

Green Liquor Desilication *via* Black Liquor Combustion Process for Bamboo Pulping

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The presence of silicon in non-wood raw materials is known to interfere with the causticization of green liquor and the calcination of white mud, which has provided motivation for advances in alkali recovery technology. Therefore, reducing the silicon content of green liquor is the fundamental way to solve the problem. However, there are certain defects in conventional green liquor desilication, so this study provides a basis for desilication from green liquor *via* black liquor combustion and studies the desilication effect of a compound desilication agent on bamboo pulping black liquor. The results show that the desilication effect was better and the desilication rate could reach 84% when the Mg/Al proportion in compound desilication agent was 1:0.6. Meanwhile, the content of residual aluminum in green liquor decreased, which can avoid the influence of residual desilication agent on subsequent stages. Scanning electron microscopic images show that green-liquor-silicon-insoluble (GLSI) substance is a granular precipitate, and the X-ray diffraction analysis shows that GLSI substance has a complex structure similar to $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{MgO}$. This implies that the desilication mechanism consists of chemical precipitation and physical adsorption.

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INTRODUCTION

The pulp and paper industry is centered on the usage of wood raw material. It plays an important role in basic supply services, but the risks of pollution to the environment and water resources have attracted increasing attention. The generation and discharge of wastewater and solid waste from the paper industry are substantial (Wei 2000; Wang 2018). Therefore, China has issued a series of laws and regulations, emission standards, and guiding opinions on comprehensive governance (NDRC *et al.* 2021). The main pollution of the pulp and paper industry comes from green mud and causticized white mud in alkali recovery systems and biochemical sludge from wastewater treatment systems. The simple discharge, landfill, or incineration treatment methods can no longer meet the requirements of environmental protection. Compared with wood raw material, non-wood raw materials have high silicon content, and the silicon that enters into the black liquor

(BL) when cooking will cause the problem of “silicon interference” in the alkali recovery system (Thiagaling 1977; Pei 2012). This is the reason for the difficulty of BL processing and comprehensive utilization and recycling of white mud. Therefore, it is necessary to remove the silicon from black liquor to overcome “silicon interference” from non-wood pulping.

Now, with the application of “high temperature passivation technology” and “black liquor crystallization evaporation technology”, the rheology and combustion performances of non-wood pulping black liquor with high solid content have been improved (Yuan *et al.* 2011; Chen *et al.* 2016; Li 2018). However, the silicon is not removed from the BL, and the silicon is transferred from the BL to the green liquor (GL). This means that the “silicon interference” problem occurs and finally focuses on the white mud component CaSiO_3 , which is produced in the process of causticization. Although the CaSiO_3 content in white mud is not so high, this is indeed responsible for the main disadvantages with high residual alkali content and low dryness of white mud, making the white mud from non-wood pulping difficult to calcine for reuse and comprehensive recycling. Although the amount of green mud generated is not as high as white mud, its treatment is also a problem that must be handled (Xia *et al.* 2014; Fang *et al.* 2016). The landfill treatment of green mud and white mud not only occupies land resources but also produces high concentration of waste liquid (leachate), resulting in the risk of secondary pollution (Yuan *et al.* 2016). Therefore, there have been many explorations on how to utilize the green mud and white mud from non-wood pulping, primarily papermaking filler, building materials, and so on (Ma *et al.* 2016; Qin *et al.* 2016). However, the non-wood pulping is difficult to completely achieve a non-polluting, environmentally friendly process, and the goal of carbon balance cannot be achieved because those above technologies do not have wise application on an industry scale.

Domestic and foreign scholars have proposed a series of new ideas and methods to solve the problem of high silicon content in non-wood pulping BL and the inability of comprehensive utilization of silicon-contained white mud. The white mud and shale can be used as sintered shale brick, and it has better compressive strength and performance of frost resistance when there is 10% white mud in sintered shale brick (Yang *et al.* 2021). An artificial stone decoration material could be synthesized by using the unsaturated polyester resin and white mud, which has low cost and high performance, and the results show that white mud can effectively prevent the expansion of artificial stone section cracks (Ling 2018). In adopted *in-situ* modification technology, the modified solidifying material was used to deal with the white mud, which can overcome the disadvantage of white mud of high moisture content and so on (Peng and Song 2018). White mud can also be utilized as single desulfurizer in flue gas desulfurization technology (Li *et al.* 2012; Liu *et al.* 2019). Industrial practice has shown that the problem of “silicon interference” in alkali recovery system for non-wood pulping mainly focuses on the stages of GL causticization and white mud calcination at present. Therefore, reducing the GL silicon content is the basic way to solve the GL silicon interference and white mud silicon interference. An aluminum salt was used in GL desilication in the process of BL combustion, and the results showed that the desilication rate increased rapidly with increasing the dosage of aluminum salt (Xu *et al.* 2013). However, the effect of the residual aluminum salt in the GL on the causticization has to be considered and solved.

