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Research Article

Study on Sodium Modification of Inferior Ca-Based Bentonite by Suspension Method

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Hunyuan Ca-based bentonite is one of large-type bentonite deposits in China, the reserve of which is more than 0.15 billion tons. However, they are not completely utilized in the pellet production. Process mineralogy investigation shows that the bentonite is a kind of typical Ca-bentonite (Ca-Bent). The sodium modification of the sample is studied by suspension method in this study. Results present the alkali coefficient K of modified Na-bentonite that is increased from 0.34 to 1.33, and the 2HWA, dilation, and colloid index are, respectively, increased to 601%, 32.4 mL/g and 87.6 mL/(3 g) under optimal conditions of Na_2CO_3 dosage 3.0%, pulp density 20%, sodium temperature 55°C, and sodium time 0.5 h. The XRD patterns show that $d(001)$ of the sample bentonite is reduced from 1.5539 nm down to 1.2467 nm, and $2\theta(001)$ of the sample bentonite is increased from 5.6875° to 7.0907°, indicating that the sample Ca-Bent is effectively modified into Na-Bent.

1. Introduction

Being high dispersity, hydrophilic property, and viscosity, bentonite is widely used in the pellet production to improve the strength of green and dry pellets as well as the bursting temperature of green pellets [1–5]. In commercial production, bentonite quality has obvious effects on the production cost and the quality of products. The practice has shown that about 90% of bentonite is residual in the finished pellets, reducing total iron (TFe) grade of roasted pellets. For blast furnaces, the coke rate is lowered by 2%, and output is increased by 3% if TFe grade of charging is enhanced by 1%. Thus, improving the bentonite quality has great importance to the iron and steel industry.

Presently, average dosage of bentonite, most of them are Ca-Bent, is between 2.5% and 4% in domestic pellet plants. Generally speaking, the balling effect using Na-Bent is better than that using Ca-Bent if the dosage is equal [6]. Therefore, in order to reduce the bentonite dosage, it is necessary to modify the inferior Ca-Bent into superior Na-Bent.

Hunyuan bentonite is one of large-type bentonite deposits in China, the reserve of which is more than 0.15 billion tons. It is a typical kind of Ca-Bent, and the dosage of it is high to 3.0% ∼3.5% when used as pellet binder. So, they should be firstly subjected to sodium modification so as to be widely used in pellet production. Three methods are usually used to sodium modification [7, 8]: suspension method, semidry process, and screw extrusion method. Comparatively, suspension method makes the sodium reaction happen in solution, and the time for this method is the shortest.

In this investigation, based on the physicochemical properties and process mineralogy of the Ca-Bent, effects of different factors on the sodium modification by means of suspension method are studied, which provides an effective route for the utilization of Hunyuan Ca-Bent.

2. Materials

The main chemical compositions of the sample bentonite are shown in Table 1. According to the formula $K = (E_{Na^+} + E_{K^+})/(E_{Ca^{2+}} + E_{Mg^{2+}})$, the alkali coefficient K is 0.34 (<1), indicating that this bentonite is a typical Ca-Bent [1].

The chemical phases of silicon in the Ca-Bent show that 94.08% SiO_2 exists in silicates, and 5.92% SiO_2 exists as the dissociated form. As far as calcium is concerned, 78.06% of CaO exists in Ca-montmorillonite, and 12.66% of CaO is in the insoluble silicates.

Table 1: Chemical compositions of the sample Ca-Bent (wt.%).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P	S	LOI*
66.73	14.05	1.86	2.37	1.20	1.06	0.84	0.010	0.015	9.79

* Note: LOI is loss of ignition.

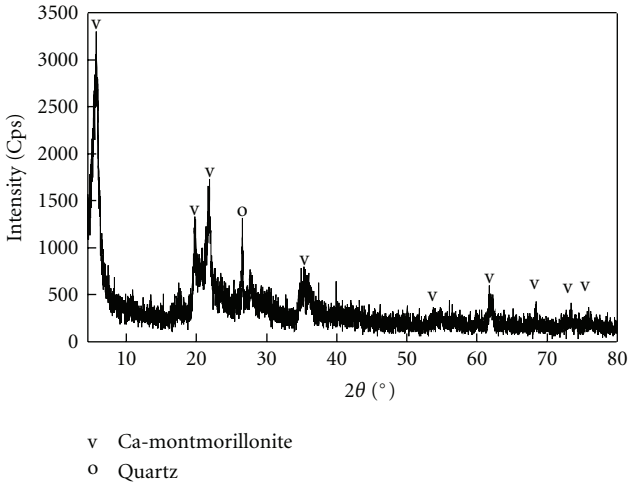

Figure 1: XRD pattern of Hunyuan Ca-Bent.

