Causticized Calcium Carbonate From Alkali Recovery Process of Non-Wood Pulping Mill as Filler of Paper

Jian Wang [1,2*], Dan Zhang [1,3], & Yong-Jian Xu[1]

ABSTRACT

Causticized calcium carbonate (CCC), known as lime mud, is a by-product of green liquor causticizing process. There are many advantages to use this by-product as paper filler. Lime-kiln operation can be shortened or stopped, resulting in the reduction of fuel oil for calcination of calcium carbonate. Furthermore, accumulated impurities in the lime cycle can be removed constantly. Especially, for non-wood materials, this using way can prevent its secondary pollution. From the mill trials in China, the application scope and loading of CCC had been limited by its shortcoming of the lower brightness. In this study, influencing of insoluble matter in green liquor on optical properties of CCC was investigated. The results showed that the insoluble matter in green liquor had the crucial influence on the brightness of CCC, the more content of insoluble matter, the lower brightness. When the green liquor was filtered by slow filter paper, the brightness of CCC reaches 91.98%ISO which was approximately close to PCC. The silicon in green liquor existed with colloidal state and had no influence on the brightness. Reduced insoluble matter was beneficial for decreasing the chromatic aberration between CCC and precipitated calcium carbonate (PCC).

Keywords *Causticized calcium carbonate, brightness, chromatic aberration, insoluble matter, alkali recovery process*

Introduction

Pulping is the process by which wood or other plant fiber source are reduced to a fibrous mass. Pulp can be obtained by several methods, such as mechanical, semi-chemical or chemical method. Chemical method is the dominant pulping process in the pulp and paper industry. Over 130 million tons/year of chemical pulp are produced globally, accounting for two-thirds of the world's virgin pulp production [1]. The aim of pulping is to break down the bulk structure of the fiber source, such as chips, stems or other plant parts, into the constituent fibers. Chemical pulping achieves this aim by degrading the lignin and part of hemicellulose into small, water-soluble molecules which can be washed from the cellulose fibers without depolymerizing the cellulose fibers. Approximately half of the wood is dissolved during chemical pulping process, together with the spent chemicals, forms a liquid named black liquor. The black liquor is separated from pulp by washing, and then sent to the alkali recovery system, where the inorganic pulping chemicals are recovered for recirculation, while the dissolved organics are used as a fuel to make stream and power.

During alkali recovery process, the sodium carbonate (Na_2CO_3) is converted into active sodium hydroxide (NaOH) by causticizing reaction as follow in two steps:

Slaking: $CaO+H_2O \rightarrow Ca(OH)_2$

Causticizing: $Na_2CO_3+Ca(OH)_2 \rightarrow 2NaOH+CaCO_3\downarrow$

1. College of Light industry and Energy, Shaanxi University of Science and Technology, Xi'an - 710021 (China)
2. State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou-510640 (China)
3. Key Laboratory of Auxiliary Chemistry & Technology for Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an Shaanxi - 710021 (China)

The causticizing process has two targets, which are obtained from separating the causticized liquor. One is the white liquor containing mainly NaOH, the other is the lime mud [2]. The white liquor can be reused in cooking process. The lime mud, for woody materials, after dewatereing, can be calcined in a rotary lime kiln and reused in the causticizing process. However, this reusing way is not suitable for non-wood materials due to its serious silica problems [3].

The traditional treatment of lime mud from the non-wood materials is discarded as solid waste or filled bury field after dewatering. The secondary pollution occurs because of a small amount of $Ca(OH)_2$ in the lime mud [4]. As a kind of $CaCO_3$, the lime mud can be purified and manufacture the causticized calcium carbonate (CCC) which can be used as filler of paper [5-6]. The using of CCC products as paper filler not only brings appreciable environment benefits but also reuses the waste resource. Especially, the price of CCC is 30 to 50 $/ton lower than that of commercial PCC. If the properties of CCC are suitable to paper fillers, remarkable social and economic benefits can be achieved for paper industry [7].

