Silica Removal using Aluminium Sulphate and Sodium Aluminate during the Bamboo Cooking Process

Yongjian Xu,[a,b,]* Weipeng Zhang,[a,]* Xiaopeng Yue,[a] and Dingjun Zhang [b]

The desilication effects of aluminium sulphate and sodium aluminate on kraft bamboo pulp during the cooking process were investigated in this study. Furthermore, the residual aluminium ion concentration in the resulting black liquor was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) to evaluate the scaling properties of black liquor during the evaporation process. Atomic force microscopy (AFM) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) analysis showed that aluminium salts could react with silica to form a silica-alumina compound, which can adhere to the fibre surface during the cooking process. As a result, the silicon content in the black liquor could be effectively decreased by the addition of aluminium sulphate and sodium aluminate. A silica removal ratio of 74% could be achieved when the loadings of aluminium sulphate and sodium aluminate were 2.0 wt.% and 1.5 wt.%, respectively. Finally, the concentration of aluminium ions was 7.31 ppm under optimised conditions. Based on these considerations, any amounts of aluminum ion passing into the black liquor are unlikely to contribute to scaling problems.

Keywords: Bamboo pulp; Cooking; Silica removal; Black liquor; Scale

*Contact information: a: College of Light Industry and Energy, Shaanxi University of Science & Technology, Xi'an 710021, China; b: Guizhou Chitianhua Company Limited, Chishui, Guizhou, 564700, China; *Corresponding authors: xuyongjian@sust.edu.cn; zwp041315@163.com*

INTRODUCTION

Because of the scarcity of forest resources in China, wood resource industrial applications are limited, especially in the pulp and papermaking industry. Meanwhile, rich non-wood resources, specifically bamboo, are widely distributed in Asia. According to statistics, a total area of 5.5 million hm^2 of bamboo forest is available in China, composing 1/3 of the world's bamboo resources. Therefore, it is known as the “second forest” (Hezhang and Chaomao 2002). Utilisation in the papermaking industry is the main area of application for bamboo materials. However, in comparison with wood materials, the utilisation of bamboo materials in the papermaking industry has been restricted by a handful of disadvantages, such as high silicon content. As reported, 60% of the ash content in non-wood materials is SiO_2 (Zhong 2002). During the kraft digesting process, the silicon in the raw material reacts with sodium hydroxide to form sodium silicate (Isono and Ono 1967; Rao *et al*. 1988). The silicate enters the black liquor and then gets into the green liquor, which causes a series of problems that are known as “silicon influence”. Pulp and papermaking processes such as material preparation, digester operation, brown stock, chemical recovery system, recausticising, and paper machine operations are adversely affected by the presence of silica in bamboo (Jeyasingam 1986; Yong-jian and Xue 2013;

Lin *et al*. 2014). Moreover, the scaling of black liquor in the alkali recovery system is closely related to the silica problem.

Black liquor evaporation scaling is a bottleneck problem in the process of preparing kraft pulp for papermaking. Several methods to solve this problem have been published, and they can be grouped into the categories of cleaning, preventing, and correcting (Darton 1999; Neofotistou and Demandis 2004). Prevention and correction of scaling are preferred, as they avoid difficult to clean deposits. The yield of aluminosilicate scaling is often associated with the concentration of silicon and aluminium element. As a result, determining the residual aluminium ion content in black liquor, to obtain information regarding the scaling properties of black liquor during the evaporation process, is important.

Many studies have been conducted to reduce or eliminate the silica problems to improve the valuable utilisation of non-wood materials, and numerous reports focusing on silica removal have been published (Tutus and Eroglu 2004; Gang and Yongjian 2010; Lin *et al*. 2014). Impurities and some non-associative silicon can be removed during the material preparation process. Silica can be removed during the cooking and alkali recovery process as well. Additionally, desilication reactions can take place by means of the addition of some chemicals, such as calcium salts and aluminium salts.

