Main Factors Affecting the Stability of Liquor Causticization Indexes in Aluminium Production

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Abstract

As the core process for alumina production, the Bayer process accounts for over 90 % of global alumina output. Its fundamental principle involves dissolving Al_2O_3 in bauxite using a so-called Bayer liquor (a NaOH solution, weak in sodium aluminate), possibly under high temperature and pressure conditions to form sodium aluminate solution. Subsequent dilution, cooling, and seeded precipitation processes yield $Al(OH)_3$, which is subsequently calcined into alumina (Al_2O_3). However, the accumulation of Na_2CO_3 in circulating process liquor reduces the caustic ratio (molar ratio of NaOH to (NaOH + Na_2CO_3) in solution), directly impacting bauxite digestion efficiency and the system caustic soda balance. To reduce caustic soda consumption and enhance alumina production efficiency, industrial trials of liquor causticisation were conducted to convert sodium carbonate into usable caustic for process make up. Notable fluctuations in key technical indicators of causticized liquor during these trials disrupted alumina production stability. To prevent such instability in large-scale operations, this study integrates theoretical foundations of liquor causticisation with industrial trial data to analyse critical factors influencing indicator stability. The research aims to optimize control strategies for carbonated spent liquor causticisation indicators and maximize operational efficiency.

Keywords: Bayer process, Alumina production, Liquor causticisation, Caustic ratio, Indicator stability

1. Introduction

The Bayer method is the core process of alumina production, and over 90 % of the alumina worldwide is produced by this method. The core principle is to dissolve the aluminous compounds in bauxite with Bayer liquor (a NaOH solution weak in sodium aluminate) possibly at high temperature and high pressure to generate sodium aluminate solution and then precipitate $Al(OH)_3$ through dilution, cooling and seeded decomposition, and finally calcined into alumina. However, in the circulating spent liquor, the accumulation of Na_2CO_3 leads to a decreased caustic ratio (molar ratio of NaOH to (NaOH + Na_2CO_3) in solution), which directly affects the dissolution efficiency and system caustic balance. In order to reduce the system caustic consumption and improve the alumina production yield, the industrial test of spent liquor was started to convert sodium carbonate into caustic. However, in the industrial test of spent liquor, the main technical indices of caustic liquor fluctuate greatly after extraction, which has an influence on the production of alumina. In order to avoid the fluctuation of the caustic technical indicators in future large-scale production, the main factors of the caustic index of spent liquor were analysed, so as to better control the caustic index of carbonated liquor, to maximize the efficiency of carbonated liquor.

2. The Theory of Process Liquor Causticization

Causticisation of spent liquor is the process of mixing the spent liquor with a certain amount of lime slurry to complete the causticisation reaction under certain conditions, so that the sodium carbonate in the spent liquor is converted into caustic which is favourable for the production of alumina. The advantage of the process is that the caustic is added into the Bayer process, to improve the critical ratio of the circulating spent liquor of the Bayer process to a certain extent and then increase the dissolution rate of soluble alumina and promote the production by the Bayer process. At the same time, the caustic production can consume a certain amount of carbonate liquid, which is conducive to do more carbonate content, alleviate the burden of carbonate evaporator, reduces carbonate evaporation steam consumption, and reduces the total amount of sintering mixing red mud, which is more conducive to the production capacity of sintering method.

2.1 Chemical Reaction Mechanism of Caustic Reaction

The causticisation is the reaction of the hydrated lime with the carbonate ions as per Bi Shiwen 1:

$$\mathrm{Ca(OH)_2(s) + CO_3^{2-} \rightarrow CaCO_3(s) + 2OH^-} \tag{1}$$

Equilibrium constant of this chemical reaction:

$$\mathrm{K} = \frac{2[\mathrm{OH^-}]}{\mathrm{CO_3^{2-}}} = \frac{\mathrm{K_{Ca(OH)_2}}}{\mathrm{K_{CaCO_3}}} \tag{2}$$

In the caustic formula, $K_{Ca(OH)_2}$ and K_{CaCO_3} are the dissolution product constants of $Ca(OH)_2$ and $CaCO_3$ in water, respectively. They are 4×10^{-6} and 4×10^{-8}, respectively, namely, the equilibrium constant is about 100, which means that the equilibrium conversion rate will eventually reach about 90 %.

