Pretreatment Technology of Gibbsitic Bauxite with High Organic Matter Content

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Abstract

Organic matter in the alumina production process is the main technical problem that concerns the alumina refinery at present. This paper proposes to solve this problem by bauxite pre-treatment technology. The organic content can be reduced to 0.05 % by calcination at about 850 ℃. The roasted ore was digested using a conventional high temperature Bayer process, and the relative digestion rate of alumina reached about 98 %. By using this technology, the organics problem impacting the alumina process can be completely solved, the freight costs of bauxites transportation can be saved by one-third, and evaporation costs can also be significantly reduced by reducing water intake in the alumina production process, as water accounts for one-third of the weight of raw bauxites. This technical solution will be more competitive if low-cost energy is available at the mining sites of bauxite resources.

Keywords: Gibbsite, Organics, Roasting, Digestion.

1. Introduction

With the continuous expansion of China's alumina industry and the ongoing depletion of domestic bauxite resources, the country's bauxite imports have steadily increased, from less than 10 million tonnes in 2010 to 159 million tonnes in 2024. Due to the geological and climatic conditions of mineral formation, the organic content in bauxite has gradually increased [1, 2–6]. As a result, the organics issue has become one of the primary technical challenges faced by China's alumina industry. This leads to a series of problems, such as increased foam in the precipitation system, reduced precipitation rate, decreased product quality, and increased alkali loss [7, 8–11]. The presence of organics in the process severely affects the continuous and stable operation of alumina production.

Based on different treatment processes, the removal of organics is broadly categorized into two types, removal from the Bayer alumina production process and removal from the bauxite. The more extensively studied approach is the removal of organics from the Bayer production process. In the context of organics removal from the alumina production process, the main targeted organics are humic substances and sodium oxalate. Methods for removing sodium oxalate include solution causticization, salting-out crystallization, oxalate pellet method, and the common ion effect method, among others [12, 13]. Some of these methods have already been applied at various scales within alumina refineries. Research on the removal of humic substances is relatively limited. The primary methods include wet oxidation [14], cooling crystallization, liquid combustion, and activated carbon adsorption. An alternative approach involves reducing the organics entering the process through bauxite pretreatment. Compared to removing organics within the process, this method can remove organics before they enter the alumina production process, thus completely preventing their impact on production. Domestically, when dealing with high-sulphur diaspore bauxite, research and practical applications have explored the calcination of high-sulphur bauxite as a means of removing sulphur from the bauxite. During the desulphurization process, it is also possible to partially remove the organics from the bauxite [15].

This paper adopts the core technical approach for pretreatment of bauxite by calcination to remove organics. It presents preliminary research and analysis on the bauxite pretreatment process, the digestion effects of the calcined bauxite, and its techno-economic assessment (TEA). The research findings serve as a reference for alumina production enterprises using imported bauxites.

2. Test Material and Method

2.1 Test Material

The imported bauxite was used as the primary test material, and the chemical and mineral composition of the ore are shown in Tables 1 and 2.

Table 1. Chemical composition of the ore used for testing (%).

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	LOI	C_{org}
Content, %	48.48	4.69	18.49	0.97	0.018	0.039	0.11	0.032	25.82	0.24

Table 2. Mineral composition of the ore used for testing (%).

	Gibbsite	Kaolinite	Quartz	Goethite	Hematite	Anatase
Content, %	66.50	8.20	0.90	15.40	6.60	1.00

The recycling spent liquor used in the digestion test was sourced from an alumina refinery, and its main chemical composition is shown in Table 3.

Table 3. Chemical composition of the recycling spent liquor (g/L).

	Na_2O_T	Al_2O_3	Na_2O_K
Concentration	253.72	122.39	232.00

2.2 Test Method

The main experimental procedures were divided into two parts, the bauxite calcination test and digestion test of calcined bauxites.