At present, several CCC filler production lines were completed in China, and the CCC was used as filler in papermaking. In comparison with PCC, there are some differences such as shape, surface properties, size distribution and so on [7-8]. However, from the mill trials [9-10], the application scope and utilization amount of CCC is considerably restricted by its lower brightness than PCC (85%ISO vs. 92%ISO) [11]. In present study, the effect of insoluble matter in green liquor on the optical properties of CCC was investigated in order to provide technical support for quality improvement of CCC in alkali recovery process.

Experimentation

Preparation of green liquor with different insoluble matter

The insoluble matter was removed from the green liquor by slow filter paper, and then the clarified green liquor was obtained. Then the clarified green liquor and original green liquor were mixed as given ratio as indicated in Table 1. (In this study, the clarified green liquor was regarded as without insoluble matter.)

Table 1 Preparation of green liquor with varied insoluble matter content

No.	Ratio of clarified green liquor /%	Ratio of original green liquor /%	Content of insoluble matter /mg/L
1	100	0	0
2	95	5	149
3	90	10	298
4	80	20	596
5	60	40	1192
6	40	60	1788
7	20	80	2384
8	0	100	2980

Preparation of CCC

A simple apparatus was used for preparing CCC in laboratory as shown in Fig. 1 [6]. Quicklime was added to the flask, which was filled with water and stirred at 300 rpm to achieve slaking. Then the green liquor filtered by slow filter paper was added to the flask at a constant rate with a transfusion tube, and the causticizing reaction was carried out. The mole ratio of Ca: CO_3^{2-} was 1.05:1. The reaction temperature was varied from 70°C to 90°C. The reaction time was 2 hours. After these reactions, the CCC was filtered and washed out with water, and then deliquated to 20% and inleted CO_2 until the pH reached to level of 9.5~10. After carbonation, the CCC passed 800 meshes was washed out with water and subjected to measure the whiteness and brightness according to the Chinese national standard GB/T 5950-2008.

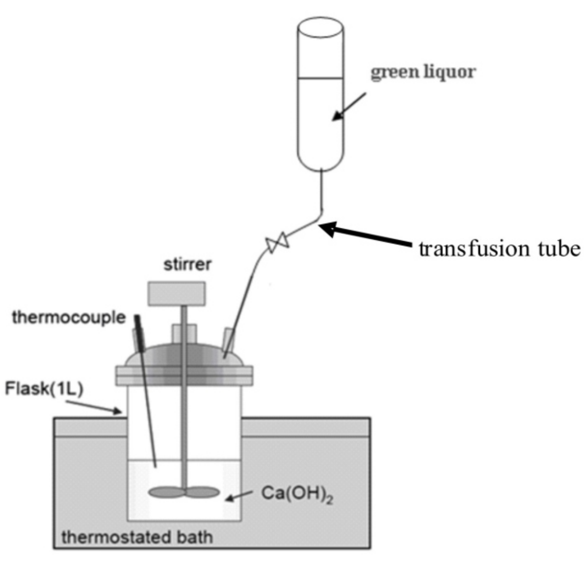

Fig. 1 Experimental apparatus for causticizing reaction

Results And Discussion

ro er es o ree or

Basic composition of green liquor is shown in Table 2.

Table - 2 Green liquor basic composition

Composition	Na_2CO_3	NaOH	SiO_2	insoluble matter
Content / g.L^{-1}	134.17	29.05	6.17	2.98

