

Study on Silicon Removal From Green Liquor With Pre-Causticization and Improved Method in the Alkali Recovery Process Of Bamboo Pulping

Lin Tao,^{1,2} Li Xue,^{*1,2} Yin Xuefeng,^{1,2} & Xu Yongjian^{1,2}

ABSTRACT

The high silicon content in green liquor of bamboo pulping affects the progress of alkali recovery, and it is also disadvantageous to the recycling of quicklime mud. The effects of quicklime charge and free-CaO content in quicklime on silicon removal with pre-causticization as well as adding Aluminum salt modified Bentonite in the process of silicon removal with pre-causticization were studied in this paper. The results showed that when quicklime with 62% and 81% free-CaO were charged 20% to 30%, the silicon removal rate in the process could be up to 48%-58% and 60%-77% respectively. When quicklime dosage was increased to 30%-40%, silicon removal rate increased little. As adding Aluminum salt modified Bentonite in the process of pre-causticization, silicon removal rate could be reached to 99.9%.

Key words: bamboo pulping, silicon removal, green liquor, pre-causticization

Introduction

Bamboo resources are rich in China which account for one-third of the world[1] and widely distributed in Fujian Province, Sichuan Province, Guangxi Province, Guangdong Province, Hunan Province, Guizhou Province, Yunnan Province and so on. The quality of bamboo fiber is between the softwood fiber and hardwood fiber, while it is better than that of ordinary non-wood raw fiber. Therefore, aiming at being lack of wood resource in China, improving the proportion of bamboo pulp in papermaking raw materials has important strategic significance. However, due to high silicon content in bamboo whose element is belonged to the non-process elements in green liquor [2-3]; Reaction of silicon with sodium hydroxide during Kraft pulping generates a lot of sodium silicate which goes into the black liquor. Finally, it causes a series of problems in alkali recovery system; Silicon element is not so removed and will tend to build-up in the liquor system with increased system closure [4]; In the evaporation process, because of the presence of silica, the viscosity of black liquor will increase with the concentration of silica, thereby affecting the evaporation of black liquor and resulting in scale [5-6]; due to the high melting point of sodium silicate, the combustion of black liquor requires a higher temperature and energy consumption; during the process of causticizing, sodium silicate in green liquor is transferred into calcium silicate, the particles of which are so fine that they are difficult to precipitate and filter, so washing white mud is difficult, residual content of alkali in white mud is high and the loss of alkali is also high; as white mud is calcined and quicklime is recycled, high energy consumption is required due to the calcium silicate. These are collectively known as "Silicon Interference" [7].

Aiming at the "Silicon Interference" in the process of causticization and recycling quicklime, researchers have proposed many solutions and have done some useful explorations which have played a positive role in the reduction of the silicon interference. The economically and technically feasible methods are: 1. Carbon dioxide is applied to pass through green liquor, and the pH of green liquor reduces, so the silicon element is precipitated in the form of silicic acid. After filtration, the silicic acid is separated from the green liquor, the silicon removal rate is up to 90%. When the desilicated green liquor is passed multi-effect evaporation system, the concentration of green liquor can increase to enough level for causticizing. But the pH of desilicated green liquor is low, and needs to adjust back to high alkalinity [8]. 2. Chemical precipitation and evaporation. A recent experiment is reported by Huuha et al. [9], where the treatments are applicable and effective to remove target pollutant from the samples. At the same SiO₂ concentration of 200 mg/L, 0.10 g/L of dose, pH 10.5 and 303 K, the integrated chemical precipitation using Fennofix type FF40 and evaporation could remove 96% of silicon. This finding is slightly higher than those of similar precipitation using CaO and electro-coagulation in other studies, which could accomplish 93% and 95% of silicon removal respectively at initial SiO₂ concentrations of 954 and 250 mg/L. 3. Quicklime is added to the green liquor with two stages of causticization in this silicon removal method. In the first stage, only 30% quicklime is added in pre-causticizing, and white mud produced in pre-causticizing was discharged outside of factory. In the second stage, the rest 70% quicklime is added in causticizing, the white mud is calcined and quicklime is recycled to causticization. The mechanism is that when adding the small amount of quicklime in pre-causticization process, the diffusion rate and the reaction rate of silicate ion is higher than carbonate ion, so silicon removal rate is also high[10-12]. However, Pulping mills use the silicon removal process with pre-causticization. In this company, 30% quicklime is added in first stage, the reaction temperature is 95°C, and residence time is 2min. After first stage, 54% silicon of

