions such as Na^+, Al^{3+}, Fe^{3+}, Fe^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+}, K^+, and Cu^{2+} tend to accumulate. Among these different kinds of metal ions, Na^+ has small radius and its adhesive force to pulp is low, so it can easily accumulate to high concentrations. In addition, Ca^{2+} is also accumulated with the use of hard water and with the increasing usage of $CaCO_3$ as a filler. The results reported by Bryant et al. (1993) indicated that the most common metal ions encountered in the closing of white water circuits in papermaking processes were Ca^{2+} and Na^+ (Bryant et al. 1993; Gulbehsen and Paulapuro 1999). As the metal ions accumulate in the white water circuit, the conductivity of white water is increased, and the state of charge and the spatial structure of auxiliary agents will be affected. The bridging effect of high molecular auxiliary agents will be especially decreased. Compared to Na^+, Ca^{2+} could impact the pulp and papermaking processes more seriously because of the increasing water hardness along with the accumulation of Ca^{2+}. Ca^{2+} influences the papermaking chemistry largely by means of screening the surface charge of fibers, so it is important to research the adsorption of Ca^{2+} on fibers. Duong et al. (2005, 2006) researched the sorption and the competitive sorption of Na^+ and Ca^{2+} ions onto unbleached kraft fibers. Rudie et al. (2006) researched the ion exchange of H^+, Na^+, Mg^{2+}, Ca^{2+}, Mn^{2+}, and Ba^{2+} on wood pulp. Many related results have been reported. A majority of such studies were done basically to solve problems related to pulping and bleaching; thus, the materials in these studies were mostly unbleached pulp, where the anionic groups components of the fibers are complicated. Because of the high complexity of the adsorption of the metal ions on unbleached pulp fibers, it was impossible to describe the adsorption by one single model.

The control of multi-valent metal ions as Ca^{2+} has already been emphasized in the pulp and papermaking industry. However, the studies mostly have focused on the influence of water hardness on the outcomes of pulping and bleaching. For example, Ca^{2+} could influence the effect of chelating agents on transition metals, leading to effects on the delignification and bleaching processes (Bryant and Edwards 1996; Frederick and Grace 1979; Grace 1977; Johansson and Liunggren 1994; Ulmgren 1996). In addition, Ca^{2+} can also affect papermaking processes, cause pitch problems, and influence the retention system, sizing, and strength properties; however, there has been relatively little attaching focused on such effects.

The present study concerns the adsorption of Ca^{2+} on fibers and the precipitation of Ca^{2+} with DCS model substances, and the effect of Ca^{2+} on wet-end operation and handsheet properties. The fibers used in this study were bleached *Eucalyptus globulus* kraft pulp fibers. Bleached *E. globulus* kraft pulp, a common hardwood material (Hillman and Rooks 2002), is widely used for making writing and printing papers. Therefore, it would be meaningful to investigate the adsorption of Ca^{2+} on bleached *E. globulus* kraft pulp fibers and learn about the effects of Ca^{2+} on paper-making processes.

EXPERIMENTAL

Materials

The bleached *E. globulus* kraft pulp used in this study was supplied by Suzano, SP, Brazil in dry sheet form. The pulp was beaten in a Valley beater to 300 mL Canadian standard freeness (CSF) using TAPPI method T200 sp-01 (TAPPI 2001). Pulp freeness was measured following TAPPI method T227 om-99 (TAPPI 1999). 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 was repeated four times until the pH of the filtrate approached neutrality. The pH of the filtrate was then regulated to 7.0 by adding a minute quantity of NaOH into the pulp. The method was suggested by previous researcher (Liu and Dai 2006). Then the pulp samples were dewatered to 25±2% oven-dry and stored at 4ºC. The pulp moisture content was determined using TAPPI method T412 om-02 (TAPPI 2002). The carboxyl content of pulp was measured following TAPPI method T237 cm-98 (TAPPI 1998).

Analytical grade NaOH (Nanhua, China), $CaCl_2$ (Jiuyi, China), NaCl (Jiuyi, China), stearic acid (Guohua, China), and sodium oxalate (Shanghua, China) samples were used in the experiments. The additive agents used were polydiallyldimethyl ammonium chloride (PDADMAC Kemira Oyj, Finland), cationic starch (CS National Starch, USA), cationic polyacrylamide (CPAM, Ciba, Switzerland), colloidal silica (Eka Chemicals, Holland), and Alkyl Ketene Dimer (AKD Tianma, China). These chemicals were diluted with deionized water.

On the basis of previous researchers' experiments and analyses, three kinds of DCS model substances including sodium rosinate, sodium stearate (simulating the resin acid and fatty acid from wood materials and sizing agent), and sodium oxalate (simulating the dissolved mineral salts from non-wood materials) were chosen for the experiment. Deposits can be formed with these negatively charged DCS model substances and Ca^{2+}. Sodium rosinate and sodium stearate were prepared with given amounts of NaOH and rosin or stearic acid at certain temperatures (sodium rosinate: 85 ^oC, sodium stearate: 75 ^oC, according to the melting points of rosin and stearic acid). The rosin was obtained from Fengkai forest chemical, China (Mclean et al. 2005; Qin et al. 2003).