The authors have deeply analyzed the problems existing in conventional GL desilication and considered that silicon concentration is higher in inorganic melt than in

green liquor during BL combustion in alkali recovery furnace. Here, it is possible for a desilication agent to react with silicon to form an insoluble substance, named green-liquor-silicon-insoluble (GLSI) substance, which has larger size and is easier to precipitate. The precipitation may be minerals with complex structures such as $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$ and $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$. This hypothesis has been validated by the authors' previous studies (Xu *et al.* (2015a,b, Xu *et al.* 2017), which provides a theoretical foundation for the GL desilication in the combustion of BL by adding desilication agent before pumping into the alkali recovery furnace. The method is named GL desilication *via* BL combustion process, and a schematic is shown in Fig. 1. The authors considered that the rheological properties of thick BL can influence the atomization and combustion of BL, so the dynamic viscoelasticity and rheological properties of thick bamboo kraft pulping BL has been studied (Xu *et al.* 2016a; Yue *et al.* 2017, 2018). The results showed that it was the primary task to realize the high concentration combustion technology of non-wood pulping BL to solve the problem of high viscosity and dilatibility of thick bamboo kraft pulping BL (Xu *et al.* 2016a; Yue *et al.* 2017).

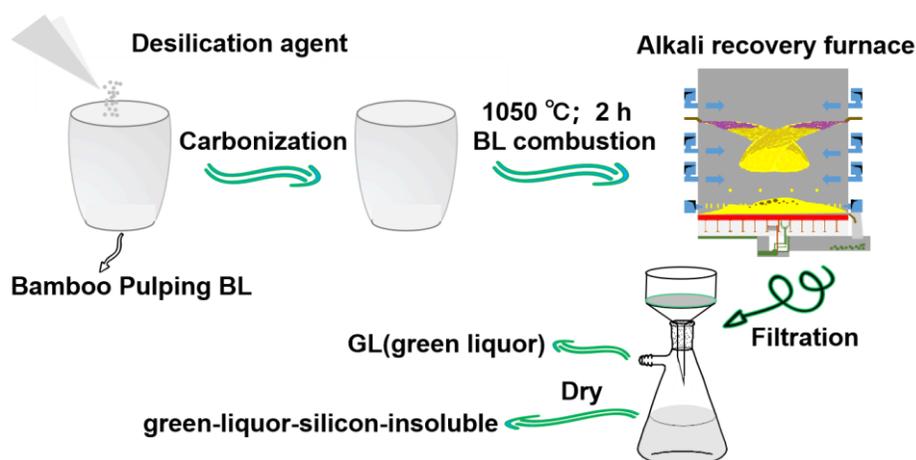


Fig. 1. Schematic of green liquor desilication *via* black liquor combustion

In this study, sodium aluminate and basic magnesium carbonate were used as desilication agents, and the desilication effect was studied deeply for both the aluminum salt and Mg-Al compound desilication agents. It is expected that magnesium salt in the Mg-Al compound desilication agent could reduce the content of residual aluminate salt. The optimum desilication conditions were determined in this study to achieve high-efficiency desilication from GL, which lays a theoretical foundation for the desilication of alkali recovery system. It can be expected to increase the utilization rate of non-wood raw materials to relieve the pressure from the shortage of raw materials in the pulp and paper industry, which can respond to the requirements for the recycling and utilization of agricultural waste proposed by the Chinese government.

EXPERIMENTAL

Materials

Bamboo pulp BL was obtained from high temperature passivation section, solids content, 71 wt%, Guizhou Chitianhua Paper Co. Ltd. (China); Magnesium carbonate basic ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), sodium aluminate (NaAlO_2) were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and sodium carbonate (Na_2CO_3) was bought from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Experiment of the GL-Desilication through BL-Combustion

A desired amount of desilication agent was blended evenly with 30 g of BL in a corundum crucible and carbonized at 300 °C on a universal electric stove until smokeless. The added amounts of desilication agent are shown in Tables 1 and 2, respectively. Subsequently, the carbonized samples were kept in a muffle furnace and burned at 1050 °C for 2 h. Finally, the melt obtained from burning was transferred into 500 mL of simulated GL containing 110 g/L Na_2CO_3 , and GL and GLSI were obtained by filtration. The GLSI substance was obtained *via* filtration using microfiltration membrane after 2 h.