1. College of Light industry and Energy, Shaanxi University of Science and Technology, Shaanxi Province of Key Lab of Paper Technology and Specialty Paper;
2. Key Laboratory of Auxiliary Chemistry and Technology in Light Industry, Ministry of Education, Shaanxi University of Science and Technology, Xi'an, 710021 China

green liquor is brought out by white mud. But white mud in the second stage has 46% silicon in the total silicon content, and silicon removal rate is much lower than that in laboratory and related reports, so "Silicon Interference" problem still exists. 4. Efficient adsorbent synergistic quicklime in pre-causticizing and silicon removal. Modified bentonite has the properties of high adsorption and expansion and is widely used in papermaking systems which showing many advantages. For example, there is great development in retention and drainage, fillers as well as paper wastewater treatment. Especially in wastewater treatment, which utilizes the high adsorption of modified bentonite to treat with wastewater [13], adsorb organic in black liquor [14] and as a coagulant to deal with wheat straw black liquor [15]. But there is no research on silicon removal of bentonite. It is the new discovery that aluminum salt modified bentonite has the high utility of silicon removal in pre-causticization by our group.

Experimental

Raw materials and reagents

The green liquor was provided by Guizhou Chitianhua Paper Industry Co., Ltd. Its composition were: total alkali 137.21g/L, active alkali 39.88g/L, Na_2CO_3 97.27g/L, Na_2S 31.94g/L, SiO_2 4.36 g/L, pH=13.64.

The main experimental chemicals were: aluminum sulfate, oxalic acid, nitric acid, ferrous ammonium sulfate, ammonium, molybdate, potassium, etc. (They were all analytical grade.). There were two kinds of quicklime in use: 1# was analytical grade quicklime; 2# was quicklime provided by Guizhou Chitianhua Paper Industry Co., Ltd. (Free calcium oxide content in 1# quicklime was 81%; free calcium oxide content in 2# quicklime was 62%. Free CaO is called f-CaO), Aluminum salt modified Bentonite (AIMB).

Experimental Methods

The silicon removal method for Green liquor

Method 1.

Silicon removal by pre-causticization: certain proportion of quicklime was added into the green liquor, and then the causticizing temperature was kept at 92°C by water bath. The reaction time was 25 min, stirring continuously. When the reaction finished, the solution was cooled to room temperature, and then the upper green liquor was took out to detect the silicon removal rate.

Method 2.

Silicon removal with AIMB in green liquor: Certain proportion of AIMB were added into the green liquor, and then the causticizing temperature was kept at 92°C by water bath. The reaction time was 10 min, stirring continuously. When the reaction finished, the solution was cooled to room temperature, and allowed to separate into layers. Then the upper green liquor was took out to detect the silicon removal rate and pH. In addition, the insoluble precipitate

were filtered off and washed repeatedly by deionized water, and then the precipitate was dried in an oven, milled and mixed. Finally, the spectroscopy analysis method was used to detect the element of precipitate.

Method 3.

Silicon removal with AIMB in the process of pre-causticization: Silicon removal with AIMB and quicklime: firstly, quicklime and AIMB were added into the green liquor and the consequent experiment was carried out as method and The insoluble precipitate was analyzed as in method 2.

The spectrophotometer was used to measure silicon removal rate. Sodium silicate was converted into silicic acid under slight acid environment. The molybdate was formed into silicon-molybdenum blue complex. Then the silicon removal rate is measured by colorimetric analysis^[16].