It can be seen from Figure 1 that Ca-montmorillonite is the leading minerals in the bentonite apart from a small quantity of dissociated quartz. Figure 2 shows the flaky and plate-like particles of Ca-montmorillonite and Figure 3 presents the dissociated quartz enwrapped by the montmorillonite.

The basic physical indexes of the sample as pellet binders are presented in Table 2.

All the sodium agents, including NaF, Na_2CO_3, NaOH, Na_3PO_4, and NaCl, are chemical pure.

3. Experimental Methods

The experimental procedures are described as follows: to begin with, the Ca-Bent is ground, of which the granularity below 0.1 mm accounts for 90%. 100 mL of distilled water is put into a 200 mL beaker. After that, a certain quality of dried Ca-Bent and sodium salt is added into the same beaker and stirred for 3 min in order to disperse the materials evenly, and, then, the beaker is laid in a homothermal water-bath and heated at a given temperature for a certain time. In the bentonite-water system, there exist plenty of Ca^{2+} and Na^{+}, the following reaction will occur:

$$\text{Ca-Bent} + 2\text{Na}^{+} = 2\text{Na-Bent} + \text{Ca}^{2+}. \quad (1)$$

After the sodium modification is finished, the slurry is filtered, then the filter residues are dried at $95 \pm 5^{\circ}$C for more than 6 hours. Finally, the dried bentonite is ground to the granularity of 99% below 0.075 mm.

Literatures indicate [7, 8] that the 2HWA and the dilation of Na-Bent are better than those of Ca-Bent, because Na-montmorillonite can be dispersed into single crystal while

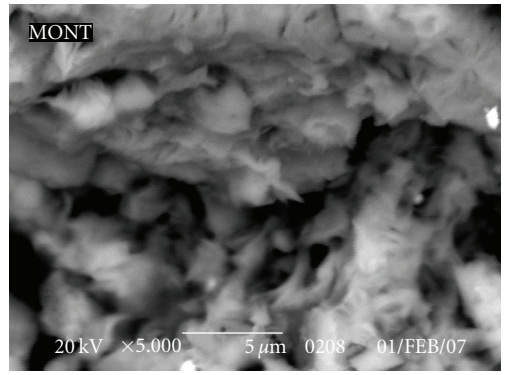

Figure 2: SEM image of Ca-montmorillonite.

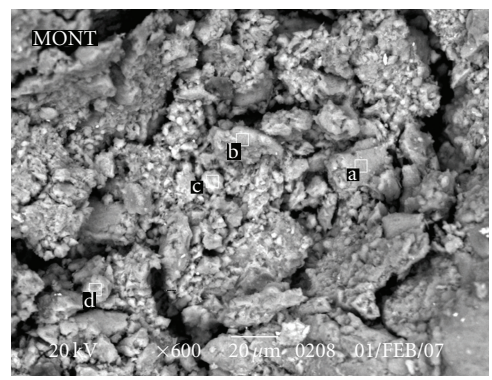

Figure 3: SEM image of quartz enwrapped by Ca-montmorillonite (a, b, d-quartz, and c-montmorillonite).

Table 2: Basic physical properties of the sample Ca-Bent.

Ca-montmorillonite (%)	2HWA* (%)	Dilation ($mL \cdot g^{-1}$)	Colloid index ($mL \cdot (3\,g)^{-1}$)
86.0	195	8.3	19.0

* Note: 2HWA refers to water absorbtion content in 2 hours.

Ca-montmorillonite can be only dispersed into the polymer composed of tens of single crystals. So, 2HWA and dilation are often used to evaluate the sodium-modification effect in these investigations, and so is in this research.

XRD is applied to distinguish Ca-Bent from Na-Bent. Literatures [7, 9, 10] reveal that the montmorillonite has the strongest intensities and bright peaks on (001) crystal face. Moreover, $d(001)$ of Ca-Bent is about 1.55 nm, and $2\theta(001)$ is 5.66°; relatively, $d(001)$ of Na-Bent is 1.25 nm, and $2\theta(001)$ is 7.1°.

