CALCIFICATION – CARBONATION METHOD FOR ALUMINA PRODUCTION BY USING LOW-GRADE BAUXITE

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Abstract

Aluminum industry is one of the most important industries in China's nonferrous metal metallurgy industry. With the development of output in alumina and the improvement of its production technology, China's high quality bauxite resources are difficult to meet. Under this condition, “Calcification-Carbonation Method” was put forward to deal with middle-low grade bauxite and red mud by Northeastern University, the main purpose of this method is to change the balance phase of red mud into 2CaO•SiO2 and $CaCO_3$ with hydrometallurgical process. Through treatment by “Calcification-Carbonation Method”, A/S of the new structure red mud lowed below to 0.5 and the Na content lowed below to 0.3%, the red mud could be used in cement industry directly. This paper mainly introduced the technological idea and principle of new method, process comparison and typical experiment results is given as well.

Preface

Technical Background

With the rapid development of the aluminum industry, China's aluminum output keeps on increasing. The total alumina output in 2011 was about 3800 million tons, while it reached 1908 million tons in the first six months of 2012. However, the bauxite resources form a sharp contrast with the rapid development of the aluminum industry in China, especially in high quality bauxite resources, which the depletion was more obvious in Henan Province, China. The average service time of the high quality bauxite resources was less than 10 years [1-2], consider the prospective reserves, can be only about 20 years. While the middle-low grade bauxite existing reserves can be acceptable support 20 to 40 years, some unproved reserves can be the supplement in the future [3-4].

How to use the low grade bauxite to produce alumina becomes an urgent problem. Most of the bauxite resources in china are diasporic with Low alumina-silica ratio. The way to extract alumina by using mixed combination process and sintering process cause long production process, high energy consumption and high production costs [5]. There are two problems in Bayer Process to produce alumina. Firstly, when low grade bauxite is used to produce alumina, it caused low recover rate of alumina and low economic benefit; Secondly, red mud with high alkali content can not reuse directly. Since the dissolution of the Bayer process residue (red mud) equilibrium solid phase is sodium aluminosilicate hydrate, both of the loss of alumina in red mud and caustic alkali consumption are increased with the increasing content of the silica in the mineral, and the theory ratio of the loss of alumina with the content of silica is 1:1. The effect of mass ratio of alumina to silica in bauxite and dissolution red mud on the actual yield of the alumina in Bayer process is showed in Figure 1. When the alumina-silica ratio is 1 in the red mud and alumina extraction rate reached 80%, the alumina-silica ratio in bauxite must be greater than 5. However, the alumina-silica ratio is greater than 1 in the red mud in actual production. When the alumina-silica ratio is 1.4 in the red mud and alumina extraction rate reached 80%, the alumina-silica ratio in bauxite must be greater than 7. Therefore, instead of the traditional combination of sodium oxide, silicon oxide and aluminum oxide, a new structure of red mud with low content of the alkali and alumina can be a fundamental solution to the efficient use and environmentally friendly of the low grade bauxite. As shown in Figure 1, when the alumina-silica ratio is 0.4 in red mud, and the alumina-silica ratio in bauxite was 2, the alumina extraction rate can reach 80% theoretically.

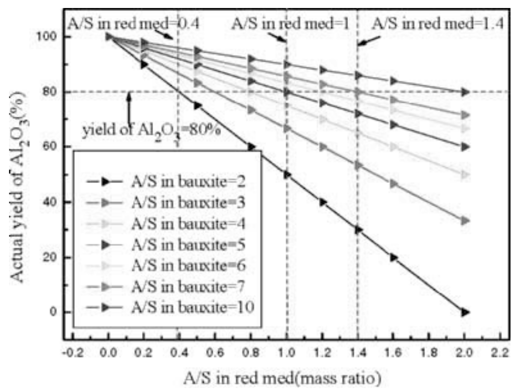

Figure 1. The effect of A/S in bauxite and dissolution red mud on the actual yield of the alumina in Bayer process

Meanwhile, China has already stored up 200 million tons red mud. As the increase of alumina yield and decrease of bauxite grade year by year, the annual output of red mud will continue increase. Promisingly, the stockpiles of red mud can be 350 million tons in 2015, which contain 80 million tons alumina and 35 million tons sodium oxide [6-7]. Many Chinese researchers have carried out lot of technology development of comprehensive utilization of red mud, but there has been never one applied to industrial production. The comprehensive utilization rate of the red mud was only 4%. There was no doubt that if researchers found a efficient process to take advantage of low grade bauxite and red mud, it will has important significance to promote alumina industry.