2.2 The Equation for Causticisation of Spent Liquor

Spent liquor causticisation is the process of converting the carbonate in the spent liquor into an effective base – i.e. caustic that is favourable for production of alumina. According to the analysis of various components in the spent liquor, the main reaction is the reaction of carbonate and lime in the spent liquor, so the chemical equation is:

$$\mathrm{Na_2O_c + CaO_f \rightarrow CaO_c + Na_2O_K} \tag{3}$$

(Na_2O_k — caustic soda as Na_2O equivalent; Na_2O_C — Na_2CO_3 as Na_2O equivalent; CaO_C — calcium carbonate as CaO equivalent)

Therefore, the ingredient formula of spent liquor is:

$$\mathrm{v_1} = \frac{56 \times \mathrm{N_c}}{62 \times CaO_\mathrm{f}} \times \mathrm{V_2} \times 90\ \% \tag{4}$$

where:

V_1 lime slurry volume

V_2 carbonate containing liquid volume

Nc carbonate concentration in carbonate containing solution

CaO_f lime slurry effective calcium oxide concentration

56 sodium oxide (Na_2O) molecular weight, g/mol

62 lime (CaO) molecular weight, g/mol

2.3 The Equation for Causticisation of Spent Liquor

At the same time, because the spent liquor contains a small amount of alumina, the reaction of dissolved alumina and lime will eventually produce calcium aluminate. Considering comprehensively, according to the phenomenon of generating $3CaO \cdot Al_2O_3 \cdot 6H_2O$ from the reaction of lime and dissolved alumina, the amount of lime reaction with alumina should be added to the caustic mixing equation, so the final mixing equation is

$$v_1 = K \times \frac{56 \times N_c}{62 \times C_aO_f} \times V_2 \times 90\ \% \tag{5}$$

K is the caustic ingredient coefficient, generally 1.1 is taken according to experience, mainly based on the dissolved alumina content in the carbonate causticisation liquid.

3. Main Technical Indicators of Master Liquor Caustic Dressing

3.1 Causticization Efficiency η

According to the main concept of causticisation, the main technical index of causticisation is the causticisation efficiency, which represents the degree and depth of causticisation reaction and is the main data to measure whether the causticisation reaction is completed. Theoretical calculation of the caustic reaction rate of the spent liquor.

Let the carbonate concentration before causticisation be N_C, the carbonate be NT, and the carbonate ratio be a_1;
After the reaction, the carbonate concentration be N_C', the carbonate be NT', and the carbonate ratio be a_2;

The amount of carbonate causticisation liquid is v_1 and the amount of lime slurry is v_2.
The theoretical reaction assumes that the total volume is equal to the total volume of spent liquor and lime slurry (Consider the density of lime slurry at a concentration of 180 g/L CaO close to the density of the spent liquor).
At the same time, it is assumed that the caustic tank system does not bring foreign alkali in, so the calculation formula of the spent liquor caustic rate is:

$$\eta = \frac{a_1 \times NT \times v_1 - a_2 \times NT' \times (v_1 + v_2)}{a_1 \times NT \times v_1} \times 100\% \tag{6}$$

Because the total amount of alkali in the system is unchanged, $NT \cdot v_1 = NT' \cdot (v_1 + v_2)$, then the reaction efficiency is:

$$\eta = \frac{a_1 - a_2}{a_1} \times 100\ \% \tag{7}$$

3.2 Carbonate Ratio of the Caustic Liquor After Causticisiation N_C / NT

Because the carbonate to total caustic ratio (carbonate and total alkali ratio) of the caustic stock solution is limited by the spent liquor, the carbonate to total caustic ratio of the stock solution is basically stable. To simplify the analysis of the production process, from the above theoretical calculation, the main index to measure the extraction ratio is the final carbonate total caustic ratio of the caustic stock solution: N_C / NT.

3.3 Caustic Concentration in the Causticized Liquor after the Causticisation Process

Since the main function of the causticisation is to balance the carbonate in the system and produce effective caustic for alumina production in the Bayer method, another important index of causticisation is the concentration of the caustic.

3.3.1 Theoretical Calculation of Caustic Concentration in Partial Causticization

Set : $f_1 = (v_1 + v_2) / v_1$ as the dilution of spent liquor
$f_2 = (v_1 + v_2) / v_2$ is the dilution ratio of lime slurry
N_K' lime slurry caustic concentration
Therefore, the concentration of caustic soda is

$$N_k = \frac{N_k}{f_1} + \eta \frac{N_c}{f_2} + \frac{N_k'}{f_2} \tag{8}$$

where:

f_1	$(v_1 + v_2) / v_1$ is the dilution of spent liquor
f_2	$(v_1 + v_2) / v_2$ is the dilution ratio of lime slurry
N_K'	lime slurry caustic concentration
Nc	carbonate concentration before causticisation

3.3.2 Another Algorithm for the Caustic Rate

From the calculation assumption of 1.3.2, another algorithm for the causticisation efficiency can be obtained.

$$\eta = (N_C/f_1 - N_C') / N_C / f_1 = 1 - f_1 N_C'/N_C \tag{9}$$

3.4 Impact of Temperature

The causticisation temperature is one of the basic conditions to ensure the causticisation reaction. From the relevant data, the optimal causticisation reaction temperature is 90–95 °C. If the reaction temperature is too high, it will cause the heat consumption to increase. If the reaction temperature is too low, the reaction time will be prolonged, which is not conducive to the continuous and stable operation of production.