Table 1. Dosage Ratio of Individual Desilication Agent

No.	Si	Al (Based on BL Solid Content (%))	Al (Calculated as SiO_2 /mol)
1	1	0.5	1.5
2	1	1	3
3	1	1.5	4.5
4	1	2	6
5	1	2.5	7.5

Table 2. Dosage Ratio of Mg-Al Compound Desilication Agent

No.	Mg	Al (Calculated as Mg/mol)	Total Amount of Desilication Agent (%)
1	1	0.4	0.58
2	1	0.6	0.66
3	1	0.8	0.74
4	1	1	0.83
5	1	1.2	0.91

Digestion Method

The treatment conditions of samples for the inductively coupled plasma (ICP) method are shown in Table 3. A certain amount of green liquor, HNO_3 aqueous solution, and H_2O_2 aqueous solution in volume ratio of 4:2 was blended in a polytetrafluoroethylene (PTFE) digestion tank and allowed to react at 80, 120, and 180 °C for 15, 30, and 30 min respectively. The sample was cooled down completely and diluted to a final volume of 100 mL with deionized water and was analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Xu *et al.* 2016b; Zhang *et al.* 2017) to measure the silicon and remnant contents of desilication agent in the GL.

Table 3. Digestion Conditions of Green Liquor Sample

No.	Power (W)	Heating Time (min)	Holding Temperature (°C)	Holding Time (min)
1	1000	10	80	15
2	1000	5	120	30
3	1000	8	180	30

Calculation of Extent of Desilication

The desilication effect of GL through the combustion of BL is expressed by the GL extent of desilication, which is the ratio of the difference in the silicon contents between the GL after adding the desilication agent and the GL control sample with the silicon content of the latter as shown in Eq. 1,

$$Y = \frac{(C_1 - C_2)}{C_1} \quad (1)$$

where Y is the extent of desilication, C_1 (ppm) is the silicon content in GL control sample without adding desilication agent, and C_2 (ppm) is the silicon content in GL after adding the desilication agent.

Characterization Methods

The operating parameters for inductively coupled plasma atomic emission spectrometry (ICP-AES, IRIS Interpid II, Thermo Fisher, Waltham, MA, USA) spectrometer 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.

A laser particle size analyzer (Mr2000, Mastersizer, UK) was used to determine the particle size of green mud precipitate and GLSI substance, the parameter was as follows: refractive index, 1.69.

Scanning electron microscopy (SEM) was used to view the solid structures present on green mud precipitate and GLSI substance. The sample consisted of suspension liquid (10 mL) comprised of green mud precipitate or GLSI substance and absolute ethyl alcohol. The SEM (SU8100, Hitachi, Tokyo, Japan), with an attached energy-dispersive X-ray spectroscopy (EDS) system, was used to determine the present elements.

X-ray diffraction (XRD, Ds Advance, Bruker, Germany) was used to analyze the chemical construction of green mud precipitate and GLSI substance. The parameters were as follows: the scope of 2θ , 15° to 90° . BET (ASAP 2426, Micromeritics, Norcross, GA, USA) was used to measure the BET surface area of green mud precipitate and GLSI substance.

RESULTS AND DISCUSSION

Desilication Effect *via* Individual Desilication Agent

In the experiment, NaAlO_2 was used as a desilication agent for GL desilication *via* BL combustion process. To evaluate the desilication effect, the silicon content was analyzed by ICP, and the residual content of desilication agent in the GL was also determined. The results are shown in Fig. 2.

It can be seen from Fig. 2 that the silicon content in the GL was reduced with increasing dosage of NaAlO₂. When the dosage of NaAlO₂ was at 0.5 wt%, the silicon content was reduced obviously compared with the control sample. The change in silicon content gradually leveled off when NaAlO₂ dosage was increased from 0.5 wt% to 2.0 wt%, and the corresponding extent of desilication also displayed the same trend and did not increase considerably. Silicon content decreased to the experimental minimum and extent of desilication was up to 70% with 2.5 wt% NaAlO₂ dosage, meaning that the desilication effect was better. Compared to the effect of NaAlO₂ on simultaneous desilication of the black liquor, GL desilication *via* BL combustion process achieved a higher extent of desilication. However, the aluminum salt content in the GL increased with the increase in the dosage of NaAlO₂, resulting in an increase in the content of residual desilication agent in the GL. Unfortunately, the increase in the content of residual aluminum salt of desilication agent would adversely affect the causticization. Therefore, the content of residual desilication agent must be controlled at a low level, which is the premise of achieving the better desilication effect.