Previous studies have demonstrated that aluminium salts, calcium oxide, and magnesium oxide are capable of removing silica (Tutus and Eroglu 2003; Ma *et al*. 2009). Among the aforementioned desilication agents, aluminium salts have demonstrated excellent silica removal efficiency (Latour *et al.* 2013). However, the silica removal techniques proposed in the literature are usually carried out during water-softening processes or by coagulation (Huuha *et al*. 2010; Hermosilla *et al*. 2012) or adsorption. Meanwhile, the product, such as magnesium silicate, is difficult to filter because of its fine particles. A silica removal method with aluminum salts added during the pulp cooking process has yet to be reported

In this paper, a novel desilication technique was established with the addition of aluminium salts (aluminium sulphate and sodium aluminate) simultaneously during the bamboo cooking process. This desilication technique is a chemical reaction process taking advantage of the pulp cooking technology to decrease the silica concentration in black liquor. Additionally, the concentration of residual aluminium ions in black liquor was herein measured by ICP-AES to make a preliminary evaluation of the scaling properties of the liquor.

EXPERIMENTAL

Materials

Bamboo chips, with an average length of 50 to 60 mm, were kindly supplied by Chitianhua Pulp and Papermaking Co., Ltd., Guizhou, China. Sodium hydroxide, with a purity of 96.0%, was supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Sodium sulfide ($Na_2S{\cdot}9H_2O$), with a purity of 98.0%, was supplied by Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China.

Aluminium sulphate ($Al_2(SO_4)_3{\cdot}18H_2O$), with a pH value of 2.5 (50 g/L, 25 °C), was supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Sodium aluminate ($NaAlO_2$) was supplied by Sinopharm Chemical Reagent Co., Ltd., Beijing, China, and the aluminium content was above 41.0% (as Al_2O_3).

Cooking Process

The laboratory cooking process was divided into two phases (the pre-impregnation phase and the pulping phase), which could simulate the actual production process.

Sulphate bamboo black liquor was obtained under the following optimised cooking conditions. The total alkali loading for oven-dried raw materials was 24 wt.%, and that for the pre-impregnation phase was 10 wt.%. The total sulfidity was 24 wt.%, and the pre-impregnation phase accounted for 12 wt.%. The remaining alkali liquor was added during the second cooking phase. The liquor-to-bamboo ratio of the pre-impregnation phase was 4:1, and that for the second phase was 4.5:1. The temperature of the pre-impregnation phase was 100 °C, and the holding time was 60 min. The maximum cooking temperature was 160 °C, and the holding time was 20 min.

After the cooking process, the Kappa value of the bamboo pulp was 28, the pulp yield was 46.35%, and the pulp ash content was 1.21%. The components of black liquor were as follows: solids content, 10.65 wt.%; organic matter content, 70.34 wt.%; and SiO_2 content, 1.14 g/L.

Evaluation and Characterisation

The method to determine the silicon content in black liquor was as follows: 1 mL of black liquor and 2 mL of formic acid were pipetted into a 150-mL beaker. Then, the suspension liquid was preheated to 65 °C and maintained for 1 min. Subsequently, 10 mL of H_2O_2 (30 wt.%) was added. Heating was continued for 15 min to make the liquor transparent under this temperature. Then, the temperature was increased to 120 °C until the sample was combusted. After the sample was cooled slightly, 10 mL of NaOH (0.1 M) solution was added to adjust the pH value to 13 to ensure the sample had the same basicity level of the original black liquor. Finally, the method of silicon-molybdic blue spectrophotometry was applied to determine the silica content (Shi *et al.* 2004; Hai, *et al.* 2015). The silicon content in black liquor was calculated as,

$$y=4.9835x-0.3548 \tag{1}$$

where y is the silica content and x is the absorbance value. The correlation coefficient R was 0.9988. The silica concentration data obtained for each sample was the average value for the determination of five times. The relative standard deviation of the element was within the range 0.25% to 1.68%.