Experimental equipment

DR-4000V spectrophotometer, Hach Company, America; Hitachi S-4800-type field emission scanning electron microscope with EDX, Hitachi, Japan; DHG-9123A electric oven thermostat blast, Yiheng Technology, Shanghai, China; A1835000 electric stirrer, Aice Technology Co., Ltd, Shanghai, China; HH-8 constant temperature water bath, Huanyu Scientific instrument plant, Jiangsu, China; PHS-3C pH meter, Shanghai Jing Branch Instrument.

Results and Discussion

The effect of the content of quicklime on silicon removal rate of pre-causticization

QuickLime is the important raw material in alkali recovery system. Therefore, the effect of the content of quicklime and f-Cao on silicon removal rate of pre-causticization was studied in this paper. In the

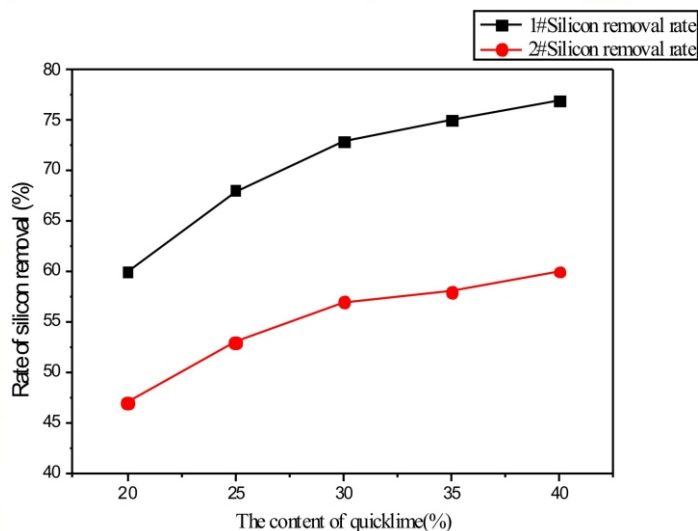


Fig.1 The effect of the content of quicklime on the silicon removal rate of pre-causticization.

■- 1# Rate of silicon removal; ●- 2# Rate of silicon removal.

Fig.1, under the same content of quicklime, 1# silicon removal rate is higher than 2# silicon removal rate due to the fact that quicklime is made up by f-Cao and f-CaO (combination of calcium oxide), f-CaO can react with H_2O , while f-CaO cannot react with H_2O . In the pre-causticizing reaction, f-CaO in quicklime first reacted with H_2O , and then the rest of chemical reactions happened. The content of f-CaO in 1# quicklime was 81%, while content of that in 2# quicklime was 62%, so the silicon removal rate of 1#quicklime was higher than that of 2#. It can be concluded that improving the silicon removal rate can be obtained by increasing the content of f-CaO during pre-causticizing green liquor.

In addition, when the dosage of quicklime in pre-causticization was less than 30% of the lime consumption in causticizing, no matter the quicklime was 1# or 2#, the silicon removal rate was increased with the increase of f-CaO content and when the quicklime dosage was 30%-40% of the lime consumption, the silicon removal rate did not increase significantly. Because the quicklime was added with a certain amount in green liquor, the entire system reached equilibrium and the silicate ions was no longer precipitated from green liquor in the form of silicate. Therefore, increasing quicklime

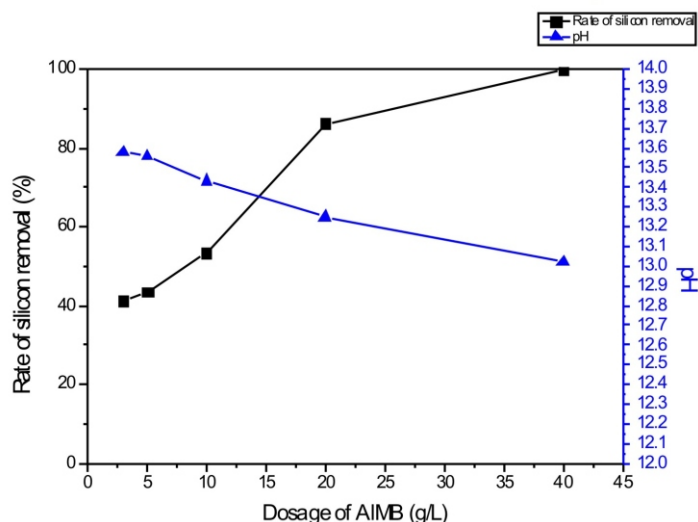


Fig2. The effect of the dosage of AIMB on silicon removal rate and pH of green liquor
 ■ - Rate of silicon removal; ▲ - pH.