Methods

Adsorption of Ca^{2+}

The adsorption tests were carried out in 250-mL screw-cap bottles. For each test about 0.5 g of pulp, which was converted to completely protonated form (deionized pulp), was mixed with 100 mL of the Ca^{2+} solution to form a slurry. The adsorption isotherms were plotted using experimental data obtained at different temperatures and concentrations of Ca^{2+}. The treated pulp was then separated from the solution by filtration, and the filtrate composition was measured by Radiofrequency Inductively Coupled Plasma (ICP 4300DV PerkinElmer instruments, USA). The specific amount of Ca^{2+} adsorbed on the fibers during the experiments was calculated using the following mass-balance equation,

$$Q = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where Q is the amount of sorbed Ca^{2+} (mmol/g) at equilibrium, C_0 is the initial concentration of Ca^{2+} in the solution (mmol/L), C_e is concentration of Ca^{2+} in the solution (mmol/L) at equilibrium, *m* is the oven-dry mass of fibers (g), and *V* is the volume of the solution (L).

Pretreatment of pulp with $CaCl_2$ or NaCl

A certain amount of deionized pulp samples was diluted and disintegrated. An excess amount of $CaCl_2$/NaCl was added in the pulp slurry, after which the pulp slurry was stirred for 90 min. The Ca^{2+} or Na^+ ions could therefore be adsorbed on the pulp fibers completely. Unbonded Ca^{2+} or Na^+ ions were removed by washed the pulp slurry with deionized water a few times, regulating the pH of the filtrate to 7.0 by adding minute quantities of NaOH into the pulp. Then the pulp samples were dewatered to 25±2%, oven-dry, and stored at 4ºC.

The precipitation effect of Ca^{2+} with DCS model substances

The analyses of precipitation were carried out in 250-mL screw-cap bottles. For each test different amounts of Ca^{2+} were added into 100 mL solutions that had 0.2g/L of model DCS. The pH of the filtrate was changed to 7.0 by adding minute quantities of NaOH/HCl into the solution. The experiments were carried out in a constant temperature shaker bath (SHA-C, Guohua, China) at 25ºC for 90min. The turbidity was measured with a turbidimeter (2100P Hach, USA).

Evaluation of pulp and hand sheets

Chemicals were added into deionized pulp (0.3% oven-dry consistency, 1 L) in the following order under 750 rpm stirring: 0.06g/L DCS (three kinds of model substances at the level of 1:1:1 in mass), $CaCl_2$ or NaCl, 0.05% PDADMAC (all the percentages are based on oven-dry fiber), 1% CS, 0.2% AKD, 0.025% CPAM (1000 rpm, 1 min), and 0.05% colloidal silica (750 rpm, 20 s, where a different stirring rate was needed for the CPAM/silica retention system). The doses of $CaCl_2$ or NaCl, CPAM, AKD, and CS were changed according to the experimental procedure. The temperature of the pulp was adjusted to 20 ^{o}C. The CSF of the pulp was measured following TAPPI method T227 om-99 (TAPPI 1999). The turbidity of filtrate was measured with the turbidimeter. The dry content of pulp was diluted to 0.2%, and handsheets were made following TAPPI method T205 sp-02 (TAPPI 2002) by sheet-making apparatus (RK-2A PTI, Austria) with the same experiment conditions and doses of chemicals as above. The Cobb value, tensile index, and folding endurance were measured following TAPPI method T441 om-98, T511 om-02, and T494 om-01 (TAPPI 1998, 2001, 2002) respectively.

Conductivity of pulp was measured by conductivity meter (DDS-11A CANY, China).

Scanning Electron Microscopy (SEM) of fibers

The pulp samples were collected on carbon tape and observed with an SEM (Quanta 200 environmental scanning electron microscopy FEI, Netherlands) instrument. The operated voltage was 20 kV, and the current changed with the vacuum under the conditions of observation.

RESULTS AND DISCUSSION

Adsorption of Ca^{2+} on Bleached *E. globulus* Kraft Pulp

It is known that water-swollen kraft fibers are porous with high specific surface. The surface of fibers usually plays a role in adsorption of various cationic substances due to the presence of carboxyl, hydroxyl, and sulfonic acid groups (Roberts 1996). In papermaking systems, various additives work only by adsorption on fibers. Carboxyl groups have adsorption capacities to metal ions by the dissociation of H^+ in aqueous media.

$$\text{Cell-COOH} \rightleftharpoons H^+ + \text{Cell-COO}^- \tag{2}$$

$$\text{Dissociation Constant: } K = \frac{[H^+][\text{Cell-COO}^-]}{[\text{Cell-COOH}]} \tag{3}$$

The dissociation constants of carboxyl groups generally are found within the range 10^{-4} to 10^{-3} (Scott 1996). From this ionization equilibrium equation, it can be seen that the extent of ionization of active groups in fibers is high under typical neutral or alkaline conditions of the papermaking system, so metal ions can be easily adsorbed on the anionic groups.

