Methods to Reduce Carbonate Content during Alumina Producing Process

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Abstract

Reaction of carbon-bearing raw materials during digestion process is the main source of carbonate in alumina production. High carbonate content in the liquor brings serious problems like negative effects on the production, deterioration of process efficiencies, resulting in alumina production cuts and rising costs. At present, carbonate removal mainly depends on the high concentration evaporation crystallization salt removal method, while red mud washing liquid causticizing and barium salt causticizing methods are also being investigated. To reduce the carbonate during alumina production process, in addition to strictly control the raw materials with high carbon content, we should also conduct laboratory research on different bauxite, understanding the anti-causticisation behavior of the ore in the process of digestion, and study the most appropriate way of evaporation crystallization precipitation and discharge, to provide theoretical support for production practice; tracking and establishing data analysis database to find out the influence law of carbonate index. Based on the laboratory results, "high temperature and low calcium" digestion process is proposed, except for adding tablet alkali and liquid alkali to assist evaporation-assisted salt removal.

Keywords: Carbonate, Carbonate Removal, Anti-causticisation, High-temperature, Low Calcium, Vaporation-Assisted Salt Removal.

1. Sources of Carbonate during Alumina Producing Process

The main sources of carbonate during alumina producing process including the anti-causticization reaction of calcium carbonate, magnesium carbonate, and magnesite containing in bauxite and lime during digestion process, that reaction between carbon dioxide in the air and liquor, in addition companies involved in sintering or chemical alumina processes may also transfer carbon-based alkaline solutions into bayer process systems.

CaO mass content in Henan bauxite is 0.6-1%, while that of MgO in Jinbei and Guizhou is about 0.5%. CaO and MgO are likely to exist in the form of limestone, magnesite and dolomite, which can react with caustic during high-temperature digestion process, resulting in caustic loss and carbonate content increasing, which is the cause of Nc/NT is higher than 10% in Huajin Aluminum using Henan bauxite, Shanxi Northern bauxite and Guizhou bauxite.

Bauxite in Shanxi Xiaoyi also contains a certain CaO, such as Chinalco Shanxi new material bauxite contains 0.9-1.3%, Xing 'an Chemical bauxite also contains 0.5-1.0%, but the total carbon ratio of these two enterprises is less than 6%, of which the form of CaO in bauxite is not limestone, but calcium salt in other minerals.

Another source of carbon alkali is the poor quality of lime as a leaching additive, which contains much unreacted limestone. Unreacted limestone content is directly related to the quality, the chemical composition, particle size, calcination conditions of limestone, which will conduct anti-causticization reaction during digestion process.

1.1 Effects of Carbonates on the Bayer Process

In the Bayer process, Nc/Nt generally has a critical point, lower than which will not have a great impact on the production system, while higher than the point, generally will have a great impact on the production system. Detailed information are shown in Figure 1.

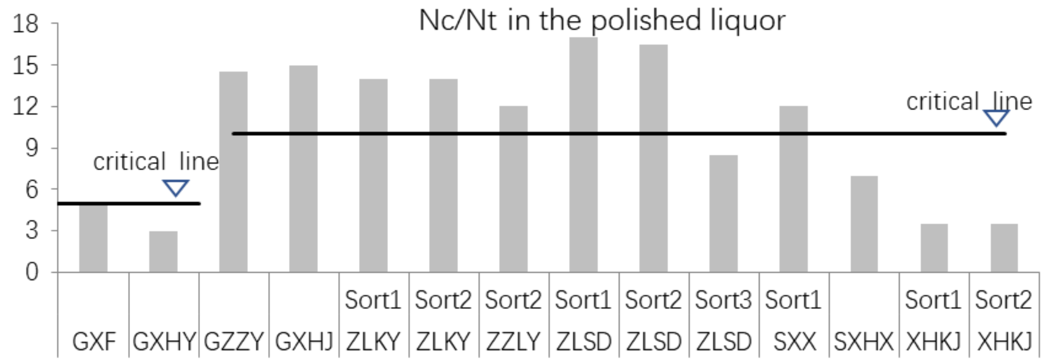

Figure 1. Nc/NT index in the polished liquor from some alumina production enterprises.

The critical point of polished liquor changes with the Bayer systems, for instance, based on the Figure 1, it can be seen that the critical point of two alumina enterprises in the south is about 5.5 %, while the critical point of other alumina enterprises is about 10 %.