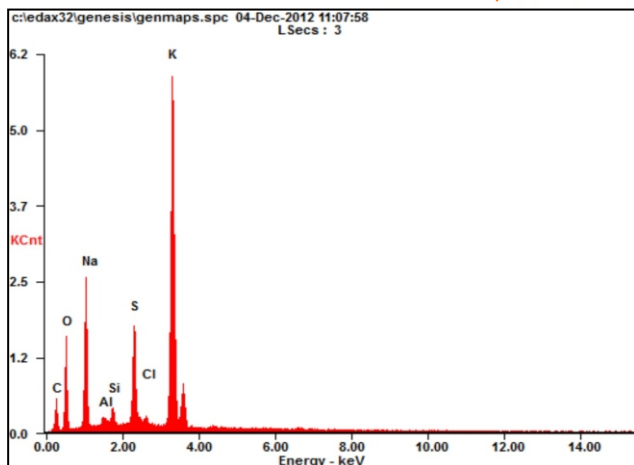


Fig3a.

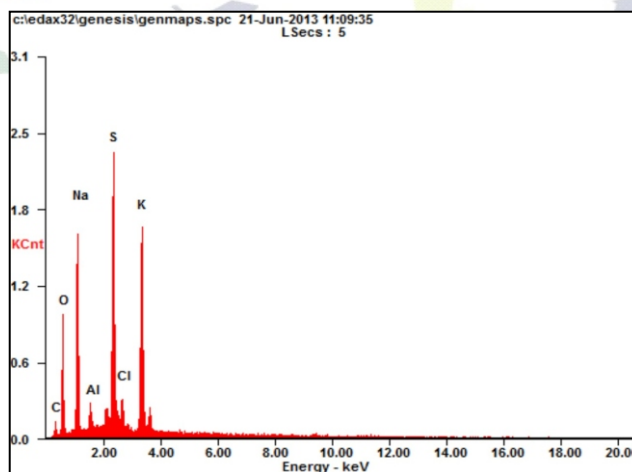


Fig3b.

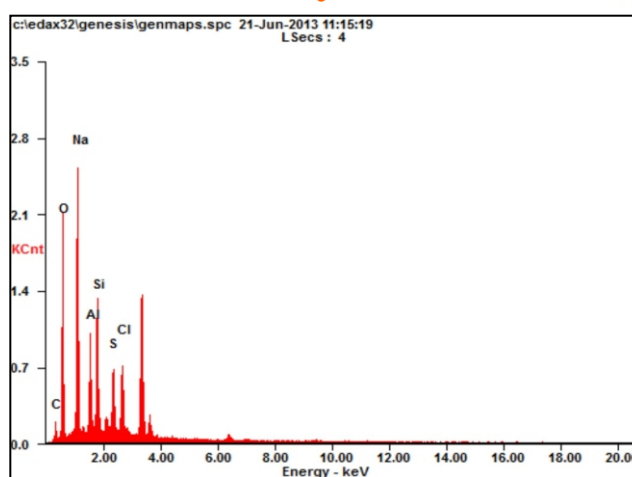


Fig3c.

Fig3. Energy spectrum of bamboo green liquor and insoluble precipitate which is added 40g/L AIMB

Fig3a. Energy spectrum of bamboo green liquor

Fig3b. Energy spectrum of bamboo green liquor which is added AIMB

Fig3c. Energy spectrum of insoluble precipitate

content was not feasible for improving silicon removal efficiency in pre-causticization.