When a saturated monolayer adsorption takes place, isotherms fit the Langmuir Model. The model can be described in terms of the following equation (Haron et al. 2009; Richard 1996; Seader and Herley 1998),

$$\frac{C_e}{Q} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{4}$$

where C_e (mmol/L) is the equilibrium concentration, Q (mmol/g) is the amount that has been adsorbed when the adsorption reaches equilibrium, and Q_0 and b are constants. Q_0 is the maximum sorption, and b is sorption binding strength.

Figure 1 shows the relationship between the equilibrium concentration of Ca^{2+} in the solution (C_e, mmol/L) and the amount of Ca^{2+} adsorbed per unit mass of deionized bleached eucalyptus pulp (mmol/g). The effects of temperature on the adsorption of Ca^{2+} to bleached eucalyptus pulp are also presented in Fig. 1. The results showed that the adsorption rate of Ca^{2+} on deionized kraft pulp was decreased, but the maximum adsorption barely changed when the temperature was increased.

Values of b and Q_0 from the Langmuir model could be obtained from Eq. (4). The results are presented in Table 1. The value of the correlation coefficient R^2 showed that there was good correlation between the Langmuir isotherm and the experimental data.

ΔH_{ads} (the heats of adsorption) for Ca^{2+} were calculated by the Van't Hoff equation as follows,

$$\ln K_a = -\frac{\Delta H_{ads}}{RT} + \frac{\Delta S}{R} \tag{5}$$

where T is the absolute temperate, and K_a is the equilibrium constant for adsorption process, taken as the Langmuir adsorption constant. The relationship between lnK_a and $1/T$ is shown in Fig. 2.

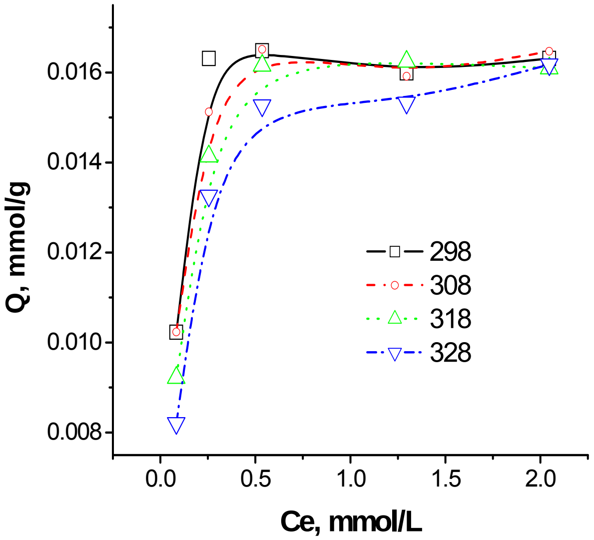

Fig. 1. Sorption isotherm of Ca^{2+} on deionized kraft pulp from mixture of Ca^{2+} and Na^{+} solution at pH 7.5

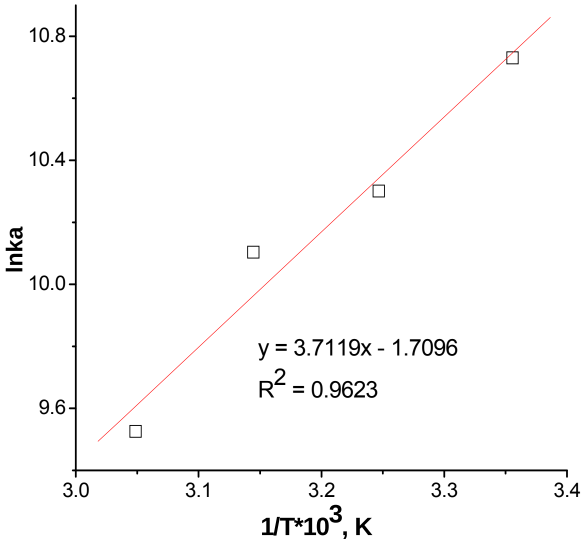

Fig. 2. Effect of temperature of Ca^{2+} adsorption on hardwood pulp

Table 1. Adsorption Capacities of Deionized Pulp for Ca^{2+} at Different Temperatures

T (K)	R^2	Q_0 (mmol/g)	b (L/mmol)
298	0.999	0.0165	45.7
308	0.999	0.0167	29.7
318	0.999	0.0166	24.4
328	0.999	0.0166	13.7

The standard free energy change (ΔG^0) was calculated using the equation,

$$\Delta G^0 = -RT \ln K_a \quad (6)$$

where R is the universal gas constant (8.31j/mol·k). The thermodynamic parameters for adsorption of Ca^{2+} were calculated and presented in Table 2.