4. Results and Discussion

4.1. Factors Affecting Sodium Modification. Many factors have obvious effects on the sodium modification of Ca-Bent. In this paper, the following primary parameters, including category and dosage of sodium agent, sodium temperature and time and pulp density, are investigated.

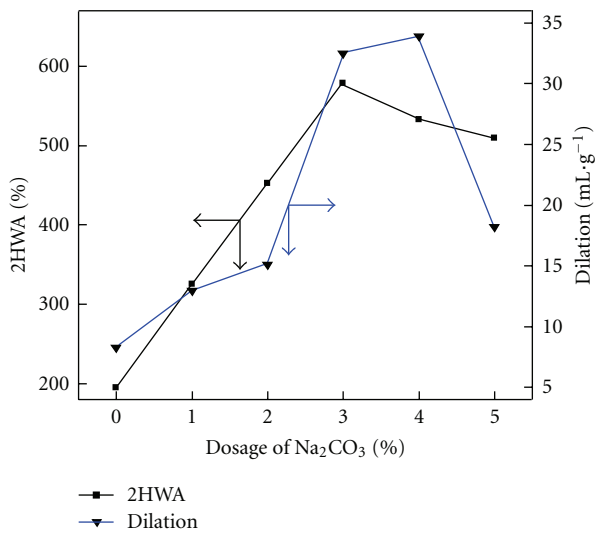

Figure 4: Effects of Na_2CO_3 dosage on sodium modification.

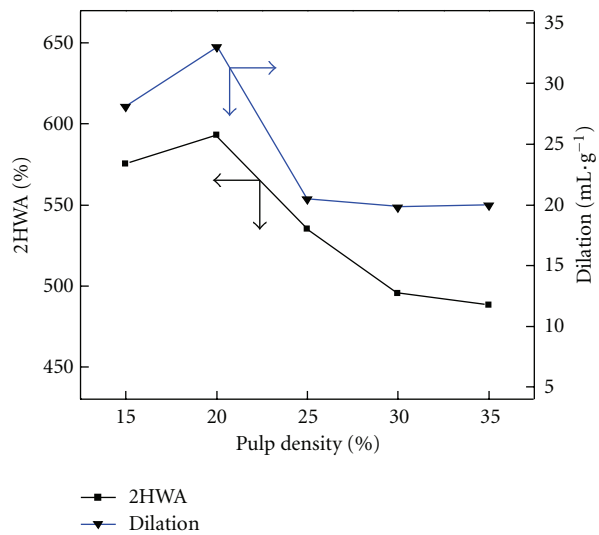

Figure 5: Effects of pulp density on sodium modification.

4.1.1. Dosage of Na_2CO_3. To start with, effects of Na_2CO_3 dosage on the 2HWA and dilation of modified bentonite are studied, fixing the conditions of pulp density 20%, sodium temperature 25°C, and sodium time 0.5 h, and the final results are plotted in Figure 4.

Seen from Figure 4, 2HWA and dilation of the unmodified Ca-Bent are far less than those of modified Na-Bent. With ascending of Na_2CO_3 dosage, 2HWA and dilation have the similar changing rule of first increase and then decrease, which reaches the maximum at the dosage of 3.0% and 4.0%, respectively. Studies mentioned above have shown that 1.85% CaO is contained in the Ca-montmorillonite. Supposing that Ca^{2+} can be completely replaced with Na^+, theoretic dosage of Na_2CO_3 is calculated as 3.5% according to reaction (1) mentioned before, which is almost equivalent to the actual dosage used. When Na_2CO_3 dosage is below the suitable quantity, Na^+ content in the liquid is evidently increased if the Na_2CO_3 dosage is heightened, which improves the reaction probability between Na^+ and Ca^{2+}. After the Na_2CO_3 dosage exceeds the right value, the excessive free Na^+ exists in the solution, and partial Na^+ ions are absorbed to the surface of the montmorillonite crystal grains to form a hydrated shell, preventing the outer moisture from entering between the crystal layers. Moreover, the balance of ion-exchange reaction between Na^+ and Ca^{2+} is destroyed owing to free Na^+ having high ionization rate and activity. The interlamellar spacing between crystal grains is compressed, so part of the interlayer water is extruded out, which is adverse to the sodium reaction [11].

From the results obtained, the suitable Na_2CO_3 dosage is 3.0% ~3.5%.

4.1.2. Pulp Density. Effects of pulp density on the sodium-modification are performed when Na_2CO_3 dosage is 3.0%, sodium temperature is 25°C, and sodium time is 0.5 h, and the variation curves of 2HWA and dilation of modified bentonite are shown in Figure 5.