The effect of the dosage of AIMB on silicon removal rate and pH of green liquor

There are 2 curves in Figure 2. The one increased with the increase of AIMB is curve 1 which is called silicon removal rate curve. It showed that when the dosage of AIMB was 40g/L, the silicon removal rate could reach 99.9% and there was a sharp upward trend of silicon removal rate after 10g/L. The other one curve decreased with the increase of AIMB is curve 2 which is named as pH curve. It is described that when the dosage of AIMB was 40g/L, pH decreased to 13.02. Generally speaking, comparing with aluminum salt, AIMB had less effect on pH of green liquor, which reduced to 11.20 when the silicon removal rate reaches at 90%. Therefore, it is indicated that AIMB did not release much aluminum ions which was free in green liquor to reduce pH,

but it adsorbs silicon on itself for silicon removal. Above all, the optimum silicon removal rate could reach at 99.9% when the dosage of AIMB was 40g/L, and AIMB had less effect on pH in green liquor relatively. Likewise, The energy spectrum of Figure 3(a, b, c) proved AIMB had high efficiency on silicon removal so that silicon element reduced significantly. And aluminum element did not increase obviously in green liquor (Figure 3b), while it was detected with a large number in the precipitation (Figure 3c). Study indicated [17] that wood fiber raw materials does not produce "Silicon Interference" problem in causticization of green liquor and calcination of white mud, due to the content of silicon was less than 0.9g/L (based on SiO_2) in the green liquor. So adding AIMB in pre-causticization can decrease or solve the "Silicon Interference" problem.

Effect on the rate of silicon removal and pH with AIMB in the process of pre-causticization

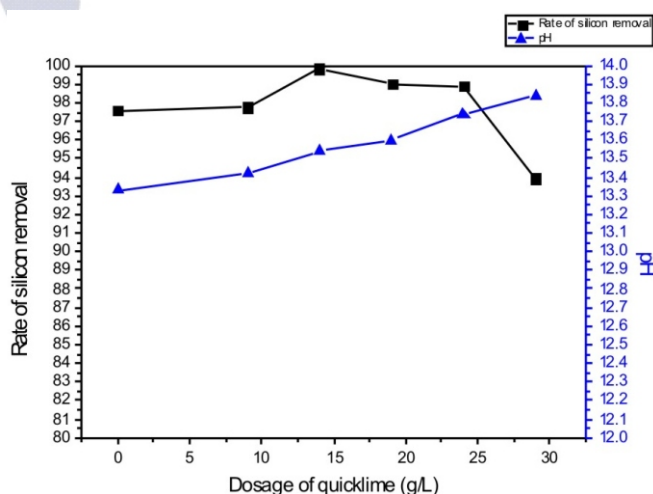


Fig4. Effect on the rate of silicon removal and pH with AIMB in the process of pre-causticization
 -■- Rate of silicon removal; -▲- pH

In the same dosage of AIMB (30g/L), changing addition of quicklime (including CaO 81%) influenced the rate of silicon removal and pH in green liquor. As it showed in Figure 4, with the increasing of quicklime, the rate of silicon removal first increased and then decreased. When the dosage of quicklime was 15g/L, the maximum rate of silicon removal could reach at 99.9%. At first, the rate was increased by quicklime which could react with silicon. Then, it decreased maybe due to the increasing of pH which inhibited silicon adsorption. In addition, the pH curve increased with the increase of quicklime. It is indicated that quicklime had the function of improving alkaline and pre-causticization. Compared to Figure 2, adding quicklime could not only increase the rate of silicon removal, but also compensated the pH which was reduced by AIMB. Moreover, it is worth noting in research that the sedimentation time of AIMB decreased from 2h to 45 minutes, comparing with Method 2. It proved that quicklime had another function to sedimentation aid. Therefore, the purposes of adding quicklime are: 1. Sedimentation aid; 2. Silicon removal aid; 3. pre-causticization; 4. Reducing the dosage of AIMB.