Table 2. Thermodynamic Parameters for Ca^{2+} Adsorption on the Bleached Pulp

T (K)	lnKa	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (J/molK)
298	10.7	-26.9	-30.9	-14.2
308	10.3	-26.7		
318	10.1	-27.0		
328	9.53	-26.3		

The results for enthalpy change, ΔH^0=-30.9 kJ/mol, indicated that the adsorption process is exothermic. In addition, ΔS^0=-14.2 J/molK, and ΔG^0 values were all negative, all of which implied that the adsorption process is spontaneous at the normal temperature. For most pulps, only a very small quantity of metal cations in the liquid phase is needed to be adsorbed on all the anionic sites of fibers (Bryant and Edwards 1996). K_a values were large, so the number of unoccupied sites of fibers was extremely small. This means Ca^{2+} is very easily adsorbed to bleached *E. globulus* kraft pulp. Furthermore, once the adsorption occurs, the bond between Ca^{2+} and carboxyl groups will be so strong that Ca^{2+} cannot be desorbed under regular pH environments in papermaking processes.

The amount of carboxyl groups in bleached *E. globulus* kraft pulp was determined to be 0.0366mmol/g. The maximum of Ca^{2+} adsorption capacity fluctuated from 0.0165 to 0.0167mmol/g in the studied temperature range. The ratio of carboxyl groups and the maximum of Ca^{2+} adsorption capacity was roughly 2:1. The same stoichiometry was also found by Karhu et al. (2002).

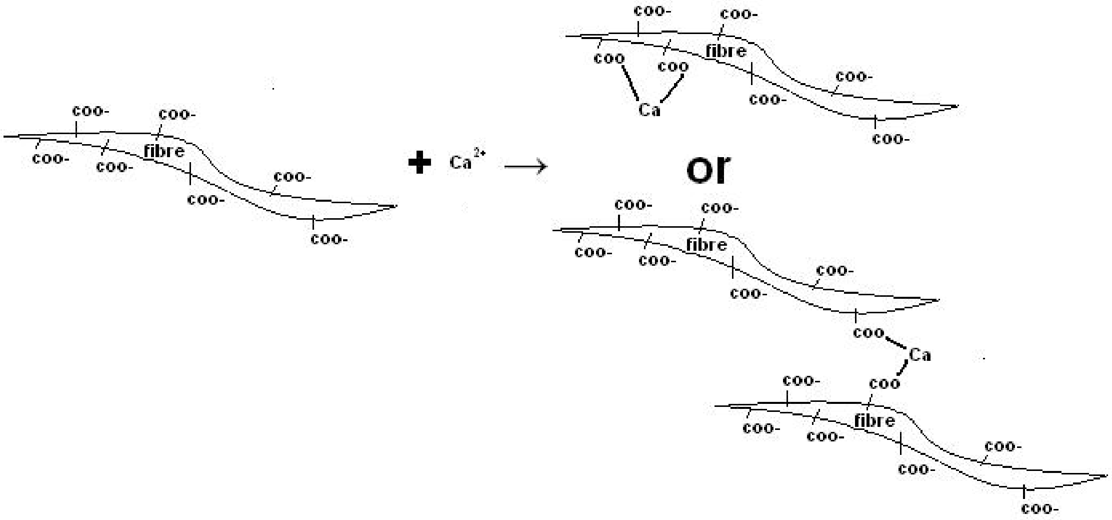

Fig. 3. The adsorption model between carboxyl groups and Ca^{2+}

As is indicated in Fig.3, one Ca^{2+} could adsorb on fiber by forming ionic bonds with two carboxyl groups in one single fiber or two carboxyl groups from different fibers. If the adsorption completely took place following the model, the maximum Ca^{2+} adsorption capacity of fibers should be 0.0183 mmol/g, a little higher than the maximum Ca^{2+} adsorption on fibers. So the adsorption of Ca^{2+} on the bleached eucalyptus pulp fibers basically agrees with the ionic reaction model. The difference between the maximum Ca^{2+} adsorption capacity and theoretical value was may caused by unionized carboxyl groups, electrostatic repulsion, and the steric effect between ions.

Different observations and explanations had been reported in previous studies. Duong's results (2006) indicated that, before being adsorbed on fibers, the calcium could form monovalent ionic pairs such as $CaCl^+$, $CaOH^+$, and some calcium may even be present in crystalline forms; thus, the calculated total charge of the sorbed Ca^{2+} may exceed the total negative sites available under some conditions of testing (Charlet and Tournassat 2005; Duong et al. 2006; Tournassat et al. 2004). The different results may be caused by different materials. In the above studies mineral materials and unbleached kraft pulp were used as adsorbing materials. Those materials have more complex chemical compositions, so the reaction between Ca^{2+} and their surfaces might take place following more than one model. Bleached *E. globulus* kraft pulp was used in the present study, and the anionic sites of fibers in bleached *E. globulus* kraft pulp were mainly carboxyl groups generated in cooking and bleaching processes. The other anionic groups in hemicelluloses and lignin would have been mostly removed after bleaching.