Figure 5 indicates that the 2HWA and dilation are relatively the best when pulp density is 20%, being 593% and 33.0 mL/g, respectively. With the rising of pulp density, the content of Na^+ and Ca^{2+} in solution is improved, increasing the probability of ion exchange between Na^+ and Ca^{2+}. While the pulp density is in excess of 20%, the montmorillonite crystal grains cannot be dispersed adequately due to the apparent increase of solution viscosity, resulting in the diffusion velocity of Na^+ decreased to a certain extent. In addition, electrical double layers of montmorillonite mutually repulse and are suppressed [12, 13], which hinder the sodium reaction. Thus, the effect of sodium modification becomes worse.

4.1.3. Sodium Temperature. Figure 6 is the changing curves of sodium temperature affecting the 2HWA and dilation of the modified bentonite. The other parameters are fixed as the following: 3.0% Na_2CO_3 dosage, 20% pulp density, and 0.5 h sodium time.

As shown in Figure 6, sodium temperature also has perceivable impact on the 2HWA and dilation. Comparatively speaking, the effect of sodium modification is the best when the sodium temperature is 55°C. In the double electric layer of bentonite-water system, Na^+ in the diffusion layer presents a trend of moving to montmorillonite surfaces [10]. When the temperature is below 55°C, the migration rate of Na^+ is increased with the temperature improved, which increases the content of Na^+ on the montmorillonite surface. Therefore, the reaction velocity between Na^+ and Ca^{2+} is growing. When the temperature is over 55°C, part of non ionization water combined with Ca^{2+} between montmorillonite crystal layers is escaped out because of the high temperature [14], resulting in the increase of migration resistance pressure of interlamination Ca^{2+}, which hinders the ion exchange between Na^+ and Ca^{2+} to a certain extent. Above the right temperature, the higher sodium temperature

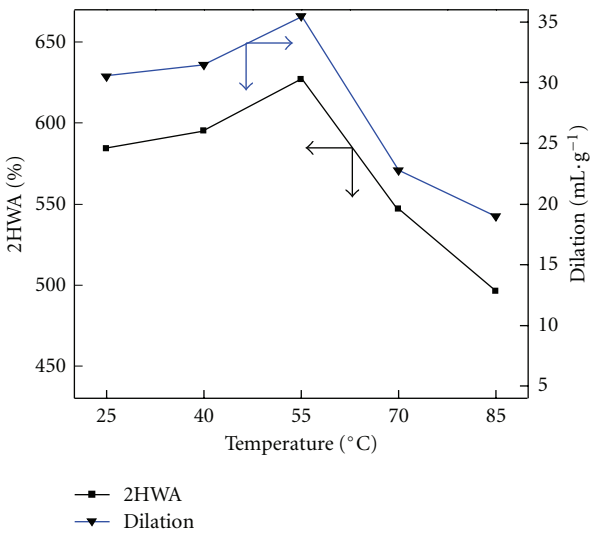

Figure 6: Effects of sodium temperature on sodium modification.

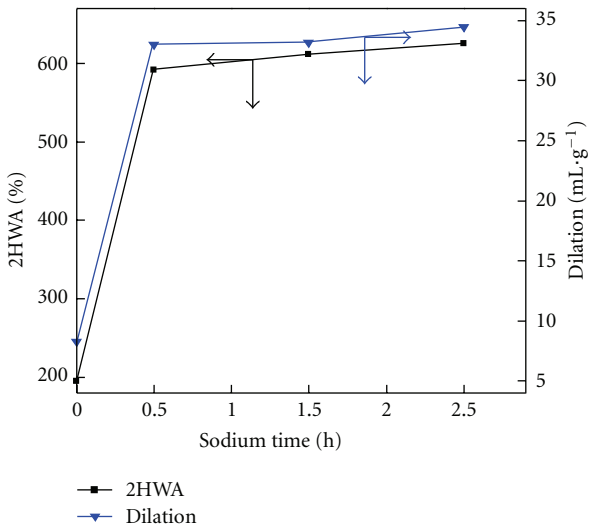

Figure 7: Effects of sodium time on the sodium modification.

is, the more interlamination water is out, and the harder Ca^{2+} is replaced of with Na^{+}.

4.1.4. Sodium Time. Effects of sodium time on sodium-modification are also studied, and the results are shown in Figure 7. The following parameters are fixed: Na_2CO_3 dosage of 3.0%, pulp density of 20%, and sodium temperature of 55°C.