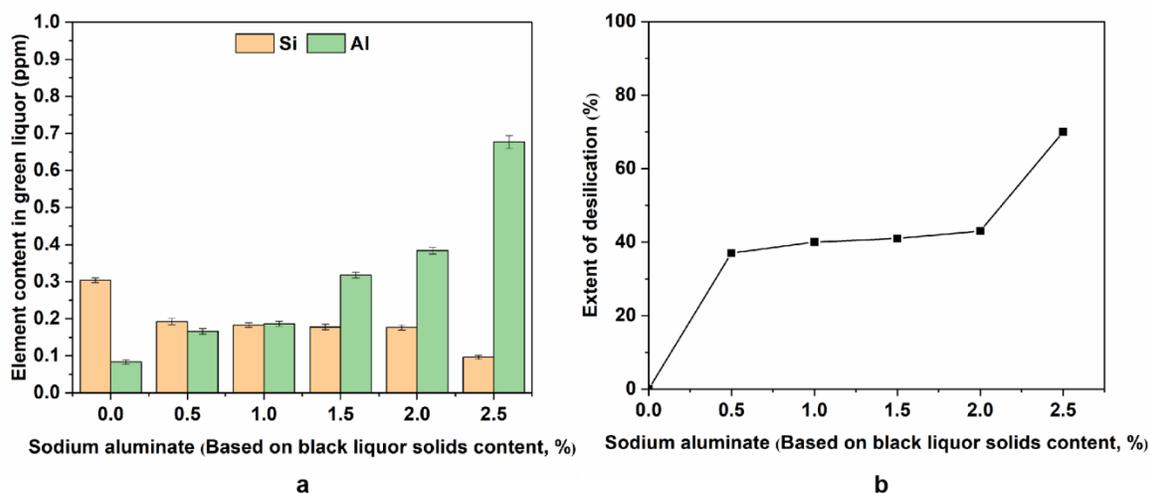


Fig. 2. NaAlO₂ as desilication agent: a: elemental content in green liquor; and b: extent of desilication

On the one hand, with aluminum salts as a desilication agent, GLSI substance is formed as a precipitate by the reaction of sodium silicate during BL combustion process, and this can be directly separated from GL. On the other hand, a colloid is generated by aluminum salt and sodium silicate in GL, which has flocculation and precipitation effect and the adsorption to silicon during its forming. Combined with these two roles stated above, the impact of “silicon interference” can be mitigated or solved because of the desilication. A possible chemical reaction is shown as follows:



The high content of aluminum salt in the GL may induce a subsequent causticization, which is difficult to achieve normally. This could be attributed to the slow precipitation of green mud or GLSI substance induced by colloid produced from magnesium and aluminum salts (Ulmgren 1987; Liu *et al.* 2021). Previous study showed the extent of desilication is higher with compound desilication agent of sodium aluminate and magnesium sulfate than that with only sodium aluminate during cooking, indicating

that there exists a synergic effect of sodium aluminate and magnesium sulfate and the residual content of the former (Xu *et al.* 2015c). Therefore, the authors put forward that the desilication is completed using magnesium salt and aluminum salt as a compound desilication agent in GL desilication *via* BL combustion process. It may be expected that the desilication effect improves and the content of residual aluminum salt in green liquor decreases. Here, magnesium salt is used to reduce the aluminum content in green liquor.

Desilication Effect *via* Mg-Al Compound

Based on the desilication process, it was determined that a basic dosage of $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ was 1.0 in molar ratio (based on SiO_2 , the same below), and the NaAlO_2 dosage was adjusted with the dosage of magnesium salt. The clear GL and GLSI substance were obtained for analyzing with different dosages of desilication agent and Mg/Al ratios of the compound desilication agent, and the desilication effect of the agent was then evaluated.

Extent of desilication via Mg-Al compound as desilication agent

The extent of desilication of compound desilication agent was calculated, and the results are shown in Table 4. It can be seen that the extent of desilication was 82% with Mg/Al molar ratio of 1:0.4 in the compound desilication agent. However, there was no obvious change in extent of desilication when the molar ratio changed from 1:0.6 to 1:1.2. The desilication effect cannot be evaluated only with the extent of desilication, but also with the influence of residual desilication agent on the subsequent stage. Therefore, the desilication effect is evaluated in extent of desilication and on the content of residual desilication agent when determining the optimal conditions.

