

A NEW METHOD FOR REMOVAL OF ORGANICS IN THE BAYER PROCESS

Bai Yingwei¹, Shen Mingliang¹, Li Junqi², Zhao Fei²

1. Guiyang Aluminum Magnesium Design & Research Institute, Guiyang, Guizhou, 550081;
2. Materials Science and Metallurgy school, Guizhou University, Guiyang, Guizhou, 550003

Keywords: Bayer process, Organics, Super-concentration, Carbonate, causticization

Abstract

This article introduces briefly the main organics sources in Bayer process alumina production and the harm due to accumulation during process flows, specifies the organics removal methods applied generally in world alumina refineries, and explains briefly advantages & disadvantages of each method. The article stresses the super-concentrated organics removal method developed successfully by GAMI with Guizhou University together, which not only has good organics removal effects (total removal percent of 57~66%), but also effectively removes the carbonates in the process flow.

1. Introduction

The organics in the Bayer liquor arise mainly from the bauxite. A few of the organics are also brought in from the flocculants, defoaming agents and dewatering agents, but with lesser amounts and smaller effects, according to the literature reports. The organic carbon content in the bauxite is generally 0.1-0.3%, but also can be lower to 0.03% or higher to 0.6% (some surface mines). The organic carbon content in tropical bauxite is higher, generally 0.2-0.4%; however, that in diasporic bauxite is lower, generally 0.1%. The organics content in the bauxite in Poncho, Africa and Australia is higher and that in Europe, Russia and China is lower [1].

There are three main kinds of organics in the Bayer liquor: natural matter (such as roots), humic acids and pitch [1] formed by precipitation of the organics (plants) and microorganisms with the chemical reaction. These organics undergo some changes during the alumina production flow, and finally become humic acids, benzenecarboxylic acids, oxalic acid etc. The organics content in the production process accumulates step by step along with the progress of production, and harms the Bayer alumina production process when it reaches a certain value. The main effects are as follows:

(1) It has effects on the digestion and red mud separation & washing [1]. Along with the increase of the organics content, the liquor viscosity will increase, the red mud settlement speed will be reduced and the overflow suspended matters in the settler will increase.

(2) It has effects on the crystal seed precipitation[1]. The precipitation speed and the alumina output rate shall be reduced, which results in the alumina size becoming fine and fragile, and especially fragile during calcination. This problem becomes one of the difficulties with producing sandy alumina in the alumina

refineries with the Bayer process. The impurities, especially Na_2O content in the product will be increased, and this is not good for aluminum hydrate settlement, filtration and classification, which results in generating foam in the settlers, reducing the alumina whiteness, and accelerating the aluminum hydrate scaling in the seed precipitation tanks.

(3) It also has effects on the evaporation of mother liquor. The organic impurities can make Na_2O_c concentration in the mother liquor increase (make Na_2CO_3 in the liquor supersaturated and concentration increased), the organics content is higher and this phenomenon is more obvious. The organics makes the liquor viscosity increase and the size of the precipitated monohydrate sodium carbonate fine, resulting in difficulties with settlement and filtration & separation. The production practice of Guangxi Branch Company of China Aluminum Company estimates that: the oxalate is easy to be precipitated from the evaporator and flash evaporator when the sodium oxalate concentration in the liquor is high, having the effects on the evaporation and increasing the scaling cleaning workload.

(4) The pitch organics often attach to the surface of filter cloths and heat exchangers, which has effects on the filtration and heat exchange.

Because the organics have some serious effects on the alumina production process flow mentioned above, alumina refineries in the world adopt varied methods for the removal of organics from the process flow. Two kinds of methods are applied in the actual production: one is to remove the organics from the liquor, mainly by spent liquor calcination, adsorption, deposition etc; the other is to totally or partly damage the organics in the liquor, mainly by the oxidization which is to partly or totally oxidise the organics to Na_2CO_3 . At present the main application methods are as follows^[2-6]: adsorption, oxidization, calcination, aluminum hydrate washing liquor settlement, crystallization etc.

2. Test principle and test method

2.1 Test principle

The super-concentrated causticization method this article puts forward is different from the traditional organic removal methods. The principle is as follows: according to the characteristic that the solubility of oxalate in the alkaline liquor is reduced, along with the increase of the alkali concentration in a certain alkali concentration range, the liquor required for organics removal is concentrated to a higher concentration (super-concentrated) so as to precipitate the most oxalate from the liquor by crystallization,

then the precipitated oxalate is translated into the insoluble compound by a causticization reaction so that the compound is removed from the process flow by washing and filtration. Therefore, the effect of factors on the solubility of oxalate in the liquor and the optimum conditions of causticization reaction is required to be found by testing, moreover, the authors have also studied the solution condition of the causticization slag in the liquor so that this method can be better applied to the industry production.