Because of the strong binding capacity with carboxyl groups as stated above, Ca^{2+} could screen the anionic charge of carboxyl acid groups. Electrostatic adsorption between cationic addition agents and the adsorption sites of fibers will be affected severely, which leads to a corresponding decrease of wet-end operating efficiency and paper sheet properties in the papermaking process (Donovan 1994; O'Brien 1996).

Charge screening effect of Ca^{2+} on retention and drainage abilities of pulp

Figure 4 shows the CSF of pulp and turbidity of filtrate with different doses of CPAM in deionized pulp and pulp pretreated with $CaCl_2$ and NaCl. Since the fibers in deionized pulp have plenty of ionized carboxyl sites to adsorb CPAM, the drainage and retention abilities of pulp increased as CPAM was adsorbed. It could be seen that the higher the dose of CPAM, the better the drainage and retention abilities of deionized pulp. As the dose level of CPAM increased from 0 to 0.04%, the freeness of pulp increased from 320 to 375 mL; meanwhile, the turbidity of the filtrate decreased from 9.72 to 4.96 Nephelometric Turbidity Units (NTU).

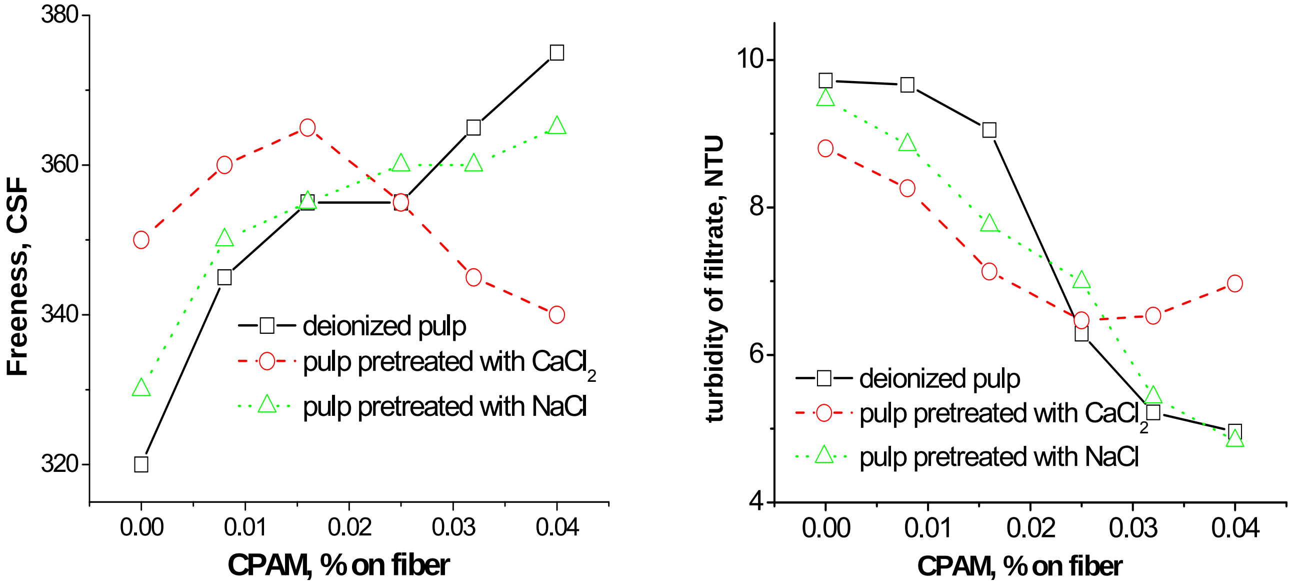

Fig. 4. Charge screening effect of Ca^{2+} and Na^+ on CSF of pulp and turbidity of filtrate (conc. of pulp was 0.3% oven-dry, different dosages of CPAM and 0.05%Silica were added sequentially)

Pulp pretreated with $CaCl_2$ showed a different result. As the dose level of CPAM rose from 0 to 0.04%, the drainage and retention abilities of pulp pretreated with $CaCl_2$

increased at first. But when the dose of CPAM was in the range of 0.016 to 0.025%, the drainage and retention abilities began to deteriorate. The freeness of pulp decreased from 365 mL (when the level of CPAM was 0.016%) to 340 mL (when the level of CPAM was 0.04%).