Table 4. Extent of Desilication of Mg-Al Compound as Desilication Agent

No.	Mg/Al Molar Ratio of Compound	Amount of Desilication Agent (%)	Extent of Desilication(%)
1	1:0.4	0.58	82
2	1:0.6	0.66	84
3	1:0.8	0.74	88
4	1:1	0.83	87
5	1:1.2	0.91	90

When the Mg/Al molar ratio was 1:0.6, the amount of desilication agent was 0.66%, and the extent of desilication reached 84%. There was a low content of residual desilication agent present in GL corresponding to the amount of 0.5% to 1.5% of the BL solid content. This indicates that the desilication effect was better. Therefore, the compound desilication agent with Mg/Al molar ratio of 1:0.6 was the best condition for GL-desilication *via* BL-combustion process.

Effect of elements from green liquor on desilication

The elemental content in GL was determined by ICP, and the calculated results are shown in Fig. 3.

Figure 3a shows the variation of Si, Mg, and Al elemental contents in clear GL after desilication with compound desilication agents at various Mg/Al ratios. It can be seen that Si elemental content was decreased with increasing dosage of Mg-Al desilication agent. Unfortunately, the Al content was also increased. The Si content decreased to a minimum

when the Mg/Al ratio of desilication agent was 1:0.4, and maintained almost the same when the ratio was increased from 1:0.6 to 1:1.2. However, Al elemental content in GL increased with the increase in NaAlO₂ proportion in compound desilication agent. Therefore, the best Mg/Al ratio was determined to be 1:0.4. Figure 3b shows the content variations in Si content and residual desilication agent with compound desilication agent at different Mg/Al ratios. The content of residual desilication agent in GL was lower when the Mg/Al ratio was 1:0.6. The Si content in GL decreased down to the lowest value with the Mg/Al molar ratio of 1:0.6 and appropriately the same as that with the ratio of 1:1.2. Additionally, the residual desilication agent from GL also had less content. Presumably, the reason may be the interaction between Mg and Al elements according to the literature (Ulmgren 1987; Xu *et al.* 2016c; Zhang *et al.* 2017).

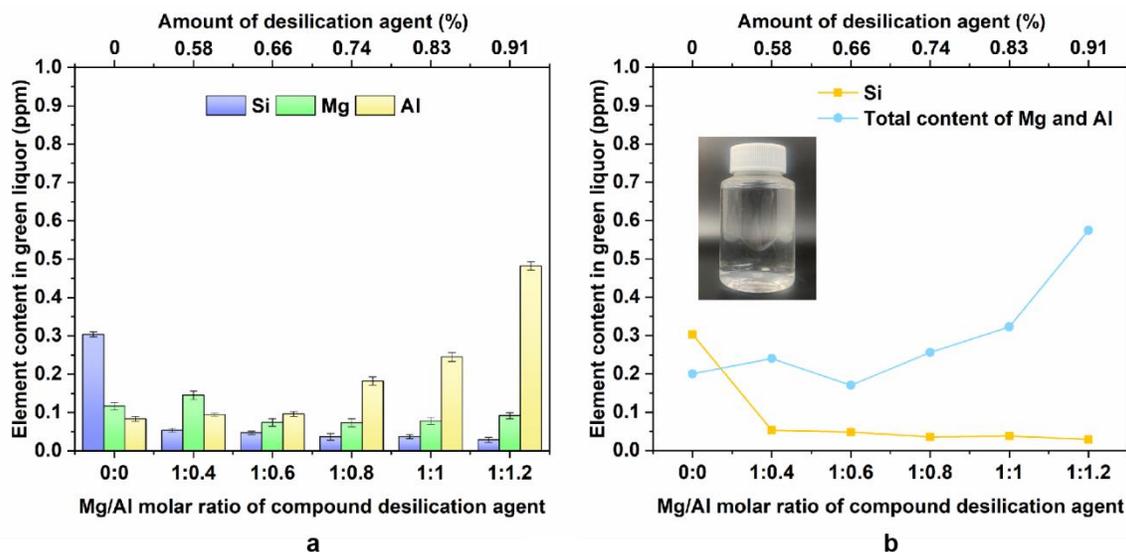


Fig. 3. Mg-Al compound as desilication agent: a: elemental content in GL; and b: content of residual desilication agent in GL

Evaluation of precipitation performance

The content of insoluble matter was determined by microfiltration membrane filtration in the experiment. The precipitation without adding compound desilication agent is called green mud precipitate and was used as the control sample. Further, the precipitate obtained after adding compound desilication agent is called GLSI substance. The particle size results of green mud precipitate and GLSI substance are shown in Table 5.