First, the tested bauxites were dried, then crushed and ground to a particle size (effective particle diameter, median diameter) of less than 15 mm, with particles in the range of 5–10 mm accounting for approximately 80 %. The grinding particle size was controlled by using a standard sieve. The ground bauxites were then subjected to static calcination in a muffle furnace, with a calcination temperature ranging from 600 to 900 °C and a calcination time of 10 to 20 minutes. The calcined bauxites were then digested using the traditional Bayer process. The digestion equipment used was a laboratory molten salt steel autoclave with a digestion temperature of 265 °C and a digestion time of 60 minutes. The concentration of recycling caustic soda was 232.00 g/L and the caustic ratio was 1.41.

The test process included testing and analysis of both solution and solid samples. The bauxite digestion performance under different conditions was evaluated to assess the effectiveness of technical solutions and the optimal process conditions were determined.

3. Test Results and Discussion

3.1 Bauxite Calcination

The processed and qualified-sized bauxites were calcined in a muffle furnace. The primary purpose of ore calcination is to induce oxidation reactions of organics present within the ore, facilitating their removal in the form of CO_2. There were two main reactions during the calcination process: firstly, dehydration reaction of gibbsite and secondly, oxidation reaction of organics, as shown in Equations 1 and 2.

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O\uparrow \quad (1)$$

$$C_{org} + O_2 \rightarrow CO_2\uparrow \quad (2)$$

The main technical parameters controlled during calcination were the calcination temperature and time. Excessively high temperature or long calcination time can cause the gibbsite in the ore to transform into α-Al_2O_3, making it difficult to extract alumina using the Bayer process. Conversely, if the temperature is too low or the time is too short, the organic carbon C_{org} will not fully react, leading to poor removal of organics. After careful consideration, calcination conditions of 600–900 °C and 10–20 minutes were selected. The specific calcination conditions and test results are shown in Table 4.

Table 4. Bauxite calcination conditions and test results.

Test No.	Tempe-rature (°C)	Calcination time (min.)	Clinker weight reduction (%)	Organic carbon (%)	Mineral composition of calcined bauxite
1#	600	10	13.57	–	–
2#	600	15	19.67	0.08	γ-alumina, hematite, kaolinite, gibbsite, boehmite, anatase, quartz, alumogoethite
3#	600	20	24.90	–	–
4#	700	10	17.93	–	–
5#	700	15	21.18	0.06	γ-alumina, hematite, kaolinite, gibbsite, boehmite, anatase, quartz, calcite
6#	700	20	23.80	–	–
7#	800	10	25.60	–	–
8#	800	15	26.23	0.05	γ-alumina, hematite, metakaolin, anatase, quartz
9#	800	20	26.40	–	–
10#	900	10	24.17	–	–
11#	900	15	26.22	0.05	γ-alumina, hematite, metakaolin, anatase, quartz
12#	900	20	26.38	–	–

As seen in Table 4, with an increase in calcination temperature or extension of calcination time, the weight loss of the dry ore gradually increased, while the organic carbon content gradually decreased. The gibbsite phase in the calcined ore gradually disappeared due to dehydration. The main mineral components in the ore transitioned from gibbsite to γ-alumina. At a calcination temperature of 800 °C, calcining for 15 minutes reduced the organic carbon content in the ore to

0.05 %. Further increases in temperature or extension of calcination time had minimal effect on reducing the organic carbon content. At this point, the loss on ignition of the ore was 26.23 %. At 900 °C, after calcining for 15 minutes, the organic carbon content in the ore was also 0.05 %, and the loss on ignition was 26.22 %. Under these conditions, the gibbsite phase in the calcined ore completely disappeared, with the main phase in the ore being γ-alumina and no α-Al_2O_3 present.

3.2 Digestion of Calcined Bauxites

Since the gibbsite in the ore had undergone dehydration reaction to form γ-alumina after calcination, the low-temperature Bayer process could no longer efficiently digest alumina. Only the high-temperature Bayer process could be used.

High-temperature digestion tests were conducted on the calcined ore, with a digestion temperature of 265 °C, a digestion time of 60 minutes and a digestion caustic ratio of 1.41. The relative digestion rate of alumina from the ore was 96 %. For comparison, all calcined ores were subjected to digestion under the above-mentioned same conditions. Additionally, to investigate the effect of lime on the digestion process, 5 % lime (based on the mass ratio of lime to calcined ore) was added in some of the digestion tests. The solution analysis results from the digestion test are shown in Table 5.