Meanwhile, the turbidity of filtrate increased from 6.47 NTU (when CPAM was 0.025%) to 6.97 NTU (when CPAM was 0.04%). These findings confirm that the screening effect of Ca^{2+} influenced the effect of CPAM on pulp. Because there were barely any unoccupied ionized carboxyl sites on the fibers of pulp pretreated with $CaCl_2$, CPAM could be adsorbed on pulp only with nonelectrostatic forces, and such forces are much weaker than the electrostatic force. As a consequence, the drainage and retention improvements as a result of the CPAM addition in pulp pretreated with $CaCl_2$ were less than those for deionized pulp.

Meanwhile, maximum CPAM adsorption capacity of pulp pretreated with $CaCl_2$ was less than that observed with the deionized pulp. So the surplus cationic charge that was provided from an overdose of CPAM increases the repulsive forces between fibers, leading to a decrease in the drainage and retention abilities of pulp due to a process of redispersion (Alince 1989).

The adsorbing ability of Na^+ is weaker than that of Ca^{2+} (Duong et al. 2005). Compared to Ca^{2+}, the anionic screen effect of Na^+ is so weak that it has little effect on the drainage and retention abilities of pulp given by CPAM. Results for Na^{2+}-treated pulp were similar to those for deionized pulp.

The ionic charge of the fibers in CPAM-free pulp was shielded by metal ions. Thus, the repulsive forces between fibers decreased, the hydration degree of fibers dropped, and the flocculation tendency of the pulp increased with the addition of Ca^{2+}. So the initial drainage and retention abilities of pulp (CPAM free) pretreated with $CaCl_2$ and NaCl were better than that of deionized pulp.

In a binary system, Ca^{2+} would displace the adsorbed Na^+, since the adsorbing ability of Ca^{2+} was higher than Na^+ at usual pH values. So even a small amount of Ca^{2+} in the pulp might shield the adsorbing sites of fibers easily, and the abilities of cationic additives would be consequently affected (Duong et al. 2006).

Charge Screening Effect of Ca^{2+} on Properties of Handsheets by Ca^{2+}

Although AKD is a non-ionic reactive sizing agent, the retention of AKD particles on paper sheets is also dependant on the electrostatic adsorption. Individual particles of AKD typically are stabilized with a layer of cationic starch or other cationic polymer. Because of the charge screening effect of Ca^{2+}, pulp pretreated with $CaCl_2$ acted as if it had less anionic adsorbing sites than deionized pulp. This would affect the adsorption of AKD on paper sheets; thus, the sizing effect decreased.

Table 3 shows the sizing properties of three kinds of pulps under different doses of AKD. The Cobb values of handsheets made of pulp pre-treated with $CaCl_2$ were obviously higher than those made of deionized pulp. The adsorption of Na^+ on fibers was so weak that the Cobb values of handsheets made of pulp pretreated with NaCl showed no significant difference from those made of deionized pulp.

Table 3. Charge Screening Effect of Ca^{2+} on Sizing Effect of AKD (conc. of pulp was 0.2% oven-dry, different dosages of AKD, 0.02% CPAM, 0.05% Silica were added sequentially)

AKD (% on fiber)	0.05	0.1	0.15	0.2	0.3
Cobb value of deionized pulp (g/m^2)	22.2	18.7	17.9	17.5	17.9
Cobb value of pulp pre-treated with $CaCl_2$ (g/m^2)	25.0	20.7	19.9	18.9	19.8
Cobb value of pulp pre-treated with NaCl (g/m^2)	22.2	19.4	18.3	18.4	18.2

Similar to AKD, the effect of the cationic starch (CS) on strength abilities of handsheets depends on the adsorption of the CS molecules and the fibers of pulp. The anionic adsorbing sites in pulp pre-treated with $CaCl_2$ were less than anionic adsorbing sites in deionized pulp and in pulp pre-treated with NaCl. The retention of CS on handsheets was reduced, and the tensile and folding strength of handsheets decreased as a consequence.

As indicated by the results shown in Table 4, there was no significant difference between the strength properties of paper sheets made by deionized pulp and pulp pre-treated by NaCl, while paper sheets made by pulp pretreated by $CaCl_2$ had lower strength properties with the same doses.

Table 4. Charge Screening Effect of Ca^{2+} and Na^+ on Strength Properties of Handsheets (conc. of pulp was 0.2% oven-dry, different dosages of CS, 0.02% CPAM, 0.05% Silica were added sequentially)

CS (% on fiber)		0.25	0.5	1	1.5
Deionized pulp	Tensile index (Nm/g)	45.9	47.3	49.6	47.4
	Folding endurance (Times)	24	27	41	47
Pulp pre-treated by $CaCl_2$	Tensile index (Nm/g）	38.6	37.7	40.9	41.9
	Folding endurance (Times)	23	24	32	36
Pulp pre-treated by NaCl	Tensile index (Nm/g)	43.1	47.8	48.7	48.5
	Folding endurance (Times)	25	26	39	47

The precipitation effect of Ca^{2+} with DCS model substances and the effect of deposits on wet-end operation

Besides adsorption on fibers and the screening effect on the ionic charge of fibers, Ca^{2+} can form deposits with DCS model substances. Under this circumstance, the colloidal properties of DCS materials would change.