Table 5. Particle Size via Green Mud Precipitate and GLSI Substance

No.	Mg/Al Molar Ratio of Compound Desilication Agent	Particle Size (μm)
1	0	17.62
2	1:0.4	21.30
3	1:0.6	27.64
4	1:0.8	28.42
5	1:1	29.06
6	1:1.2	32.70

It can be seen that particle size of GLSI substance gradually increased. In a view of common sense, the precipitation rate is higher if the precipitate has larger particle size. Therefore, the precipitation rate also increased with the increase in the dosage of Mg-Al compound desilication agent. The precipitation performance of GLSI substance was better than that of green mud precipitate. Moreover, better precipitation performance can shorten the precipitation time of GLSI substance or green mud precipitate in the process of GL clarification. Therefore, the addition of Mg-Al compound desilication agent not only can improve the “silicon interference” problem, but it also can improve the precipitation performance of GLSI substance. The desilication effect is found better based on the previous analysis, meaning higher of desilication rate was obtained. The precipitation time of GLSI substance was shortened when the ratio of compound desilication agent was up to 1:0.6.

Most of BL is composed of organic substances, such as lignin, and inorganic substances such as salts. Therefore, some substances other than the required raw materials will transfer to the BL to form a complex system during pulping. The black liquor that contains more substances indicates that silicon exists in different forms and is thus difficult to remove. The results showed that the desilication effect is better using Mg-Al compound as desilication agent, but the mechanism of desilication could not be understood, and must be further considered and illustrated.

Desilication Mechanism

This study aimed to mainly compare the difference between two kinds of precipitates—one is green mud precipitate and the other is GLSI substance with 1:0.6 Mg/Al molar ratio of compound desilication agent. The two kinds of precipitates were mainly analyzed by SEM, EDS, and XRD analyses to illustrate the mechanism of GL desilication *via* BL combustion.

The microscopic morphologies of green mud precipitate and GLSI substance as analyzed by SEM are shown in Fig. 4. The morphology of green mud precipitate appeared as contiguously layered (Fig. 4a). Nonetheless, the GLSI substance, obtained with the ratio of 1:0.6, exhibited granular morphology (Fig. 4b). The microscopic morphologies of the two kinds of precipitates were different. The reason may be that the reaction between silicon and desilication agent during the combustion of BL is different with or without adding Mg-Al compound desilication agent. Some silicon reacts with desilication agent to form precipitate, and the other part of unreacted silicon is adsorbed on the precipitates, thus forming a complex insoluble silicon compound. From EDS results, C, O, Al, Mg, Si, Ca elements were the main elements found in green mud precipitate and GLSI substance, and the Si elemental content of GLSI substance was more comparable with that in green mud precipitate. This demonstrates that the Mg-Al compound desilication agent can successfully remove silicon.