The essence of sodium modification is the ion exchange between Na^{+} and Ca^{2+}. Sodium time will have obvious effects on the sodium reaction balance. It can be seen from Figure 7 that 2HWA and dilation has a sharp increase when the sodium time is less than 0.5 h. With the sodium time increased to 0.5 h, the ion exchange reaction is almost balanced, and the effects of sodium modification nearly reach the optimum. When the time is changed between 0.5 h and 2.5 h, 2HWA and dilation of modified bentonite are kept constantly. So in the commercial production, the sodium time is recommended as about 0.5 h.

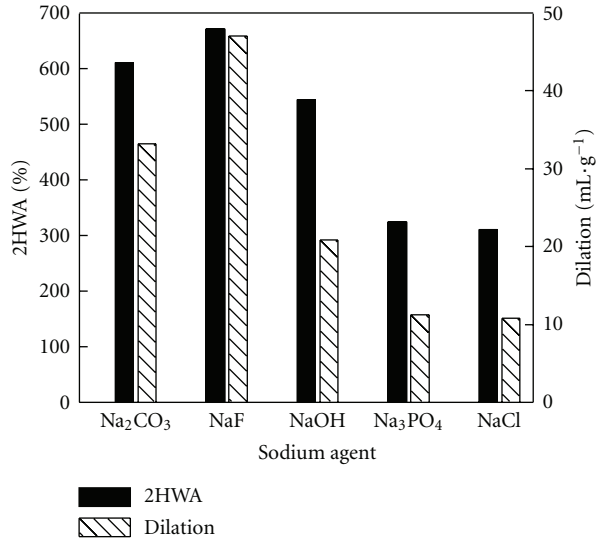

Figure 8: Comparison of different sodium agents affecting sodium modification.

Table 3: Na^{+} mole number of different sodium agents at the same mass percent.*

Sodium agents	Na_2CO_3	NaF	NaOH	Na_3PO_4	NaCl
Na^{+} (mol)	0.057	0.071	0.075	0.018	0.051

* Note: The sample bentonite is 100 g, and the sodium agent is 3.0 g.

4.1.5. Comparisons of Different Sodium Agents. Effects of different sodium agents on sodium modification are performed and the results are displayed in Figure 8. The experimental parameters are fixed as follows: sodium agent dosage of 3.0%, pulp density of 20%, sodium temperature of 55°C, and sodium time of 0.5 h.

At the same mass percent, Na^{+} mole number of different sodium agents has obvious difference, which is listed in Table 3.

From Figure 8, it can be apparently observed that the sodium modification effects of different sodium agents is NaF > Na_2CO_3 > NaOH > Na_3PO_4 > NaCl.

As given in Table 3, Na^{+} mole number of NaF and NaOH is relatively the most, that of Na_2CO_3 and NaCl is less, and that of Na_3PO_4 is the least. When we use NaF, NaOH, and Na_2CO_3 as sodium agents, there are sediments, colloids, or slightly soluble substances formed in the bentonite-water system, which has promoting effects on the sodium reaction. Although NaCl and Na_2CO_3 have the equivalent Na^{+} mole number, Cl^{-} and Ca^{2+} cannot form colloid or sediments, which is the real reason for the sodium effect of NaCl worse than that of Na_2CO_3. At the same mass percent, Na_3PO_4 only provides 0.018 mol of Na^{+}, far less than the theoretic quantity of 0.066 mol.

Table 4: Main physical properties of the bentonite.

	2HWA (%)	Dilation ($mL \cdot g^{-1}$)	Colloid index ($mL \cdot (3\,g)^{-1}$)
(1)	586	30.6	86.0
(2)	624	35.3	89.5
(3)	593	31.3	87.4
Average	601	32.4	87.6
Ca-bent	195	8.3	19.0
Average/Ca-bent	3.08	3.90	4.61

Table 5: Chemical compositions of the modified bentonite.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O
65.57	14.03	1.74	0.77	0.90	1.05	2.33

As well known, fluorine is a harmful element. So, Na_2CO_3 is the best sodium agent for the sodium modification of Ca-Bent.

4.2. Integrated Experiments. From the results mentioned above, the suitable conditions of sodium modification for Hunyuan Ca-Bent are including Na_2CO_3 dosage 3.0%, pulp density 20%, sodium temperature 55°C and sodium time 0.5 h.