DCS model substances were able to dissolved in water without Ca^{2+}, and the turbidity values of the solutions were very low. With Ca^{2+} added into the solution, Ca^{2+}

formed deposits with the DCS model substances gradually. The turbidity of solutions increased almost linearly. As results in Fig.5, with no Ca^{2+} present, the turbidity of three kinds of DCS model substances solutions were 11.1, 1.1, 4.5 NTU. As the added amount of Ca^{2+} increased to 0.944 mmol/L, the turbidity of three kinds of DCS materials respectively reached 971, 995, and 182 NTU, which are several times the values reached without Ca^{2+}. The different trends for the turbidities of samples were caused by the different properties of the respective DCS model substances.

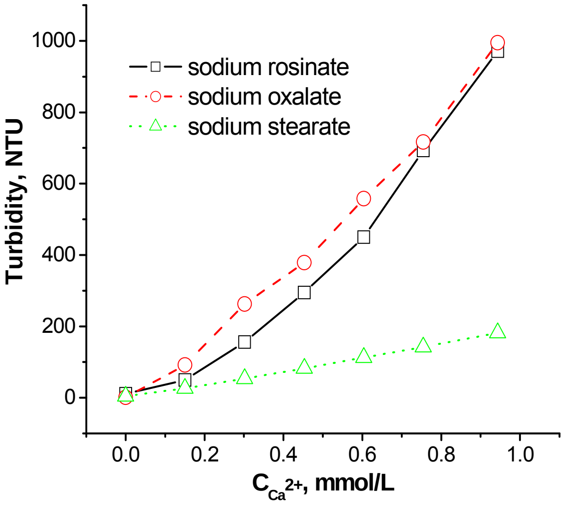

Fig. 5. Effect of Ca (II) on the turbidity of DCS model substances solutions

Pulp samples with and without deposits formed by Ca^{2+} with DCS were observed by SEM. Figure 7 shows the surfaces condition of fibers. In the pulp with deposits formed by Ca^{2+} and DCS materials, the surfaces of fibers adsorbed many sedimentary particles. There were no similar deposits on the surfaces of blank samples (Fig. 6).

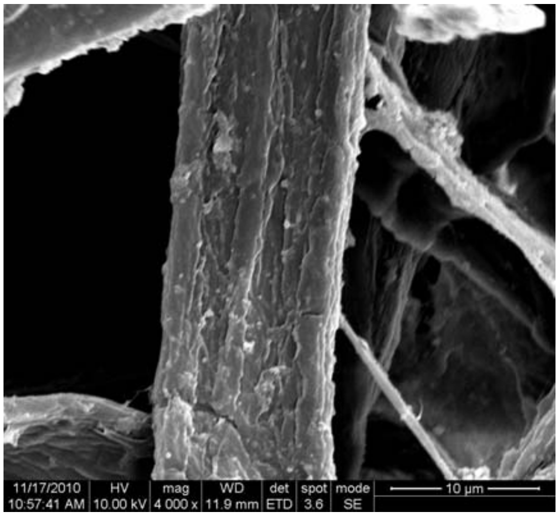

Fig. 6. Fibers of bleached eucalyptus pulp

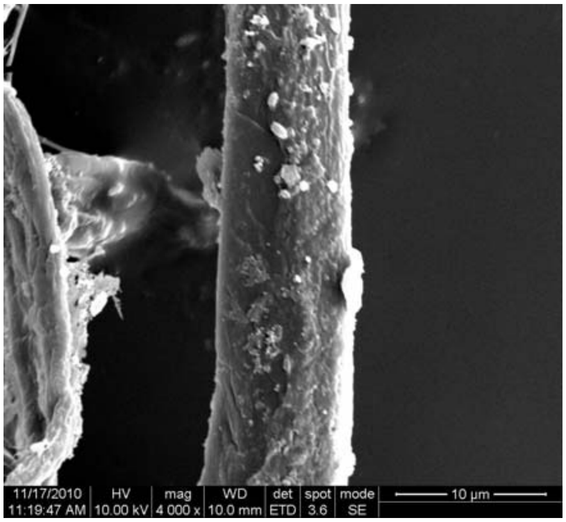

Fig. 7. Fibers of bleached eucalyptus pulp with deposits formed by Ca^{2+} and DCS model substances

The interactions between fibers and additives such as drainage and retention aids would been affected by the presence of any precipitated particles formed by DCS model compounds and Ca^{2+} (Fig. 8). When the conductivity of pulp regulated by $CaCl_2$ increased to 6.066 mS/cm, the freeness of pulp dropped from 440 to 290 mL, along with a rise in the turbidity of the filtrate from 11.9 to 34.6 NTU.