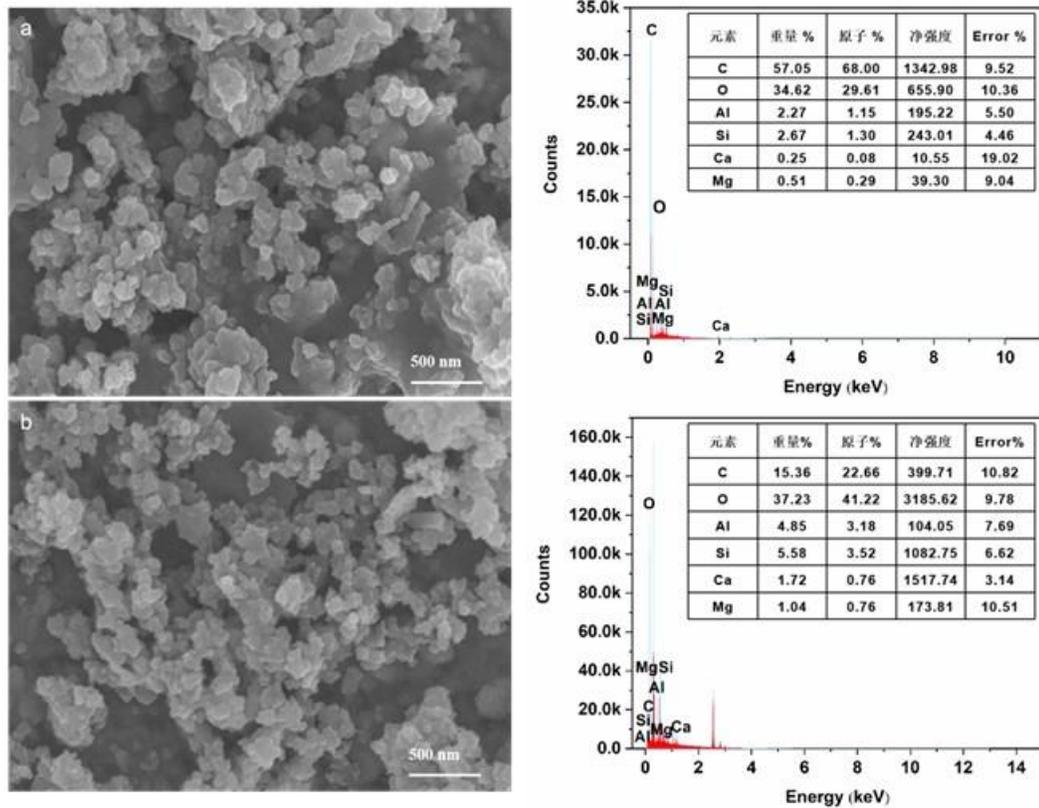


Fig. 4. SEM images and EDS results: a: green mud precipitate; and b: GLSI substance

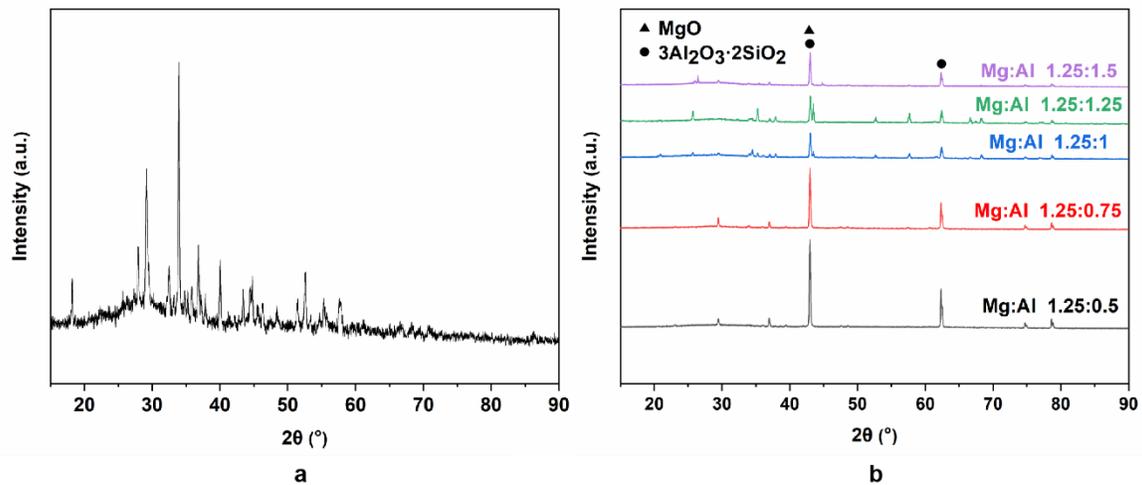


Fig. 5. X-ray diffraction patterns: a: green mud precipitate; and b: GLSI substance

Figure 5a shows the XRD detection of green mud precipitate. It can be seen that the diffraction peaks of green mud precipitate appeared disorderly and unsystematic, and the characteristic peaks were not obvious, indicating that the composition of green mud precipitate was complicated. The peak positions of green mud precipitate, which was composed of Al, Si, Ca, and other elements, was roughly the same as that of hydrated garnet reported in the literature, so it may be hydrated garnet or similar to hydrated garnet based on the composition and structure (Zheng *et al.* 2015; Yan *et al.* 2020). The diffraction

peak of the GLSI substance was clear, and there were less impure peaks, as shown in Fig. 5b. According to the diffraction pattern analysis, it infers that the GLSI substance may contain MgO, SiO₂, and Al₂O₃ oxide forms and that its structural composition may be 3Al₂O₃•2SiO₂•MgO based on the literature data (Liu *et al.* 2006).

According to the analyses of green mud precipitate and GLSI substance, the desilication mechanism for the GL desilication *via* BL combustion may be composed of two parts. On the one hand, the silicon in the BL reacts chemically with the sodium aluminate desilication agent in the combustion melt cushion to form a silicon-aluminum compound, which will be directly precipitated when the melt is dissolved into the thin GL. On the other hand, silicon adsorbs on the surface of magnesium oxide generated by the high-temperature combustion of basic magnesium carbonate desilication agent when it reacts with sodium carbonate in green liquor and is removed from the green liquor.