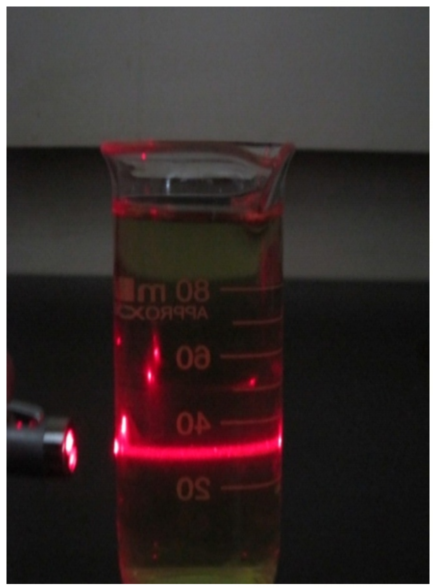

Fig. 2 Tyndall effect of clarified green liquor

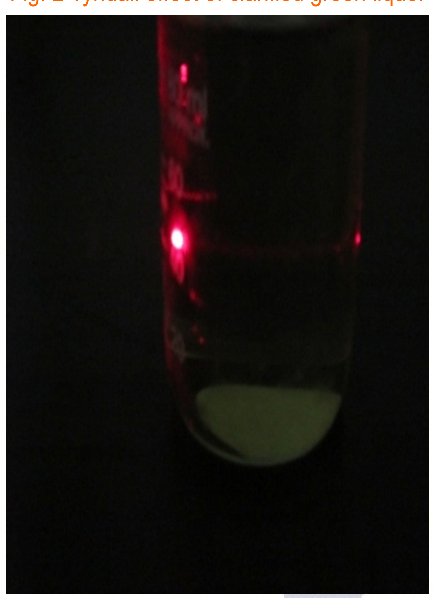

Fig. 3 Tyndall effect of clarified green liquor after sol-gel method treatment

From Table 2, the main components of the green liquor are sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH), followed by a small amount of silicon, and insoluble matter. The clarified green liquor and the clarified green liquor after solgel method treatment were used to test the Tyndall effect. The images were shown as Fig. 2 and Fig. 3.

As shown in Fig. 2, there is some colloid in clarified green liquor. When the clarified green liquor was treated with solgel method, the colloid disappeared. The silicon content in the two green liquors was separately measured. After solgel method treatment, the silicon content decreased from 6.17g/L to 1.36g/L and the silicon was the main component of the sol-gel derived powders. Therefore, the conclusion can be drawn that the silicon in the green liquor existed in a colloidal state, such as the complex of sodium silicate and metal ion.

Fig. 4. Appearance of insoluble matter (air-dried)

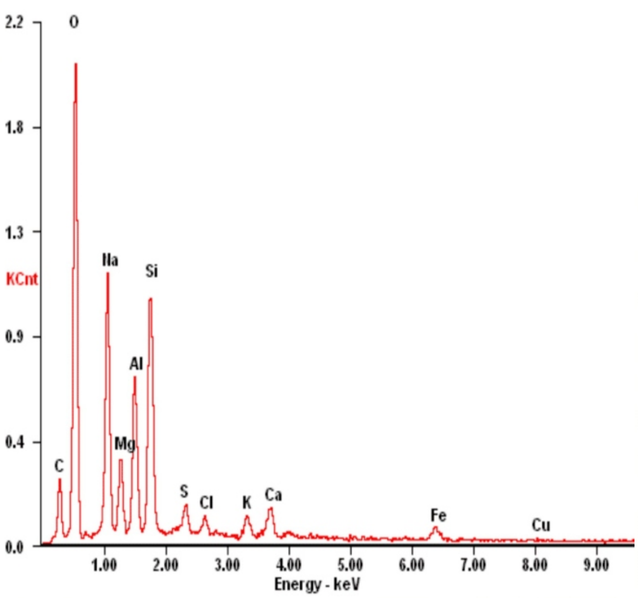

Fig. 5. Energy spectrum of insoluble matter

ro er es o so e er ree or

The insoluble matter was obtained from the green liquor by slow filter paper. It was shown in Fig. 4, and its elemental composition was shown in Fig. 5.

It can be seen from Fig. 4 that the color of insoluble matter is black. This is the reason why the brightness and whiteness of CCC are affected by insoluble matter. The insoluble matters may be come from the ash alkalinity of black liquor combustion furnace. Its elemental composition is complex. It should be a mixture of hydroxide, sulfide or silicon compounds of Fe, Cu, Al, Mg, Ca, etc.