The morphological characteristics of pulp were observed using atomic force microscopy (AFM 5100, Agilent, USA). The AFM images were recorded with a Nanoscope IIIa microscope, equipped with the extender electronics module enabling phase imaging in tapping mode. Silicon cantilevers, with a resonance frequency of 250 to 300 kHz, were used. Prior to analysis, the pulp samples were dried on sample stubs and covered by double-sided adhesive tape. Images were collected from 30 to 40 different fibres for each sample, so that the main axis of the fibre was parallel to the slow scan axis of the AFM.

Scanning electron microscopy (SEM) was used to view the solid structures present on the fibre surfaces, and the sample was prepared as a paper sheet with dimensions of 2 mm × 2 mm. The SEM apparatus (S4800 RIGAKU, Japan), with an attached energy-dispersive X-ray spectroscopy (EDS) system, was used to determine the present elements. The morphological analysis was conducted under high vacuum conditions, using an operating voltage of 20 kV.

Inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS InterpidⅡ, Thermo Fisher, USA) was used to measure the concentration of residual aluminium ions in the black liquor, which was digested by HNO_3 and H_2O_2. The ICP spectrometer operating parameters were as follows: RF power, 1200 W; RF frequency, 27.12 MHz; auxiliary gas flow rate (Ar), 1.0 L/min; nebuliser pressure, 0.22 MPa; observation height, 11.2 mm; and wavelength, 309.2 nm.

RESULTS AND DISCUSSION

Desilication Effects of Aluminium Sulphate and Sodium Aluminate

The pulp (with an ash content of 1.21%), without the addition of a desilication agent, was regarded as the control specimen. As can be seen from Fig. 1, the silica content in the black liquor decreased, and the pulp ash content increased, with increasing sodium aluminate loading. The silica content was found to be 0.36 g/L at the sodium aluminate loading of 1.5 wt.% and a silica removal ratio of 68.19% was achieved. From this point, it can be indicated that sodium aluminate exhibited a favourable desilication effect in the cooking process. The silica content can be regarded as the foremost parameter to evaluate bamboo pulp ash. Thus, one can infer that the silica from raw materials remained on the fibre surfaces, or in the fibre cell cavities. This means that the desilication technique inhibited the transfer of silicon into the black liquor. Meanwhile, the silica remained on the pulp, such that it can act as a filler for the paper making process.

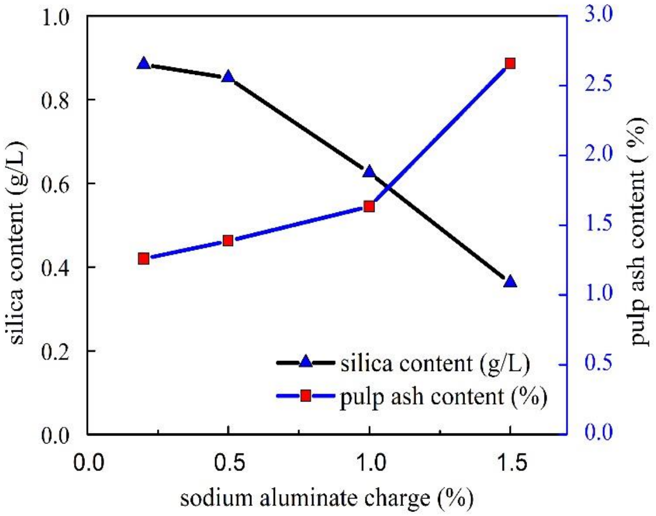

Fig. 1. Sodium aluminate dosage *vs*. silica content in black liquor and pulp ash content