In the test:

N_k expresses the caustic sodium oxide concentration in the liquor (Na_2O_k) g/l

N_c expresses the carbonate sodium oxide concentration in the liquor (Na_2O_c) g/l

N_T expresses the total soda concentration in the liquor (Na_2O_T) g/l

AO expresses the alumina concentration in the liquor (Al_2O_3) g/l

$C_{organics}$ expresses the organics content in the sodium oxalate ($Na_2C_2O_4$) in the liquor

$\Delta C_{organics}$ expresses the precipitation (settlement) percent (%) of $C_{organics}$

Crystal seed coefficient of sodium oxalate

$$= \frac{\text{Added } Na_2C_2O_4}{Na_2C_2O_4 \text{ in the liquor}} \text{ (mass ratio)}$$

Crystal seed coefficient of sodium carbonate

$$= \frac{\text{Added } Na_2C_2O_4}{Na_2C_2O_4 \text{ in the liquor}} \text{ (mass ratio)}$$

The organics removal percent formula can be expressed as the followings:

$$C \% = \frac{C_0 \times V_0 - C_i \times V_i}{C_0 \times V_0} \times 100\%$$

C_0 and V_0 respectively express the concentration and the volume of organic carbon ($C_{organics}$) in the test liquor.

C_i and V_i respectively express the concentration and the volume of organic carbon ($C_{organics}$) in the concentrated liquor.

2.2 Test method

- Effect of initial organic carbon concentration on organics removal percent: initial organic carbon concentration = 2.46-8.0 g/l
- Effect of concentrated N_k on organics removal percent: concentrated N_k = 300 g/l. 320 g/l. 340 g/l. 360 g/l. 380g/l

- Effect of crystal seed addition on organics removal percent
- The optimum super-concentrated conditions of organics removal are adopted for concentration and slag making. The concentrated slag is dried and milled to be fine for 1-section causticization test, using the orthogonal method. The chemical compounds in the liquor and solid after causticization and separation, is analyzed and the organics removal percent is calculated so as to determine the optimum 1-section causticization conditions.
- The 2-section causticization treatment with different causticization conditions is done based on the 1-section causticization. The organics removal condition after 2-section causticization separation is analyzed so as to determine the optimum 2-section causticization conditions.
- The anti-solution test of the slag obtained after causticization is done so as to study the anti-solution condition of the organics in the caustic slag during the washing.

3. Test result and analysis

3.1 Effect of initial organic carbon concentration on organics removal percent

When the mother liquor (super-concentrated green liquor) ($N_k=153g/l$; $C_{organics}=2.46-8.0g/l$) is super-concentrated to about N_k 300g/l, table 1 shows that the crystal precipitation percent of sodium oxalate is directly proportional to the concentration of $C_{organics}$ in the green liquor.

Table 1 Relation of initial organics concentration and organics removal percent

BSC= Before super concentration ASC= After super concentration

No.	Item Result Conditions	N_T (g/l)	A_O (g/l)	N_k (g/l)	N_c (g/l)	$C_{organics}$ (g/l)	N_c/N_T (%)	$\Delta C_{organics}$ (%)
1	BSC	163.8	91.35	153.0	15.3	2.46	9.1	66.89
	ASC	335.4	191.38	314.0	21.4	1.81	6.4	
2	BSC	168.3	91.35	153.0	15.3	4.0	9.1	71.39
	ASC	331.2	213.35	309.0	22.2	2.51	6.7	
3	BSC	168.3	91.35	153.0	15.3	6.0	9.1	73.36
	ASC	321.2	181.84	303.0	18.2	3.6	5.7	
4	BSC	168.3	91.35	153.0	15.3	8.0	9.1	75.97
	ASC	312.6	179.27	298.0	14.6	4.31	4.7	

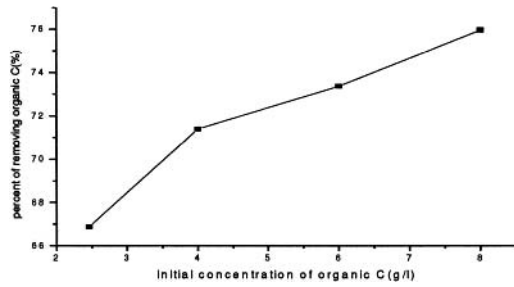


Figure 1: Relation of initial organic carbon concentration and organics removal percent

The organics removal percent has a direct relationship to the initial organic carbon content, and will increase along with the increase of the organic carbon content in the green liquor. There are main two reasons for this: one is that the more organics shall be precipitated by the crystallization after the initial organics content increases, the first precipitated organics itself can be the crystal seed for the later precipitated organics so as to promote the crystallization precipitation of the organics during the concentration and improve the organics removal percent. The other one is that the solubility of the organics in the sodium aluminate liquor has no big change under certain conditions, the organics removal percent must be increased if the initial organic carbon concentration is increased.