The increase of carbonate in alumina production will cause steam with alkali during evaporation process, making production difficult. The influences of carbonate rise on Bayer process are as follows [1]:

1. Increasing material stream traffic, affecting the increase of power consumption. Making the fluidity of materials poor, separation and filtration difficult, decomposition increasing, and the performance deteriorated.
2. Reduced cycle efficiency.
3. Making the preheater and evaporator scarred, which affects the heat transfer efficiency, increases the steam consumption and reduces the dissolution rate.
4. Influencing the granularity and grading efficiency of AH products.

2. Methods to Carbonate Removal

There are three common ways to remove carbonate from the production system, including high concentration evaporation crystallization, red mud washing liquid causticization, and barium salt coprecipitation methods.

2.1 High Concentration Evaporation Crystallization Method

High concentration evaporation crystallization method is to evaporate the seed mother liquor to high concentration through the evaporator, so that the sodium carbonate reaches the supersaturation state of crystallization precipitation, which is discharged in the form of filter cake through sedimentation filtration, followed by dilution with water, lime causticization, Na_2CO_3 is converted into NaOH and returned to the production process.

Guili Yang, et al studied the precipitation mechanism of natrium salt during the evaporation process of Bayer spent liquor [2], which demonstrates that the equilibrium concentration of Na_2CO_3 decreased with the increase of caustic concentration, while increased with the decrease of solution αk and elevated temperature. Low temperature, high concentration and high caustic ratio are favorable for the crystallization of Na_2CO_3.

Lili Song conducted an experimental study on causticization of salt discharge with evaporation [3], which pointed out that Al_2O_3 content in the solution should be reduced as much as possible in the process of causticizing, otherwise the causticizing efficiency would be reduced, resulting in Al_2O_3 loss. The caustic efficiency decreased with the increase of Na_2CO_3 concentration in caustic solution, while increased with prolonging causticizing time. Too much lime will increase Al_2O_3 loss, too little will reduce caustic efficiency. Zhenwen Gao et al. [4] proposed that the salt removal efficiency can be improved by adding appropriate carbonate crystal seeds and high concentration of caustic soda in the process of forced circulation or flash evaporation, and most of the discharged salt is anhydrous Na_2CO_3 with good sedimentation and filtration performance. Yamei Xu [5] pointed out that adding liquid and solid alkali in some outlet of III flash evaporation could raise levels of Nk and make salting out, which needs low operation cost and investment compared with the salt removal by forced evaporation. Haijun Wang et al. [6] proposed a Method for carbonate elimination in alumina Production by adding the liquid alkali needed to be supplemented in the Bayer process directly to the salt discharge sedimentation tank. Hongfei Wu et al [7] studied the effect and mechanism of Na_2SO_4 seed and H_2O_2 addition on enhanced salt discharge of evaporation of high-sulfur seeded precipitation spent liquor, which showed that salts discharging can be promoted by adding Na_2SO_4 and H_2O_2.

2.2 Red Mud Washing Liquor Causticization

The caustic method of red mud washing liquor is to select the appropriate red mud washing liquor for caustic with lime caustic method, removing Na_2CO_3 from the washing solution though lime causticization, and the filtrate after caustic is returned to the washing system for recycling, to achieve the purpose of adding caustic soda.

Jianhui Liu [8] studied the optimistic parameters of red mud causticization and its application in Jajarm Alumina Plant, Iran., which demonstrated that the main factors affecting caustic rate were Na_2O_k concentration, Na_2O_C concentration and lime addition, and the order of influence was Na_2O_T concentration > Na_2O_C concentration > lime addition >Na_2O_k concentration, besides the caustic efficiency increased with elevated temperature.

Yingzi Guo et al proposed a side caustic method [9], in which the side caustic raw liquid is the second or third washing liquid of red mud separation washing process, and the caustic temperature and addition amount of lime milk [Ca]/[Nc] (mole) are 95 ~ 98 ℃ and 1.2. This method is suitable for bayer process alumina plant with bauxite as raw material and can replace evaporation and salt removal process in the initial stage of plant construction.

The causticizing process of red mud washing liquor is simple, but the efficiency is low. The effect of reducing the content of sodium carbonate in the production process solution is slow, and the alumina loss rate is high while the causticizing rate is pursued.

2.3 Barium Salt Causticization

Huajun Yuan et al. [10] conducted a systematic study on BaO adding mechanism, adding part, adding amount and process conditions in the Bayer process, and pointed out that the selection of mother liquor for BaO adding part is more appropriate and has practical application value.

In Salinde Plant in France, barium salt causticization is very effective, and the Na_2CO_3 content of circulating mother liquor can be effectively controlled in a low range. As a result, the evaporator capacity is improved, and the alumina production capacity is increased from 250 000 t/a to 280 000 ~ 300 000 t/a [11]. Greece's St. Nicholas factory introduced the barium salt causticizing technology, which could effectively control the sodium carbonate content in the solution below 6 %, and make the factory production capacity increased by nearly 10 %.