Technical Principle of New Technology

Our group puts forward the "Calcification-Carbonation Method" which deals with the low-grade bauxite or red mud and other aluminous materials after many years of research [8]. First the low-grade bauxite or red mud are calcified, which changes from the containing silicon phase to the calcium silicon aluminum compound as the main phase of hydrogarnet. Second uses the CO_2 gas for carbonation decomposition. The phases of decomposition products are mainly composed of calcium silicate, calcium carbonate and aluminum hydroxide. Then alumina is extracted by the alkaline solution at low temperature. The main components are the new structure red mud with calcium silicate and calcium carbonate. They can be directly used in the cement industry. This technology ensures valuable elements recycling such as alumina,

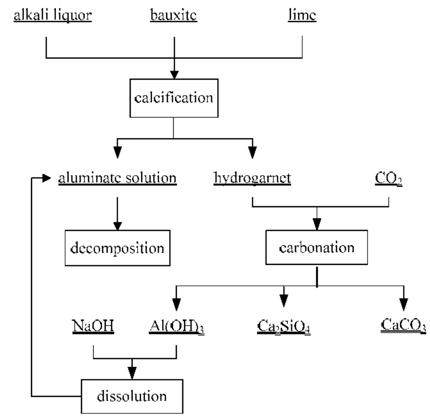

Figure 2. Process chart of calcification-carbonation method to treat bauxite

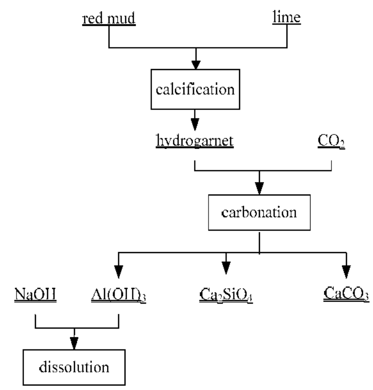

Figure 3. Process chart of calcification-carbonation method to treat red mud

alkali in the low-grade bauxite or red mud. And also it can realize the comprehensive utilization of in production process. Figure 2 and Figure 3 show the process chart.

Calcification and carbonation process are the key processes in the "Calcification-Carbonation Method". The goal of the calcification process is achieving calcification transformation for the containing silicon phase in the low-grade bauxite or red mud completely. It can provide precondition in further carbonation transformation of the digestion slag. Calcification transformation process is not in pursuit of the extracting rate of alumina. For bauxite and red mud, calcification transformation reaction is as follows:

$$Al_2O_3\cdot 2SiO_2\cdot 2H_2O+CaO+Al(OH)_3\rightarrow 3CaO\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O+H_2O \quad (1)$$

$$Na_2O\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O+3CaO\rightarrow 3CaO\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O+Na_2O \quad (2)$$

But for the carbonation process, the calcified transformation slag will decompose into aluminum hydroxide, calcium carbonate, and calcium silicate with CO_2 as the main material in the lime baking furnace or others. The reaction is as follows:

$$3CaO\cdot Al_2O_3\cdot xSiO_2\cdot(6-2x)H_2O+(3-2x)CO_2\rightarrow xCa_2SiO_4+(3-2x)CaCO_3+2Al(OH)_3+(3-2x)H_2O \quad (3)$$