3.5 Influence of Reaction Time

The reaction time of the causticisation. According to the related test and related data of the carbonate containing liquid, the reaction time necessary for the causticisation reaction at 90–95 °C is generally from 2 hours to 2 hours and 30 minutes. Although increasing the temperature accelerates the causticisation reaction to a certain extent and it increases the heat consumption.

4. Key Factors Affecting the Stability of Causticisation Production Indicators

In previous industrial tests of spent liquor causticisation, there were often instances where the carbonate-to-total-alkali ratio and the caustic alkali concentration of the causticized liquor fluctuated significantly after the causticisation process. This had a certain impact on the alkali supplementation in the subsequent alumina production. Therefore, it is necessary to analyse the main factors affecting the stability of causticisation production indicators in order to better utilize the technological advantages.

4.1 Carbonate Concentration of the Parent Solution N_C

In case of a certain ratio of lime slurry and spent liquor, the concentration of carbonate in the caustic stock is the main factor affecting the stability of caustic concentration. At the same time, a high carbonate concentration will lead to a low reaction efficiency, at a low carbonate concentration, the reaction efficiency will be high. Therefore, the concentration of the spent liquor will affect the caustic concentration and cannot reach the ideal concentration.

4.2 Lime Slurry Quantity Compared with the Effective Calcium Concentration CaO_f

In the case of extracting efficiency and certain concentration of effective calcium CaO_f, if the amount of lime slurry is small, the actual extraction efficiency will not reach the ideal extraction efficiency, and the ideal concentration of caustic soda will be affected.

At the same time if the amount of lime slurry added is too big, because of the ultimate end is 90 %, therefore adding too much lime slurry increases the dilution of bulk solution, causes the surface caustic rate increased, but actually caused more negative impact on production, the lime slurry dosage is too large, higher costs, at the same time affect the settlement of caustic slag operation, settlement tank run muddy, filter cake moisture is too large, hinders the stable operation of alumina production.

At the same time, under the condition of certain caustic rate, if the concentration of effective calcium CaO_f of lime slurry is large, the dilution ratio of the spent liquor is small, and the concentration of caustic soda will be high. On the contrary, if the concentration of lime slurry is low, the dilution of carbonate increases, and the concentration of caustic soda is low.

The added amount of lime slurry and the effective calcium oxide concentration of lime slurry are factors that can be controlled to affect the caustic production index.

4.3 Lime slurry is Brought into the Caustic N_K

As can be seen from the above (8) formula, the caustic soda attached to lime slurry will eventually affect the caustic soda concentration in the caustic fluid (Lin Xiancun 2). However, in the causticisation reaction, the caustic soda does not participate in the reaction under certain conditions, and the caustic soda brought into the lime slurry only increases the total amount of the whole alkali in the system. If the reaction of the causticisation reaction begins, the amount of what in the system does not change. From the definition of caustic rate, the caustic attached to lime slurry has no effect on the final caustic rate. However, it will cause the phenomenon that the carbonate ratio of the caustic solution is low, and the carbonate in the caustic is still high, which is unfavourable to the production of alumina. At this time, it is necessary to adjust the ratio index to obtain a lower value of carbonate concentration.

In this regard, we conducted a causticisation experiment on the carbon-alkali filter cake. The solutions were prepared with NT concentrations of 100, 80, and 60 g/L after dissolving the filter cake. The lime dosage was added at 1.0, 1.25, and 1.5 times the theoretical calculated amount, respectively.

Table 1. Properties of carbonate and causticizing liquor under different lime dosages and reaction times.