A favorable silica removal ratio can be obtained with the addition of sodium aluminate. However, the price of $NaAlO_2$ (AR) is 45 RMB / 500 g, and $Al_2(SO_4)_3$ (AR) is 6.5 RMB / 500 g. Considering the cost factor, the desilication effects of aluminium sulphate were studied. As illustrated in Fig. 2, the silica content in black liquor was 0.66 g/L at a aluminium sulphate loading of 1.5 wt.%. Under such technological parameters, a desilication ratio of 41% was obtained. Aluminium sulphate can react with sodium hydroxide to generate sodium aluminate. For this reason and from what has been discussed above, it could be concluded that a promising silica removal effect can be achieved with the addition of aluminium sulphate during the kraft bamboo cooking process. However, the desilication effect of aluminium sulphate was relatively weak in comparison to sodium aluminate. This is most likely due to the high adsorption capacity of aluminium sulphate. Organic substances obtained during the cooking process can be absorbed by aluminium sulphate, which weakens the activity of aluminium sulphate. Furthermore, the solubility of aluminium sulphate is closely related to the pH value of the liquid. Consequently, partial aluminium sulphate loaded in the system cannot perform well to remove the silica. In order to reduce the production cost and obtain better desilication effects, the synergistic effects of combining aluminium sulphate and sodium aluminate were investigated and are further discussed.

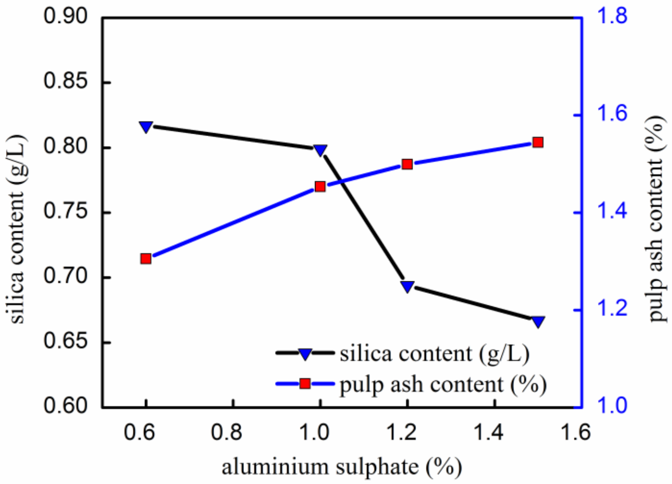

Fig. 2. Aluminium sulphate dosage *vs*. silicon content in black liquor and pulp ash content

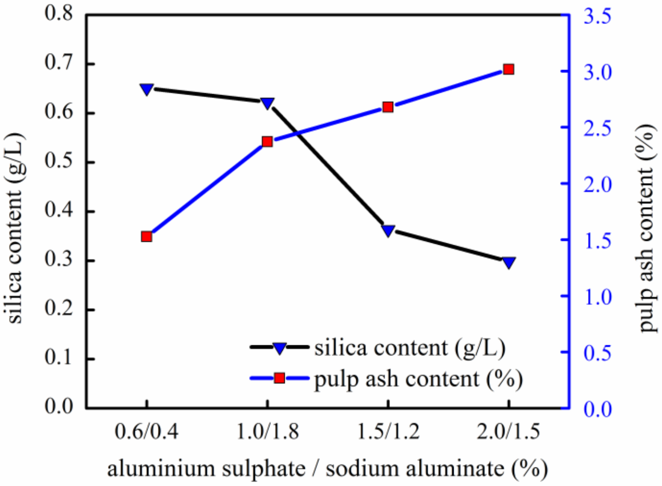

Fig. 3. Aluminium sulphate / sodium aluminate dosage *vs*. silica content in black liquor and pulp ash content

It was apparent that the silica content in black liquor decreased with the incorporation of the two aluminium salts (Fig. 3). A silica removal ratio of 74% could be achieved with an aluminium sulphate/sodium aluminate ratio of 2.0/1.5. Correspondingly, the content of pulp ash was 3.01%, which was much higher than that of the control specimen (1.21%). As discussed above, the additive amount of sodium aluminate cannot be too high. However, the addition of aluminium sulphate offsets this disadvantage and a more outstanding desilication ratio can be obtained. Based on these considerations, one may preliminarily draw the conclusion that silica from raw materials can react with the sodium metasilicate to form other silica-alumina compounds during the bamboo cooking process. It also can be concluded that the compounds can adhere to the fibre surface and hinder the passage of the silica into the black liquor.