Technical features and advantages of "Calcification-Carbonation Method" are as follows: Firstly, it changes the structure of red mud. In theory, it does not contain alkali or aluminum in red mud. And the ratio of alumina-silica and sodium-silica can reach zero. Secondly, it can treat with low ratio of alumina-silica bauxite, and make the bauxite resources which can be used for the industrial production in our country improve 4~5 times. Thirdly, the technology could solve this situation of high solid waste in the alumina industry. Red mud can be directly applied to the production of cement. It reduces more than 40 million tons of red mud emissions; gets rid of high solid waste in the alumina industry completely. It realizes the resource circulation of alumina production and the cement industry. Fourthly, it can be able to eliminate the existing stacking of Bayer red mud, recycle more than 40% of alumina and more than 80% alkali in red mud. So the red mud can be used directly. It solves the stockpiling problem of the red mud completely.

Experiments

Materials

Gibbsite, diasporic and red mud used for experiments come from an alumina plant in Shandong and Henan. The chemical compositions of these materials are shown in Table 1.

Table 1 Chemical composition of bauxite and red mud (mass fraction, %)

Component		Al_2O_3	SiO_2	Fe_2O_3	TiO_2	L.O.I
Content(%)	Gibbsite	49.60	11.36	14.65	0.44	24.37
	Diasporic	54.41	16.55	7.20	2.86	25.45
	Red mud	31.57	20.68	14.37	0.84	9.04

The reagents in the experiment are as follows:

Sodium hydrate, aluminium hydroxide, calcium oxide and codium silicate (analytically pure);

Carbon dioxide (Industrial bottled, purity＞99%);

Sodium aluminate solution (circulating mother liquid from alumina plant, prepare the solution according to the need of mother liquor molecular ratio);

Distilled water (self-made in Lab).

Experimental Method

Calcification and carbonation experiments were carried out by using WHFS-1 reaction vessel. By analyzing chemical composition of Stripping solution and red mud, the content of Al_2O_3 and Na_2O in liquid, and the content of Al_2O_3、Na_2O and SiO_2 in the red mud were obtained. The effect of temperature and calcium oxide-silica ratio on alumina relative digestion rate was inspected.

The computational formula of alumina relative digestion rate is as follows.

$$\eta=\frac{(A/S)_{ore}-(A/S)_{mud}}{(A/S)_{ore}}\times100\% \quad (4)$$

Results and Discussion

Pure Substances Experiments

In order to avoid the impurity elements affecting the balance of the experimental phase, firstly, we use the pure substances ($NaOH$、$Al(OH)_3$、CaO、Na_2SiO_3) to synthesize hydrogarnet, and study the carbonation decomposition of hydrogarnet, and investigate effects of the main factors on the process of calcification and carbonation.

The Effect of CaO Addition on The Calcification Process. The fixed experimental leaching temperature is 240℃, holding time is 1 hour, stirring speed is 270r/min, investigate how different CaO addition affect the Na_2O-SiO_2 ratio and Al_2O_3-SiO_2 ratio in the dissolved red mud. The results are shown as Figure 4.

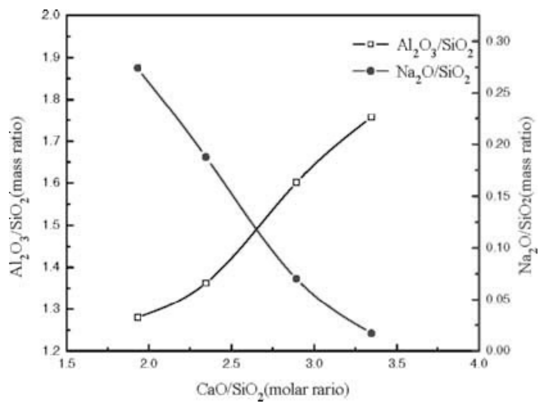

Figure 4. The effect of different lime addition on Al_2O_3-SiO_2 ratio and Na_2O-SiO_2 ratio

From the experiment results that Figure 4 shows, with the increasing of CaO addition, the Al_2O_3-SiO_2 ratio in the dissolved red mud shows a clear upward trend, otherwise, the Na_2O-SiO_2 ratio shows a downward trend. This is because when adding a small amount of CaO, the main phase in the produced red mud is sodium aluminosilicate hydrate, which lead to the increasing of the Na_2O-SiO_2 ratio, with the increasing of CaO, the main phase becomes into calcium aluminum-silicon hydrated (hydrogarnet), the Al_2O_3-SiO_2 ratio of hydrogarnet is higher than sodium aluminosilicate hydrate, resulting in the increasing in Al_2O_3-SiO_2 ratio of the red mud .