Table 5. The ccomposition of liquor from the digestion test of calcined bauxites.

No.	Digestion conditions			Digestion liquor composition, g/L				
	Dig. Temp. (°C)	Digestion time (min)	Lime addition (%)	Na_2O_T	Al_2O_3	Na_2O_K	SiO_2	α_k
R1#	265	60	0	168.01	184.51	152.00	1.91	1.36
R2#			5	231.44	251.37	210.00	1.66	1.37
R3#			0	181.39	193.80	160.40	1.91	1.36
R4#			0	168.36	177.34	150.00	1.75	1.39
R5#			5	175.16	185.95	158.40	1.24	1.40
R6#			0	182.80	198.07	162.00	2.07	1.35
R7#			0	223.51	243.03	203.60	2.33	1.38
R8#			5	237.62	252.73	216.00	1.69	1.41
R9#			0	221.99	239.93	199.00	2.40	1.36
R10#			0	232.33	249.92	210.00	2.41	1.38
R11#			5	234.45	252.34	214.40	1.74	1.40
R12#			0	223.99	239.93	202.40	2.38	1.39

As shown in Table 5, the caustic ratio of the digestion liquor under all test conditions was lower than the set value of 1.41, indicating that the ore digestion performance was favourable and the actual digestion rate was higher than the estimated rate. As the calcination temperature increased, the caustic ratio of the digestion liquor tended to increase, suggesting a slight decline in the digestion performance of the calcined ore. Considering all four temperature conditions, the addition of lime reduced the alumina digestion rate. However, it played a certain role in desilication. In the liquor with lime addition, the silica content decreased, and the siliceous modulus of the liquor increased. The solid-phase results from the digestion test are shown in Table 6.

Table 6. The solid analysis results of digestion test of calcined bauxites.

No.	Lime addition (%)	Chemical composition of the digested bauxite residue, %					Digestion result		
		Al_2O_3	SiO_2	Na_2O	Fe_2O_3	CaO	A/F	N/S	$\eta_{A(\%)}$
R1#	0	13.97	11.91	7.36	54.74	0.26	0.26	0.62	90.27
R2#	5	14.40	11.65	5.20	46.80	9.74	0.31	0.45	88.26
R3#	0	14.06	11.97	7.06	56.12	0.48	0.25	0.59	90.44
R4#	0	13.88	11.9	7.31	54.88	0.29	0.25	0.61	90.35
R5#	5	14.07	11.37	5.10	47.22	9.81	0.30	0.45	88.64
R6#	0	14.47	11.81	7.27	55.12	0.31	0.26	0.62	89.99
R7#	0	16.27	11.87	7.08	54.09	0.26	0.30	0.60	88.53
R8#	5	15.24	11.56	5.32	47.12	9.32	0.32	0.46	87.66
R9#	0	16.56	11.65	7.01	54.24	0.26	0.31	0.60	88.36
R10#	0	15.87	11.93	7.16	54.49	0.28	0.29	0.60	88.89
R11#	5	15.15	11.21	5.24	47.81	9.04	0.32	0.47	87.91
R12#	0	16.96	11.51	6.91	53.23	0.26	0.32	0.60	87.85

From the test data in Table 6, it can be observed that after calcination at 600 °C, the actual alumina digestion rate from the calcined ore was consistently above 90 %. As the calcination temperature increased, the alumina digestion rate decreased to around 88 % at 900 °C. From the solid analysis results, it is evident that the addition of lime lowered the alumina digestion rate, decreased the N/S ratio of the bauxite residue, and increased the A/F ratio. This suggests that though the addition of lime could reduce soda consumption, it also led to increased alumina loss. This was consistent with the conclusion derived from the liquor analysis. Within the range of test conditions, as the digestion temperature increased from 600 °C to 900 °C, the alumina crystallization in the sintered bauxites became more mature and compact. Even under high-temperature digestion conditions, the digestion performance of alumina showed a downward trend. Under identical temperature conditions, the alumina digestion performance was better at 600 °C with a calcination time of 30 minutes. However, at temperatures between 700 °C and 900 °C, the digestion performance was better with a calcination time of 15 minutes. Since the bauxites had undergone calcination, theoretically, the alumina digestion performance of the calcined bauxites will always be poorer than raw bauxites.