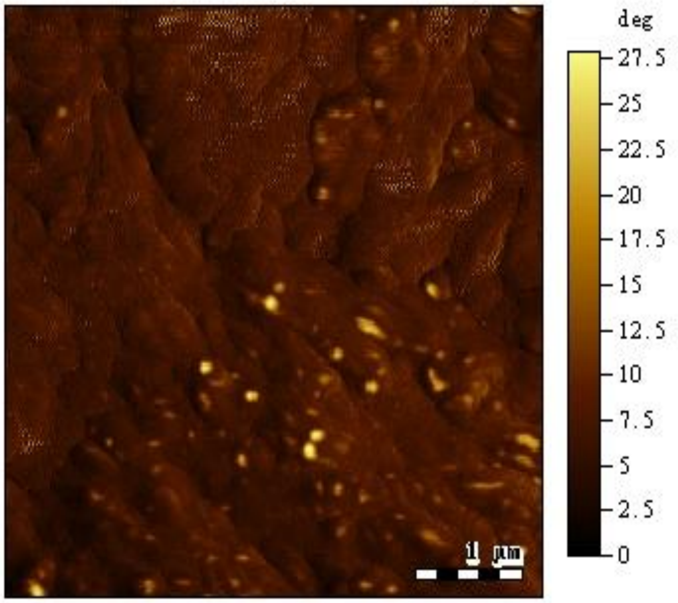

Fig. 4. AFM phase of the pulp

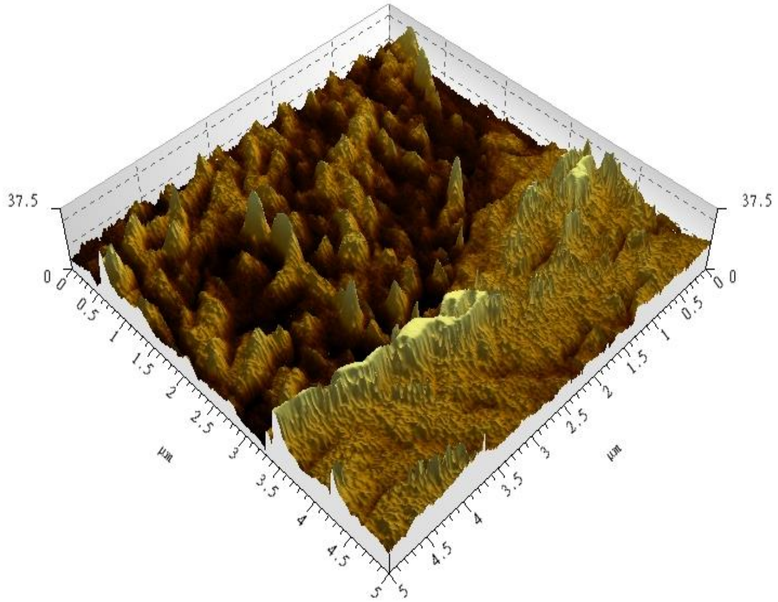

Fig. 5. AFM phase of the pulp (3D)

To further support the conclusions obtained above, AFM and SEM-EDS were employed to analyse the morphology of the pulp (Figs. 4, 5, and 6). AFM has rapidly become a commonly used tool for surface characterization since its invention in 1986, and it has been widely applied to polymeric systems (Gustafsson *et al*. 2003a). The SEM-EDS technique can be used to analyse the morphology of the pulp and show major composition of the sample. The contrast in the phase image of AFM clearly shows that the fibre surface is mechanically inhomogeneous (Gustafsson *et al*. 2003b). Figures 4 and 5 show that substances with differing characteristic stiffness values are distributed on the surface of the pulp fibres. It can be seen that some non-cellulosic, hydrophobic substances appear light in the phase image, which are considered the reaction product of silica and the desilication agent. Furthermore, these unknown particulate substances on the pulp surface were investigated by SEM-EDS (Fig. 6). As can be seen from Fig. 6, bright particles existed on the fibre surface and can be considered silica-alumina compounds derived from the reaction of aluminium salts (aluminium sulphate and sodium aluminate) with sodium metasilicate. The EDS spectrum analysis shows that the particulate substance consisted of Si, Al, Ca, K, Na, *etc*. Among these elements, the silicon content was the highest, and the second was aluminium (Fig. 6). Therefore, it can be concluded that aluminium sulphate and sodium aluminate cause the beneficial desilication effects. Consequently, one can draw the conclusion that aluminium salts can react with silica and generate another silica-alumina particulate phases in the pulp cooking phase. The particles obtained in the system remain or adhere to the pulp surface, by which, the objective to decrease the silica content of the black liquor can be completed. Meanwhile, those particles in the pulp can be considered as favourable fillers during the paper making process.