Preliminary study on mechanism of Silicon removal with AIMB in the process of pre-causticization.

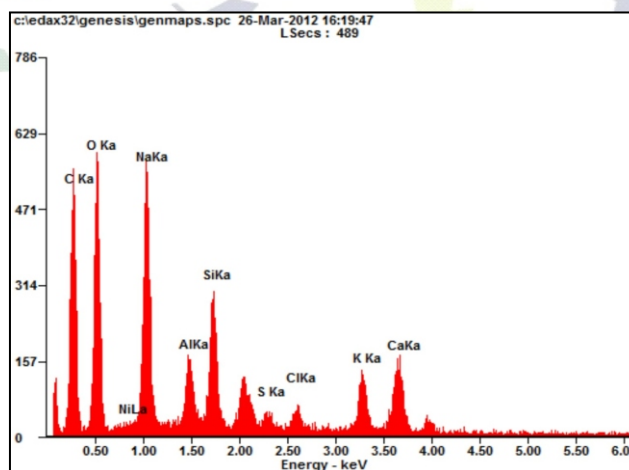


Fig5. Energy spectrum of insoluble precipitate which is added 15g/L quicklime and 30g/L AIMB in green liquor

There is no relevant reports about silicon removal by bentonite, but researchers had done various jobs on silicon removal by aluminum salts and the form of silicon in green liquor. Several studies have provided evidence [18] that mineral acid is neutralized sodium silicate and the product is silicic acid in different structures which is condensed into the fine particles in the range of colloidal disperse phase. In addition, if there is high concentration of soluble salts in the solution, the fine particles of silicic acid can exist in alkaline solution. While it is suggested that when the aluminum sulfate is added into green liquor, the content of silicon decreases due to the product of sodium aluminosilicate by Ping Wang [19] and Bing-yue Liu et al. [20]. The EDS was used to analyze the insoluble precipitate element when 30g/L AIMB and 15g/L quicklime were added in green liquor. As shown in Fig.5, the insoluble precipitate elements all had Al, O, Na, and Si. It was probably that AIMB adsorbed silicon, but it was no denied that the sodium aluminosilicate was formed into the precipitate. Therefore, It probably had calcium silicate, sodium aluminosilicate and the unknown form of silicon which is adsorbed by AIMB in the precipitate (Figure 5). Guihua Liu et al.[21] has studied on the structure of silicon and aluminum in the strong alkalinity. It suggested that silicon and aluminum was formed into sodium aluminosilicate in different alkalinity, while the structure of sodium aluminosilicate was diverse. Therefore, except for calcium carbonate and calcium silicate in the precipitate of pre-causticization, the new precipitate were sodium aluminosilicate or AIMB-Si (the mixture of AIMB adsorb silicon).However, the structure of silicon which is adsorbed by AIMB has not yet been fully defined, and further studies are needed to carry out on the reaction of adding AIMB on green liquor and white mud.

Conclusion

1. Increasing the content of f-CaO in the quicklime can improve the silicon removal rate of pre-causticization in green liquor. When the addition of quicklime with 62% and 81% f-CaO were 20%-30% and, the silicon removal rate are at 48%-58% and 60%-70% respectively. When the addition of quicklime increased to 30%-40%, the silicon removal rate did not

increase significantly.

2. When the dosage of AIMB was 40g/L, the maximum reached at 99.9%. AIMB had high efficiency on silicon removal. The improved method in pre-causticization was when 30g/L AIMB and 15g/L quicklime were added in green liquor, the rate of silicon removal also could reach at 99.9%. There are many advantages for adding quicklime, which are: the purposes of adding quicklime: (1). sedimentation aid; (2). silicon removal aid; (3). pre-causticization; (4). reducing the dosage of AIMB.
3. There are two possible reasons for silicon removal by AIMB in pre-causticization: One is that silicon is adsorbed by AIMB and grafted on it, the other one is aluminum ion reacts with silicon and forms a new precipitate called sodium aluminosilicate. It has more inclined to the first saying which is proved by the change of pH in green liquor.

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