Application Evaluation of Green Mud Precipitate

The size distribution and BET surface area of green mud precipitate and GLSI substance are shown in Fig. 6. The mean grain size of green mud precipitate and GLSI substance were 17.62 μm and 27.64 μm, respectively. There were obvious peaks in the particle size distribution curves of two kinds of precipitates that tended to normal distribution and they basically overlapped. The size distributions were the same and distributed mostly from 1 to 100 μm, as shown in Fig. 6a. The BET surface area of green mud precipitate and GLSI substance were 63.0 m²/g and 35.3 m²/g, respectively, as shown in Table 6.

Table 6. BET Surface Area of Green Mud Precipitate and the GLSI Substance

Sample	BET Surface Area (m ² /g)	Single Point Surface Area (m ² /g)	Correlation Coefficient
Green Mud Precipitate	63.0	61.40 (at P/P ₀ = 0.2499)	0.9998
GLSI Substance	35.3	34.40 (at P/P ₀ = 0.2499)	0.9998

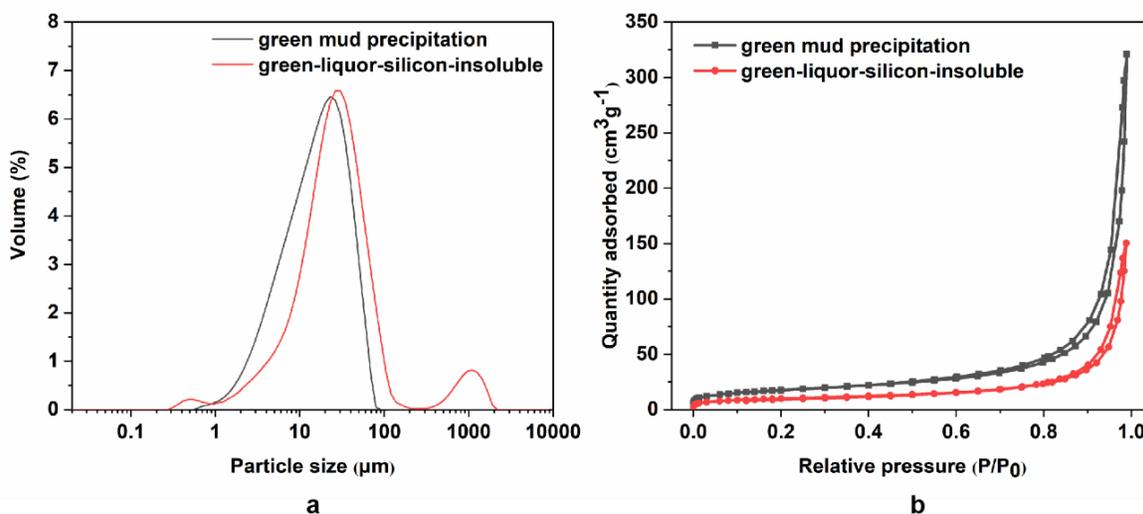


Fig. 6. Analysis of green mud precipitate and the GLSI substance: a: particle size; and b: BET surface area

The particle size of GLSI substance was larger than that of green mud precipitate, which is deposited in granular form. These granular precipitates display serious aggregation and deposition, and become larger agglomerates, or these agglomerates produce secondary aggregations to form larger size of GLSI substance. Further, the GLSI substance is aggregated with each other, resulting in the overlap of some areas and the decrease in the outer surface area. This leads to a decrease in the specific surface area.

It is speculated that green mud can be used for the preparation of adsorption materials due to the fact that green mud could be reused and comprehensively recycled based on the analyses above. The study of green mud provides new ideas for the recycling of green mud.

CONCLUSIONS

1. The effect of green liquor (GL) desilication *via* black liquor (BL) combustion was better when Mg-Al compound desilication agent was used. When the Mg/Al ratio of compound desilication agent was 1:0.6, the extent of desilication reached 84% and the content of residual desilication agent in green liquor was lower because of the interaction between magnesium and aluminum.
2. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) results showed that the GLSI substance formed corresponded to $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{MgO}$, indicating that the interaction occurred between magnesium and aluminum and the desilication mechanism involved chemical precipitation and physical adsorption.
3. The GL desilication *via* BL combustion can be used not only to achieve the purpose of efficient desilication, but also to avoid the influence of residual desilication agent on subsequent stages through process control. The study provides a theoretical basis for the alkali recovery system desilication technology and a new idea for the comprehensive reuse and recycling of green mud precipitate.

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