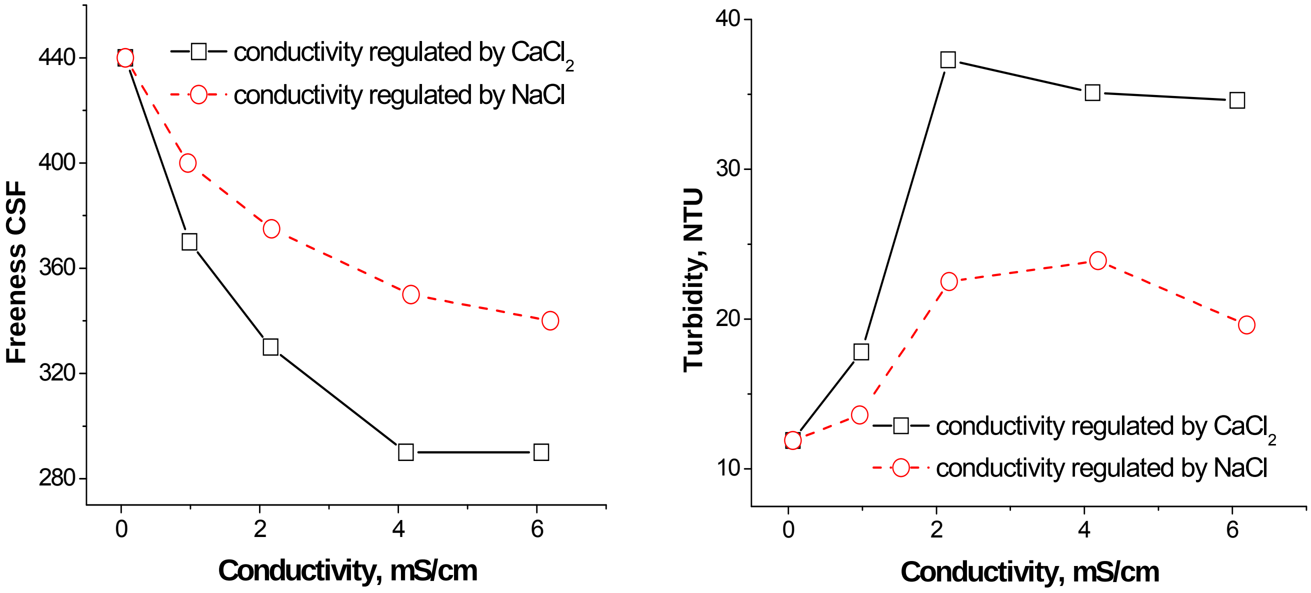

Fig. 8. Effect of conc. of Ca^{2+} on CSF of pulp and turbidity of filtrate when conc. of DCS was 0.06g/L (conc. of deionized pulp was 0.3% oven-dry, different dosages of $CaCl_2$ or NaCl, 0.02% CPAM and 0.05% Silica were added sequentially)

Because no deposition resulted from the interaction between Na^+ and DCS model substances, Na^+ in pulp would not change the colloidal properties of the DCS. The decreases in the drainage and retention abilities of pulp were less when the conductivities of pulp were regulated by NaCl, compared to the conductivities of pulp regulated by $CaCl_2$. In this situation, the decreases in the drainage and retention abilities of pulp were mainly caused by the effect on the character of the molecular chains of retention and drainage aids from the high conductivities.

CONCLUSIONS

1. The adsorption isotherms of Ca^{2+} on bleached kraft eucalyptus pulps follow the Langmuir model. The adsorption is exothermic, reversible, and spontaneous. The adsorption of Ca^{2+} on the bleached eucalyptus pulp fibers basically agrees with the ionic reaction model between carboxyl groups of fibers and Ca^{2+}. The molar ratio of carboxyl to Ca^{2+} is close to 2:1.
2. Because of the strong binding capacity with carboxyl groups, Ca^{2+} can screen the anionic charge of carboxyl acid groups. Consequently, the electrostatic adsorption between cationic addition agents and the adsorption sites of fibers are affected

severely, which leads to the corresponding decrease of wet-end operations and sheet properties in the papermaking process. With DCS model substances, Ca^{2+} is able to form deposits than can absorb onto the surfaces of fibers, thereby affecting wet-end operations and sheets properties, as well as leading to pitch problem.

3. Na^{+} is another common metal ion in papermaking systems. Like Ca^{2+}, it can raise the conductivity of white water. However, the charge screening effect of Na^{+} is weaker than Ca^{2+}. Furthermore, it will not form deposits with DCS model substances, and thus Na^{+} has a small effect on the drainage and retention abilities of pulp compared to Ca^{2+}.
4. Ca^{2+} is an important factor that greatly affects closing of the white water circuit. To exploit potential performance of cationic addition agents through the complete adsorption to fibers, Ca^{2+} in the system should be controlled initially. Even though the conductivity of white water is still high, the properties of wet-end operation and paper sheets will be improved by means of removing of Ca^{2+} from the papermaking system.

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