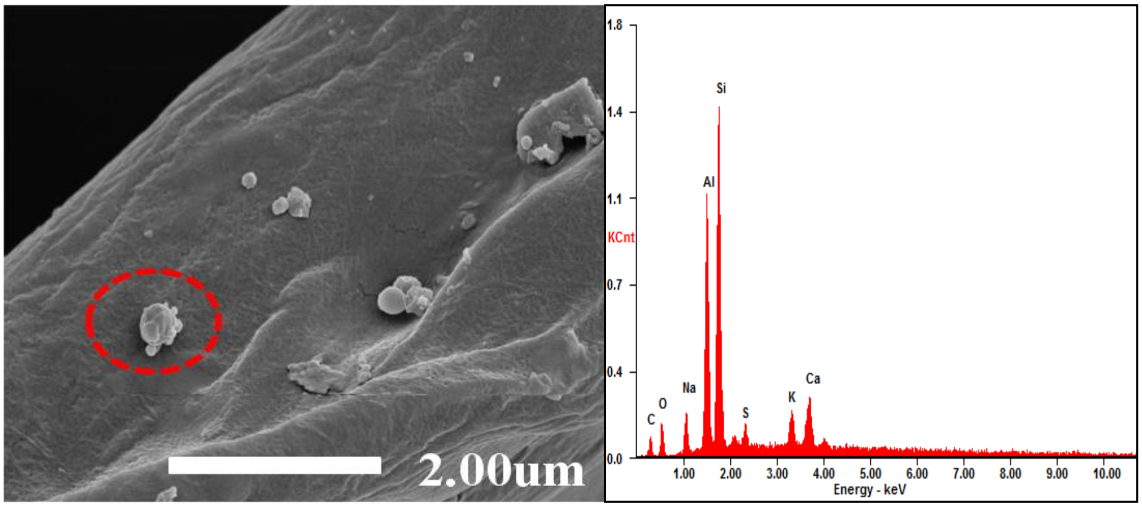

Fig. 6. SEM image and EDS spectrum of the pulp fibre

Preliminary Evaluation of the Influence of Residual Al and Si Ions on the Scaling Properties of Black Liquor

Sodium aluminosilicate scaling is a common problem with respect to black liquor during the evaporation process. Sodium aluminosilicates are sparingly soluble in alkaline liquor and often form hard glassy scales on the appearance of the evaporators (DeMartini and Frederick Jr. 2008). The scales occur only when there is a build-up of alumina and/or silica in the recovery cycle, which has a significant relationship with the pH value of the black liquor (Hartler and Libert 1972). As illustrated in Fig. 7, the desilication ratio increased as the desilication agent contents increased. Meanwhile, the aluminium salt loading affected the concentration of aluminium ions in the black liquor to some degree. The aluminium concentration in the black liquor was 7.31 ppm when the desilication agent loading was 1.23% (on Al_2O_3), and the silica removal ratio was 74%.

It has been demonstrated that the scaling of the evaporators in alkali recovery system is correlated to a series of factors, such as liquid concentration, evaporation temperature, and the amount of residual alkali in the black liquor. However, aluminosilicate scale is mostly generated under the conditions of high aluminium and silicon contents (Lauren 1966; Dessouky *et al*. 2000). The solubility of aluminosilicates in an alkaline solution has been shown to depend on the concentration of aluminium ions and silicon, as well as on the hydroxide ion concentration and temperature (Zheng *et al.* 1997; Wannenmacher *et al*. 2005).