NT concentration	Lime Dosage	Sample Name	NT	Al2O3	Nk	NC	aK	C/N Ratio	Causticisation Efficiency (%)
		carbonate	100.2	19.8	37	63.2	3.07	0.631	/
100 g/l	1.0×	1h	101.4	4	91.5	9.9	37.6	0.097	84.63
	1.0×	2h	98.2	2.9	89	9.2	51.386	0.093	85.27
	1.25×	1h	106.7	1.4	96.5	10.2	117.77	0.095	84.94
	1.25×	2h	106.7	1.4	97.5	9.2	118.95	0.086	86.37
	1.5×	1h	107.3	0.9	95	12.3	175.81	0.115	81.85
	1.5×	2h	104.6	1.1	94	10.6	140.57	0.101	83.92
80 g/l		carbonate	81.8	16.2	30	51.8	3.05	0.633	/
	1.0×	1h	80.9	8.1	72	8.9	14.62	0.11	82.62
	1.0×	2h	79.8	6.9	71	8.8	16.93	0.11	82.62
	1.25×	1h	83.9	3.1	76	7.9	40.33	0.094	85.15
	1.25×	2h	84.4	2.2	77	7.4	57.58	0.088	86.09
	1.5×	1h	79.4	1.6	72	7.4	74.03	0.093	85.31
	1.5×	2h	76.6	1.3	70	6.6	88.58	0.086	86.41
60 g/l		carbonate	61.6	12.6	21	40.6	2.74	0.631	/
	1.0×	1h	59.8	7	53	6.8	12.46	0.114	82.7
	1.0×	2h	58.4	5	52	6.4	17.11	0.11	83.31
	1.25×	1h	63	2.3	57	6	40.77	0.095	85.58
	1.25×	2h	62.6	1.3	57	5.6	72.13	0.089	86.49
	1.5×	1h	59	0.7	54	5	126.9	0.085	87.1
	1.5×	2h	57.1	0.5	52	5.1	171.08	0.089	86.49

In this regard, we conducted causticisation experiments on carbonate filter cakes. The solutions were prepared with NT concentrations of 100 g/L, 80 g/L, and 60 g/L after dissolving the filter cakes. The lime dosage was calculated based on theoretical values. The actual carbon alkali causticization experiments revealed the following:

a. When the lime dosage was added at 1, 1.25, and 1.5 times of the theoretical value, the causticisation efficiency essentially reached its maximum at 1.25 times of the theoretical lime dosage. Further increasing the lime dosage did not significantly enhance the causticisation efficiency.

b. The effective calcium in lime is crucial for causticisation. At a given dosage, a higher content of effective calcium results in better causticisation performance.

c. With the same lime dosage, the causticisation efficiency after 2 hours was higher than that after 1 hour. However, the rate of increase in causticisation efficiency exhibited a declining trend over time.

5. The Way to Stabilize and Improve the Caustic Index

5.1 Improving the Accuracy of the Caustic Ingredients

From the extraction theory, we can see that the correct degree of causticisation is the premise of stabilizing and improving the caustic production index. It is important to establish accurately the correct lime slurry addition level. Both more or less lime slurry will affect the production level. Therefore, in the caustic ingredients, improving the accuracy of the addition levels will result in greater stability and improve the caustic production technical indicators.

5.2 Improve the Critical Rate

Under the case of the correct caustic compound ratio, it is an important condition to ensure the stability of the caustic index and improve the caustic production technical index. However, according to the relevant extraction theory, the end point of extraction is 90 %, so the final extraction efficiency is controlled at 90 %, that is, the total alkali ratio of extraction liquid is controlled at about 10 %, which is an important guarantee for the maximum extraction efficiency.

5.3 Raise the Lime Slurry Level into the Caustic Alkali (N_K) within a Certain Range

According to the previous calculation, increasing the caustic concentration of the caustic ingredient lime slurry within a certain range can increase the caustic soda concentration of the caustic liquid within a certain range. According to the industrial test of spent liquor, when the concentration of caustic soda in lime slurry is 30–40 g/L, the concentration of caustic soda can be increased by about 15 g/L which will not greatly impact the causticisation.

5.4 Improve the effective calcium — CaO_f content of caustic slurry slurry

In the causticisation reaction, stabilizing the concentration of lime slurry is the first condition for the stability of the temperature and time of the causticisation reaction. At the same time, the concentration of effective calcium CaO_f of added lime slurry can reduce the dilution ratio of the spent liquor and increase the concentration of caustic soda to a certain extent, which is beneficial to the production of alumina. After the test, the effective calcium oxide concentration of lime slurry increased by 10 g/L, which can increase the concentration of caustic soda by about 5 g/L.

6. Conclusion

In order to reduce caustic soda consumption and enhance alumina production, industrial trials of liquor causticisation were conducted to convert sodium carbonate into usable caustic. The application of the aforementioned theoretical analysis in these trials demonstrated that: post-causticisation, the causticisation liquor consistently maintains a carbonate-to-total alkali ratio around 10 %, with a caustic alkali concentration typically above 90 g/L. Currently, the key production technical indicators of liquor causticisation remain stable, yielding significant economic benefits.

7. References

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