<u>The Effect of Different Temperature on The Carbonation Process</u> The fixed ventilation pressure is 0.4MPa, liquid-solid ratio is 10:1 , reaction time is 1 hour, stirring speed is 200r/min, the results are shown in Figure 5.

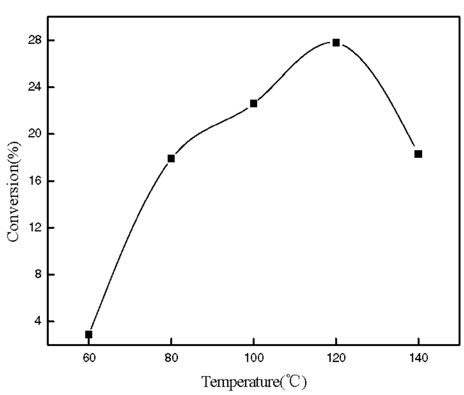

Figure 5. The effect of different temperature on the carbonation conversion rate

From the results that Figure 5 show, it indicate that with the increase of temperature the carbonation conversion rate is increased and then decreased, when the temperature is 120 ℃ the conversion rate reaches to the maximum. This is because of at higher temperatures, the decomposition rate of hydrogarnet is faster, the time that the reaction reached the end is shorter; when the temperature rise from 120 ℃ to 140 ℃, the saturated vapor pressure of the water increases from 198.48 kPa to 361.19 kPa, which increases nearly doubled, and therefore the effective concentration of the carbon dioxide gas is inevitably reduced , which is adverse to the conversion of the reaction .

<u>The Effect of Different Pressure on The Carbonation Process</u>

The fixed temperature is 120℃, liquid-solid ratio is 10:1, reaction time is 1 hour, stirring speed is 200r/min, examining how different pressure affect carbonation decomposition process, the results are shown in Figure 6.

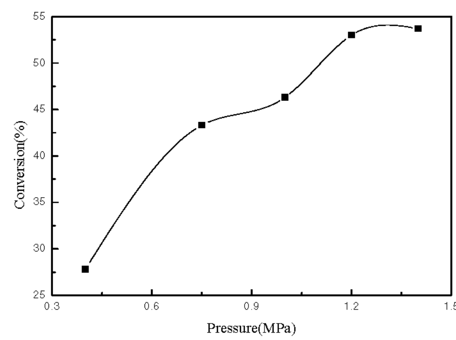

Figure 6. The effect of different pressure on the carbonation conversion rate

From the results that Figure 6 show, as the partial pressure of carbon dioxide in the decomposition process increases from 0.4MPa to 1.2MPa, the carbonation rate of hydrogarnet raises from 27.8% to 53.0% , But with the further increased of the carbon dioxide partial pressure , the rate of carbonation of hydrogarnet has little change, only increases from 53.0% to 53.7%, which tends to be stable. Experimental results show that 1.2MPa is the appropriate condition for carbonation decomposition reaction.

<u>Processing Bauxite and Red Mud Experiment</u>

With low-grade bauxite and red mud as raw material, under the pure substances optimum conditions, investigated how the primary and secondary carbonation affect the calcification transformation slag carbonation effect respectively. Comprehensive considering, there is a certain amount of attached alkali in the red mud , which can also lead to a certain concentration of sodium hydroxide in the liquid phase of carbonation system. Therefore, this section also examines the carbonation effect after the calcification transition of the red mud, with the concentration of NaOH of 5g/L and 10g/L in the carbonized liquid phase, and the experimental results are listed in Table 2.