3.3 Analysis and Discussion

The main goal of bauxite pretreatment was to remove the organics. From this perspective, higher calcination temperature is more effective. However, the calcination process must not interfere with the subsequent alumina extraction, which means the calcination temperature should not be excessively high. Since the planned technical solution involved using a rotary kiln (known for its simple operation and mature technology) as the calcination equipment while using pulverized coal or peat as fuel, the calcination temperature could not be too low. Otherwise, the rotary kiln might struggle to operate in a stable manner. From the calcination data, it is evident that when the temperature exceeded 800 °C, the organic content in the ore decreased to 0.05 % and this value remained consistent when the temperature reached 900 °C. Comprehensively considering the calcination equipment, effectiveness and efficiency in industrial application, the optimal calcination temperature should range from 800 to 900 °C, with a calcination time of 10 to 20 minutes.

After calcining bauxites under the above conditions, the calcined bauxites were digested using a high-temperature Bayer process. Under the test conditions (similar to typical operating conditions, calculations based on the liquor composition and solid analysis results from the bauxite digestion), the actual alumina digestion rate of the tested ore was around 88 %, with a relative digestion rate of approximately 98 %. The addition of lime during the digestion process reduced the alumina digestion rate. Although it reduced soda consumption, the overall economic benefits were not significant. Therefore, it is not recommended to add lime during digestion.

After pretreatment, the organic content in the ore was reduced to around 0.05 %, with an organic removal rate of 79 %. This effectively eliminated the negative impact of organics on the alumina production process, preventing their adverse effect on output and the increased costs associated with subsequent organic removal. After low-cost calcination of high organiccontent bauxite at the mining site, 8–15 % of moisture in the ore will be removed and the loss on ignition will be reduced by 24–27 %. The bauxites weight would be reduced by about one-third compared to conventional wet bauxite transportation, approximately one-third savings in the transportation costs would be achieved. Compared to regular bauxites, through digestion of calcined ore, about one-third of the water that would have entered the alumina production process from the raw bauxites is eliminated, which will reduce steam consumption and significantly lower evaporation costs. However, the consumption of fresh water will increase.

This technology increases the cost of bauxites for alumina production due to calcination costs. However, the benefits are reflected in two aspects, firstly, after removing the organics, there will be no longer costs related to organic treatment in the alumina production process, reducing process disruption and cost. Secondly, if inexpensive energy is available at the mining site, calcination can be conducted there. Due to the reduction in weight of the roasted ore, the associated transportation costs will decrease accordingly. This reduction can largely offset the cost of the calcination process, thereby enhancing the overall economic viability and competitiveness of this technical solution

4. Research Conclusions

(1) After calcination pretreatment of gibbsitic bauxite with high organic content at 800–900 °C, the organic carbon in the ore is reduced to around 0.05 %, achieving effective removal of organics from the bauxites.

(2) The calcined bauxites should be digested using the high-temperature Bayer process. The alumina digestion rate of the tested ore was approximately 88 %, with a relative digestion rate of about 98 %. Lime should not be added during the digestion.

(3) After pretreatment, the organics in the ore were largely removed, eliminating the significant negative impact that organics would otherwise have on the alumina production process, thereby reducing processing costs. If low-cost energy is available for calcination at the mining site, one-third of the ore transportation costs can be saved. Due to the reduction of about one-third of the water fed into the alumina production process (by the weight of the raw bauxites), evaporation costs can be significantly saved, though the consumption of fresh water will increase.

By adopting this technology, especially when very cheap energy is available at the mining site, the ore calcination cost can be reduced. When this cost is lower than the sum of the organic's treatment costs (from the raw bauxites) and the savings from reduced transportation costs (of the calcined bauxites), this technical solution will have strong market competitiveness.

5. References

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