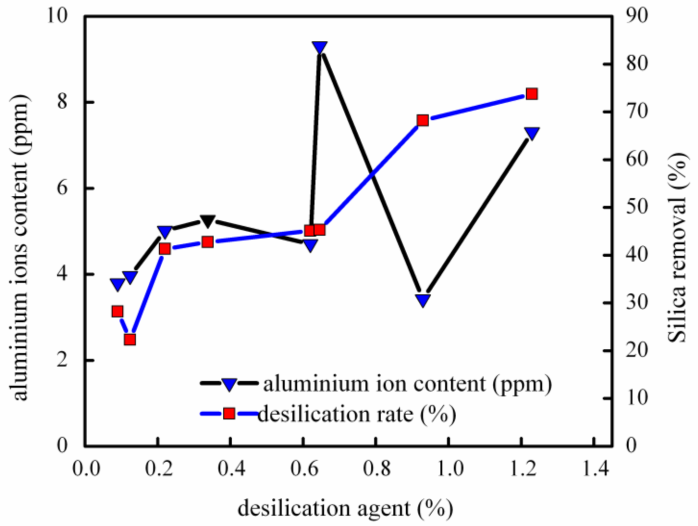

Fig. 7. Desilication agent loading *vs*. aluminium ions content in black liquor and silica removal rate

Silicon exists in the form of monosilicic acid in a diluted solution where the pH value ranges from 1.0 to 8.0, whereas it exists in the form of SiO_3^{2-} in an alkali solution. The monosilicic acid varies in the form of $H_2SiO_3^{2-}$, $Si(OH)_3^-$, and $Si(OH)_4$ in the course of changes in the pH value. When the alkali concentration is 1 M or greater, silicon primarily exists in the form of $Si(OH)_3^-$ (Sedeh *et al*. 1993). Sodium aluminosilicate scaling can be easier to take place at low pH value due to the presence of more orthosilicic acid. As reported, the critical concentration needed to transfer silicon to scale could be decreased by the addition of aluminium ions to the sodium aluminate solution (Hilonga *et al*. 2010). On the other hand, the aluminosilicate scale cannot come into being in the evaporators when the aluminium ion content is below 120 g/L and the silicon content also is below 0.7 g/L (Liang 2005). There is no gainsaying the fact that the composition of black liquor is complicated, and the scaling properties of black liquor during the evaporation process are related to a series of other factors. However, according to this study, the maximum silicon content in black liquor was 9.31 ppm, which was lower than the critical concentration of silicon precipitation. Additionally, a silicon concentration of 0.298 g/L was found in black liquor under a 74% silica removal ratio. From what has been discussed above, one may safely draw the conclusion that, the addition of salt desilication agents in the system is unlikely to contribute to scaling problems during the processing of kraft bamboo black liquor.

CONCLUSIONS

1. Silica removal carried out during the pulp cooking process is an outstanding desilication method for kraft bamboo pulp. Aluminium sulphate and sodium aluminate are considered the favourable desilication agents, and a silica removal ratio of 74% can be obtained.
2. Aluminium salts can react with silica to yield silica-alumina compounds that adhere to the fibre surface and prevent the transfer of silica into black liquor.
3. As a result of the described desilication operation, the residual silicon and aluminium in the black liquor are not likely to contribute to scaling problems during chemical recovery operations.

ACKNOWLEDGMENTS

The authors appreciate the financial support from the "Twelfth Five-Year" National Science and Technology Support Program Project of China (2012BAD23B0201) and the Shaanxi University of Science and Technology Academic Leader Training Program (2013XSD25). We are grateful to the Shaanxi Province Key Lab of Papermaking Technology and Specialty Paper for supporting this research at Shaanxi University of Science and Technology (SUST), China.

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Article submitted: May 27, 2015; Peer review completed: September 12, 2015; Revised version received: September 19, 2015; Accepted: September 20, 2015; Published: September 29, 2015.
DOI: 10.15376/biores.10.4.7704-7714