Table 2 The sodium alkali content and Al_2O_3-SiO_2 ratio in the red mud treatment by different carbonation conditions

Materials	Carbonation times	Carbonation conditions					Results			
		P(MPa)	T(℃)	L/S	t(h)	$C_{NaOH}(g\cdot L^{-1})$	Al_2O_3 (wt.%)	SiO_2 (wt.%)	Na_2O (wt.%)	A/S
Diasporic	1	1.2	120	10:1	2	—	11.09	11.02	—	1.01
	2	1.2	120	10:1	2	—	4.41	10.02	0.12	0.44
Gibbsite	1	1.2	120	10:1	2	—	11.27	10.16	0.67	1.11
	2	1.2	120	10:1	2	—	8.49	10.32	0.57	0.82
Red mud	1	1.2	120	10:1	2	—	8.79	11.08	0.35	0.79
	2	1.2	120	10:1	2	—	5.04	11.66	0.44	0.43
	1	1.2	120	10:1	2	5	10.61	10.15	0.11	1.05
	1	1.2	120	10:1	2	10	6.44	11.67	0.89	0.55

Note: P is pressure; T is temperature; L/S is liquid-solid ratio; t is time; C_{NaOH} is concentration of NaOH; A/S is alumina-silica ratio.

The experimental results in Table 2 show that the “Calcification–Carbonation Method” to treat both low grade bauxite and Bayer process red mud has a good effects, after the secondary carbonation, the Al_2O_3-SiO_2 ratio in diasporic, gibbsite and red mud dropped to 0.44,0.82 and 0.43 respectively , sodium oxide content can be reduced to 0.12% 0.57% and 0.44% respectively . The adding sodium hydroxide experimental results also show that when a certain concentration of sodium hydroxide containing in the solution, the silicon phase in red mud also changes, when sodium hydroxide concentration is 10g/L, the A/S in the tailings through primary carbonation reaches 0.55, which is better than no sodium hydroxide carbonation process, analyzing the reasons that the presence of sodium hydroxide improve system 's ability to absorb CO_2 carbonation transformation process, thereby promoting the carbonation process. But the presence of sodium alkali make the final tailings sodium content also increased , so the sodium hydroxide should be controlled at a certain concentration range in this system .

Using this method to process either low grade bauxite or the Bayer process red mud, the Al_2O_3-SiO_2 ratio in the tailings can be reduced to 1, which break the binding mode of alumina and silica in red mud and reduce the effect of silicon in Bayer process production process. The experimental results show that when using the technique to process the diasporic with the alumina-silica ratio of 3.29, the recovery of alumina in minerals reaches to more than 85%, and the red mud alkali content is below to 0.5%, it can fully meet the requirements of the cement industry, low grade bauxite which account for more than 70% of the total reserves of bauxite in China can achieve high efficiency and clean production of alumina.

Conclusion

(1) The Synthetic experiment of pure substance indicates: with the addition of CaO increasing, the balanced phase in the red mud transformed into the hydrogarnet from sodium aluminosilicate hydrate. However, the alumina-silica ratio increases, the sodium-silica ratio reduce. The produced hydrogarnet was decomposed by carbon dioxide at 120℃, under partial pressure of carbon dioxide of 1.2 MPa. The extraction efficiency of alumina could reach 63.6%, the alumina-silica ratio of the final product was reduced to 0.54.

(2) The diasporic, gibbsite and red mud treated by the “Calcification-Carbonation Method”. The results show that, under the condition: calcification temperature is 240 ℃ (diasporic),180 ℃ (for gibbsite and red mud), calcium

oxide-silica ratio is 3:0.64(molar ratio); carbonation temperature is 120℃,pressure is 1.2MPa, the A/S of the final red mud is reduced to 0.44, 0.82 and 0.43 respectively. At the same time, the content of sodium oxide in the final red mud is reduced to 0.12%, 0.57% and 0.44%. The Calcification-Carbonation method for trading the low grade Bauxite was feasible.

Acknowledgements

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