Though barium salt causticizing method to remove sodium carbonate in sodium aluminate solution is better, the high price of $Ba(OH)_2$ and BaO, the use cost of barium salt causticizing is higher, such as calcination of barite or the regeneration of $BaCO_3$ and $BaSO_4$ produced by caustic caustic recycling, not only the construction investment and production cost are higher. In addition, gases and dust harmful to human health are produced in the process of calcination, which pollutes the environment and limits the further application of this method.

In a word, the existing sodium carbonate removal technology can remove sodium carbonate from alumina production process to a certain extent, but there are a series of problems such as complicated process, low efficiency and high cost, which cannot meet the requirements of salt removal under the current complex production system.

3. Technologies to Remove Carbonate from Bayer Process

At present, most alumina enterprises use high concentration evaporation crystallization method to remove carbonate. Chalco Shandong Co., Ltd. has tried to causticize red mud washing liquor for a period of time, but the technical indicators and economic benefits are not ideal.

3.1 Laboratory Test

The laboratory studies on the equilibrium concentration of carbon and alkali, anti-causticization during digestion process, and precipitation of carbon and alkali were conducted according to different sources of ore and components of circulating mother liquor.

Liquor obtained from the evaporation process (main components are shown in Table 1), which was first evaporated to the required concentration of Nk240, 260, 280, 300 and 320 g/L, and then stirred at 95 °C for 4 h, followed by being settled for 1 h. Table 2 shows the analysis results of different concentrations after the reaction, and Table 3 shows the phase composition of the precipitated solid phase.

Table 1. Composition of evaporation raw liquor.

N_T	A	N_K	SiO_2	S_T	Nc/N_T	A/S	α_K
198.02	100.6	170	0.84	1.36	14.15	120	2.78

Table 2. Results for different concentration.

N_T	A	N_K	S_T	Nc	Nc/N_T	A/S	α_K
282.53	148.1	247	1.94	35.53	12.58	84.1	2.74
302.61	159.5	265	1.76	37.61	12.43	81.8	2.73
308.99	167.1	284	1.92	24.99	8.09	71.4	2.80
329.12	181.7	309	1.94	20.12	6.11	81.8	2.80
344.10	191.6	324	2.00	20.10	5.84	74.3	2.78

From Table 1 and Table 2, it can be seen that with the increase of Nk concentration, the equilibrium concentration of sodium carbonate decreased and the Nc/NT decreased. When Nk concentration was greater than 280 g/L, the total carbon ratio decreased slowly with the increase of Nk, and the total carbon ratio changed little when it reached 300 g/L. At 95 °C, when Nk is 265 g/L, 284 g/L, 309 g/L and 324 g/L, the carbon total ratio at equilibrium is 12.43 %, 8.09 %, 6.11 % and 5.84 %, respectively.

Table 3. Results for solid analysis.

N_K(g/L)	Na_2O	Al_2O_3	SiO_2
265	51.6	5.886	0.338
284	53.52	6.906	0.079
309	51.68	7.197	0.087
324	47.69	10.39	0.4275

Anti-causticizztion experiments during digestion process: taking raw materials such as bauxite and lime from one alumina enterprise, laboratory digestion tests were conducted to study the influence of raw materials including calcium, pre-desilication and digestion conditions on the carbonate in red mud. Composition of the bauxite and liquor are shown in Table 4 and Table 5, lime composition: available calcium 89 %, total calcium 92.56 %, total carbon 0.64 %.

Table 4. Bauxite composition (wt%).

Al_2O_3	SiO_2	FeO	K_2O	CaO	MgO	TC	TOC	S
62.39	12.4	5.61	1.13	0.53	0.16	0.36	0.23	0.096

Table 5. Liquor composition(g/L).

Nt	A	Nk	SiO_2	αk	Nc/Nt
275	135	228	1.08	2.77	0.17

From Table 6, it can be seen that elevated temperature is conducive to reducing carbonate in the polished liquor. While with lime addition amount increasing, the carbonate content in the solution increases first and then becomes slow, where there is an appropriate addition amount.

Table 6. Effects of temperature, lime dosage on the Nc/Nt of polished liquor.

Lime dosage，%	Temperature，℃	Nc/N_T，%
6	265	14.8
7	265	16.9
8	265	16
9	265	16.5
6	272	14.8
7	272	15.6
8	272	15.7
9	272	15.6

From Table 7, it can be seen that elevated temperature is conducive to sulfur entering into red mud, while lime dosage has reversed effect.