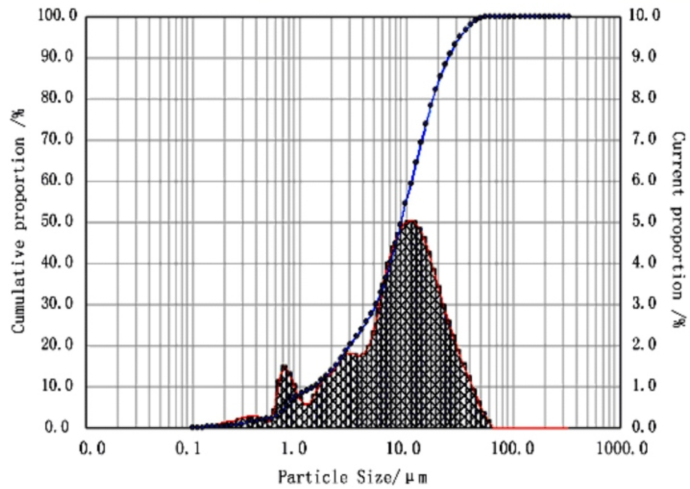

Fig.6. The particle-size distribution of insoluble matter

The particle-size distribution (PSD) of insoluble matter was shown in Fig. 6. The range of particle diameter is from 0.7μm to 45μm. The amount of the insoluble matter with diameter less than 2μm is about 13.74%. It can be inferred that the insoluble matter is difficult to remove from the green liquor by screening.

e s o so e ero r ess o

The CCC samples were prepared by causticizing reaction between quicklime and the green liquor as given in Table 1. The brightness and CIE whiteness of CCC samples were shown in Table 3.

Table - 3. Effect of insoluble matter on optical properties of CCC

No.	Content of insoluble matter/mg/L	R_{457} %ISO	L*	a*	b*
1	0	91.98	98.35	-0.74	0.98
2	149	90.07	97.87	-0.85	1.03
3	298	89.46	97.05	-1.08	1.10
4	596	88.86	96.32	-1.26	1.18
5	1192	87.32	94.97	-1.82	1.05
6	1788	86.61	94.15	-3.02	1.43
7	2384	85.78	93.82	-3.45	2.11
8	2980	84.08	92.27	-3.47	2.20

From Table 3, the brightness and the CIE whiteness of CCC samples are affected remarkably by the insoluble matter. Compared with the original green liquor (No. 8), the brightness (R_{457}) of CCC made from clarified green liquor (No. 1) raised by 7.9%ISO. For the clarified green liquor, the black insoluble matter was almost removed. Thus, it is perhaps not surprising why the brightness of CCC increased. The conclusion can be drawn that the insoluble matter in green liquor must be removed as much as possible in order to obtain high brightness CCC.

Table 4 Effects of green liquor on optical properties of lime mud

No.	Ratio of clarified green liquor %	Ratio of simulated green liquor %	R_{457} %ISO	L*	a*	b*
1	100	0	91.98	98.35	-0.74	0.98
2	80	20	91.46	98.26	-0.68	0.85
3	60	40	91.50	98.14	-0.55	0.79
4	40	60	91.52	98.23	-0.47	0.64
5	20	80	91.33	98.04	-0.42	0.63
6	0	100	91.04	97.07	-0.38	0.53

e so s o o r ess o

The sodium carbonate and the sodium hydroxide were used to simulate the green liquor. The clarified green liquor was mixed with simulated green liquor, and the CCC was prepared. The results were shown in Table 4.

It can be seen from Table 4 that there is no significant variation in the brightness of CCC samples. For simulated green liquor, there is no silicon. Therefore, it is reasonable to infer that the silicon has no effect on the brightness of CCC. When the CCC was made from simulated green liquor, its brightness was slightly lower than that of CCC made from clarified green liquor. It may be has the relationship with crystal form of CCC, as Yasunori Nanri's research [2], or the relationship with the brightness of $CaSiO_3$ which brightness is higher than that of CCC.

e so e re o ed e od o so e er o o ro er es o

As above mentioned, the insoluble matter in green liquor must be removed as much as possible in order to obtain high brightness CCC. Some different screening methods were used to remove the insoluble matter. The CCC was prepared by screened green liquor and Quicklime. The chromatic aberration was calculated according to equation (1) as the standard of CIE whiteness of PCC. The results were shown in Table 5.

$$\Delta E_{ab} = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{½} \qquad (1)$$

□E_{ab} - chromatic aberration.
□$L = L^*_{CCC} - L^*_{PCC}$
□$a = a^*_{CCC} - a^*_{PCC}$
□$b = b^*_{CCC} - b^*_{PCC}$