Repeating the experiment under the optimal conditions for three times, the main physical and chemical properties are measured and given in Tables 4 and 5.

It can be seen from Table 5 that the content of Na_2O is obviously increased to 2.33%, by contrast, the content of CaO is decreased to 0.77%. According to $K = (E_{Na}{}^{+} + E_{K}{}^{+})/(E_{Ca}{}^{2+} + E_{Mg}{}^{2+})$, alkali coefficient K of modified bentonite is calculated as 1.33 (more than 1.0).

Figure 9 presents the XRD patterns of Hunyuan Ca-bent and the modified Na-Bent obtained under the integrated experimental conditions. As shown, $d(001)$ is reduced from 1.5539 nm down to 1.2467 nm, $2\theta(001)$ is increased from 5.6875° to 7.0907°. And the peak (001) of curve 1 is cragged and dissymmetry; however, the peak (001) of curve 2 is relatively flat and symmetry. These characteristics apparently indicate that curve 1 is the Ca-Bent XRD pattern, and curve 2 is the Na-Bent XRD pattern.

4.3. Process Flow Recommended. Based on the above results, the sodium-modification process flow is recommended in Figure 10. Suspension method is an effective sodium modification for Ca-Bent. However, the drying of the slurry is the limited section of this method, which is not applied in the Na-Bent commercial production because of the low drying efficiency and long drying time.

In recent years, the spray high-speed centrifugal dryer is developed and successfully used to dry the liquids as emulsion, suspending liquid, colloid, and so on. Compared with traditional drying equipment, the spray high-speed centrifugal dryer possesses high drying speed and thermal efficiency. Practice shows that the drying time is only 5~15 seconds in general as the drying temperature is about 120~150°C. So, it is feasible that this dryer is recommended to dry bentonite.

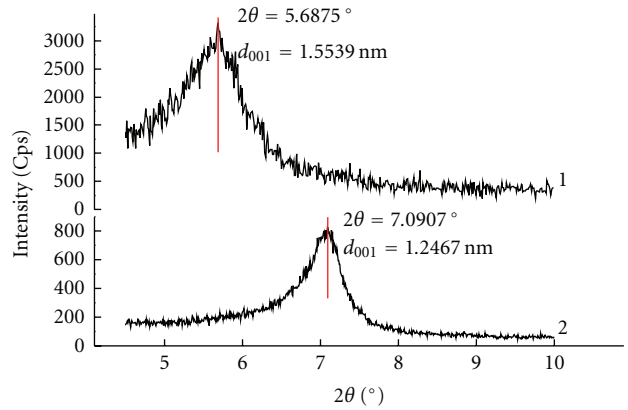

Figure 9: XRD patterns of Ca-Bent (curve 1) and modified Na-Bent (curve 2).

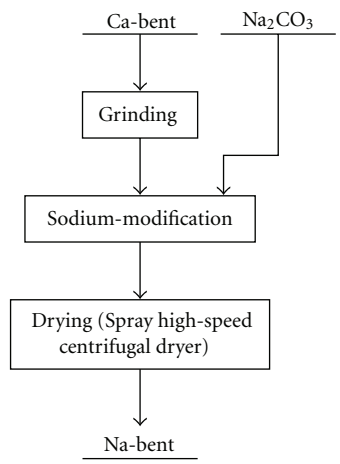

Figure 10: Process flow for sodium modification.

5. Conclusions

(1) Process mineralogy investigations show that Hunyuan bentonite, the reserve of which is more than 0.15 billion tons, is one of large-type typical Ca-Bent deposits in China. The 2HWA, dilation, and colloid index of the Ca-Bent are 195%, 8.3 mL/g, and 19.0 mL/(3 g), respectively. Presently, they are not adequately utilized in iron ore pellet production.

(2) By means of suspension method, the alkali coefficient K of modified bentonite is increased from 0.34 to 1.33, and the 2HWA, dilation, and colloid index are respectively increased to 601%, 32.4 mL/g, and 87.6 mL/(3 g), under the optimal conditions of Na_2CO_3 dosage 3.0%, pulp density 20%, sodium temperature 55°C, and sodium time 0.5 h.

(3) The XRD patterns of bentonite before and after sodium modification show that the $d(001)$ from 1.5539 nm reduces to 1.2467 nm, and $2\theta(001)$ from 5.6875° increases to 7.0907°. It indicated that the Ca-based Hunyuan bentonite changed to Na-Bent successfully.

Acknowledgments

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