Table 7. Effects of temperature, lime dosage on the ST in red mud.

Lime dosage，%	Temperature，℃	S_T，%
6	265	0.42
7	265	0.39
8	265	0.25
9	265	0.24
6	272	0.43
7	272	0.41
8	272	0.37
9	272	0.34

Results from digestion anti-causticization demonstrated that properly increasing the digestion temperature and decreasing lime dosage can make the carbonate and S impurities not enter into the liquor but into the red mud, realizing carbonate removal. In a word, the "high temperature and low calcium" digestion process is effective for most digestion anti-causticization.

3.2 Reducing Carbonate During Bayer Process

a. Establish the daily balance analysis statistics of carbonate

Making the daily balance chart of carbonate for statistical analysis of the production data involved, to guide the whole process of reducing carbonate.

b. Control raw materials

The content of calcium oxide or inorganic carbon in the grinding ore is required to be less than 0.50 % or less than 0.20 %. The content of effective calcium oxide in lime was >80% and the decomposition rate of lime was > 90 %. The carbonate in liquor was less than 0.4%, and the carbonate in solid caustic soda was less than 0.8 %.
For bauxites with high sulfur and carbon, the principle of sulfur control first and carbon control later should be followed, and bauxite blending should be reasonable and careful, and both of them should not enter the production system at the same time.

c. Control digestion

For diaspore type ore, "low calcium and elevated temperature" helps red mud to maximize the removal of sulfur, carbon and other impurities, which is also conductive to improve the dissolution rate, decomposition rate and settlement performance of red mud.

d. Solution concentration for salt disposal

Different Nc/Nt corresponding to the appropriate salt disposal concentration (Figure 2).

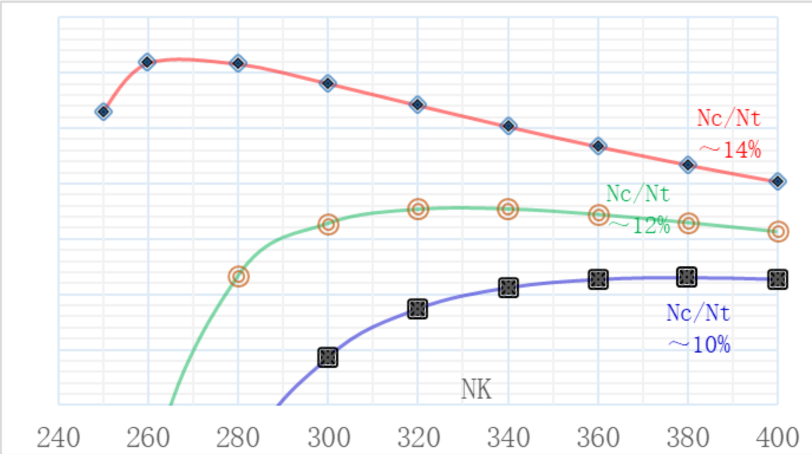

Figure 2: Effects of Nc/Nt on the appropriate salt disposal concentration

According to the production system Nc/Nt situation, determining the appropriate salt solution concentration, too high or too low are not appropriate.

e. Solid and liquid alkali assisted evaporation

It is necessary to add solid and liquid alkali continuously and evenly to stabilize the concentration of solution. Under the condition of constant solution concentration, the lower the concentration of alkaloid, the lower the amount of carbon alkaloid precipitated. With the same salt discharge concentration, the order of salt amount precipitated from low to high with different incoming chemical caustic soda is: flat plate washing liquor < using evaporative stock liquor< using flash discharge material < using liquid alkali < using solid caustic soda.

f. Causticizing efficiency

Caustic index: Nk of caustic stock is 30 g/ L ~ 50 g/ L, Nc/Nt of caustic stock is 0.5 ~ 0.7, Nc/Nt of caustic liquor is about 0.06 ~ 0.08. Causticizing time and temperature: duration time 2-4 hours, temperature of greater than 85 °C. Caustic liquid whereabouts: caustic slurry settlement separation, overflow back to the evaporation liquid, bottom flow sent settlement two washing tank.

4. Conclusions

Through strengthening raw material control, increasing red mud take away, strengthening salt removal using evaporation. In order to reduce the carbonate in alumina production system, controlling the carbonate entering, while increasing the carbonate discharge and causticizing efficiency. The solution of "high temperature and low calcium" is beneficial to maximize the removal of carbonate together with red mud, determining the optimal concentration range of carbonate fishing, strict technical conditions of carbonate causticizing, and improving the causticizing efficiency are conductive to deal with carbonate problem during Bayer process.

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