Table 5 The brightness of CCC and its chromatic aberration with PCC

No.	Disposed method	Pore diameter /μm	Content of insoluble matter /mg/L	R_{457} / %ISO	L*	a*	b*	$\triangle E_{ab}$
1	untreated	-	2980	84.08	92.27	-3.47	2.20	5.97
2	200 mesh filtered	74	2464	85.13	93.08	-2.09	2.07	4.73
3	800 mesh filtered	18	1404	88.70	95.13	-1.71	1.39	2.58
4	24 hours clarified	-	178	90.89	97.34	-0.89	1.15	0.25
5	slow filter paper filtered	1-3	0	91.98	98.35	-0.74	0.98	0.83
6	PCC	-	/	92.41	97.58	-0.91	1.23	0.00

As indicated from Table 5, the lower insoluble matter content in green liquor, the higher brightness and CIE whiteness of CCC can be obtained. The chromatic aberration (□E_{ab}) between CCC and PCC decreased with the decreasing content of insoluble matter. The brightness of CCC, made from the green liquor filtered by slow filter paper, is reached 91.98%ISO. Furthermore, its □E_{ab} is 0.83. Both are higher than that of CCC made from the green liquor by 24 hours clarified. Some parts of insoluble matter were too small to remove by clarification, resulting in the lower brightness of CCC made from the green liquor by 24 hours clarified in comparison with that of CCC made from the green liquor filtered by slow filter paper. However, its chromatic aberration is lower than that of CCC made from the green liquor filtered by slow filter paper due to its optical properties are close to PCC.

From the experiment, the filter screen with small pore diameter is adaptive to obtain the CCC with high brightness since it is effective to remove the insoluble matter.

Conclusions

1. The insoluble matter in green liquor had the crucial influence on the brightness of CCC. The more insoluble matter content in green liquor, the lower CCC brightness could be obtained. When the green liquor was filtered by slow filter paper, the brightness of CCC could reach 91.98%ISO which was approximately close to PCC.

2. The silicon in green liquor existed in colloidal state had no influence on the brightness of CCC.
3. Reducing the content of insoluble matter was beneficial for decreasing the chromatic aberration between CCC and PCC.

Acknowledgements

References

1. R Patil, JM, Genco, H Pendse. Cleavage of Acetyl Groups from Northeast Hardwood for Acetic Acid Production[C]. 2012 PEERS Conference: 2177-2226

2. Yasunori Nanri, Haruo Konno, Hideyuki Goto, and Kazuto Takahashi. A new process to produce high quality PCC by the causticizing process in a kraft pulp mill[J]. TAPPI Journal, 2008(1):19-24

3. Tutus A. and Eroglu H., An alternative solution to the silica problem in wheat straw pulping [J], Appita,2004,57 (3): 214-217

4. Yan-jun Tang, Bin-yue Liu. An Overview of Comprehensive Utilization of White Mud[J].Word Pulp and Paper, 2003, 22 (6) : 53-55

5. Jin Wang, Peng Wei, Peng Liu, Wei Sun. Identifying Appropriate Conditions for Producing Spindle-like Causticizing Precipitated Calcium Carbonate for Paper Filler Applications[J]. BioResources, 2012,7(4):5894-5903

6. Haruo Konno, Hideyuki Goto, Kazuto Takahashi,Yasunori Nanri. An Innovative Process to Manufacture Calcium Carbonate by the Causticizing Process in a Kraft Pulp Mill[C]. TAPPI PaperCon'09 Conference, St. Louis, 2009:1-18

7. Li, Z, Wang, Z. The preparation of precipitated Calcium carbonate from alkali recovery white sludge[J]. China pulp & Paper, 2007(1):60~61

8. Wang Jin, Yang Peng. Properties evaluation and application performance of white sludge from alkali recovery [J]. Paper and paper making,2011(11):51-54

9. Gui-hua Pan, Jin-shan Chen, Wang-lan Li. Straw Lime Mud as Filler of Paper [J]. Paper and Paper Making,2009,28(7):52-54

10. Gui-lin Wang. Practise of Straw CCC as Filler of Paper[J]. The Chinese Paper Industry,2008,29 2 :55-60

11. Jian Wang, Xiao-long Wang, Zhi-jie Wang, Effect Factors of Optical Properties of Calcium Carbonate Made from lime Mud [J]. Paper and Papermaking, 2011(08):57-59