3.2 Effect of concentrated N_k on organics removal percent

The mother liquor (super-concentrated green liquor) ($N_k=136.8/l$; $C_{organics}=1.44g/l$) is super concentrated. The precipitation percent of sodium oxalate is increased along with the increase of the super-concentrated liquor N_k value. The precipitation percent reaches the peak value (refer to table 2 and figure 2) when the super concentrated liquor N_k value reaches about 360g/l, moreover, the solubility of the carbonate in the liquor is continuously reduced along with the increase of the concentrated liquor N_k value, the lowest value is here when the N_k is 360g/l, and then it will be little increased along with the increase of the N_k value (refer to table 2 and figure 2).

Table 2: Relation of concentrated liquor N_k and organics removal percent (1)

No.	Item Result Conditions	N_r (g/l)	A_o (g/l)	N_k (g/l)	N_c (g/l)	$C_{organics}$ (g/l)	N_c/N_r (%)	$\Delta C_{organics}$ (%)
1	BSC	160.4	82.9	136.8	23.6	1.44	14.7	70.3
	ASC	333.4	172.04	310.0	23.4	1.06	7.0	
2	BSC	160.4	82.9	136.8	23.6	1.44	14.7	75.3
	ASC	352.6	101.78	335	17.6	0.98	14.7	
3	BSC	160.4	82.9	136.8	23.6	1.44	14.7	81.3
	ASC	374.2	200.19	364.0	10.2	0.79	2.7	
4	BSC	160.4	82.9	136.8	23.6	1.44	14.7	79.2
	ASC	399.0	219.27	386.0	13.0	0.91	3.3	

BSC= Before super concentration ASC= After super concentration

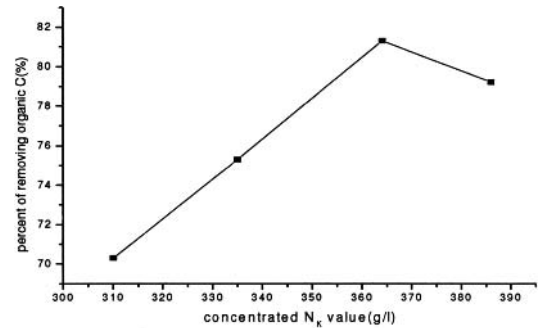


Figure 2: Relation of concentrated N_k value and organics removal percent (1)

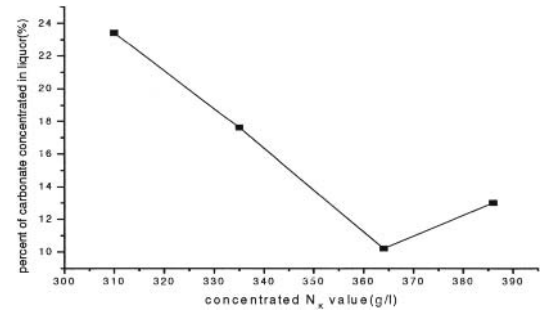


Figure 3: Relation of concentrated N_k value and solubility percent of carbonate in the liquor

The mother liquor (super-concentrated green liquor) ($N_k=153g/l$; $C_{organics}=6g/l$) is super concentrated, the study result shows that the precipitation percent of sodium oxalate is increased along with the increase of N_k value of super concentrated liquor under the condition of higher $C_{organics}$ content in the super-concentrated liquor. The precipitation percent reaches a peak value (refer to Table 3 and Figure 4) when the N_k value of super-concentrated liquor reaches about 360g/l.

Table 3: Relation of concentrated N_k value and organics removal percent (2)

No.	Item Result Conditions	N_r (g/l)	A_o (g/l)	N_k (g/l)	N_c (g/l)	$C_{organics}$ (g/l)	N_c/N_r (%)	$\Delta C_{organics}$ (%)
1	BSC	160.4	82.9	136.8	23.6	1.44	14.7	70.3
	ASC	333.4	172.04	310.0	23.4	1.06	7.0	
2	BSC	160.4	82.9	136.8	23.6	1.44	14.7	75.3
	ASC	352.6	101.78	335	17.6	0.98	14.7	
3	BSC	160.4	82.9	136.8	23.6	1.44	14.7	81.3
	ASC	374.2	200.19	364.0	10.2	0.79	2.7	
4	BSC	160.4	82.9	136.8	23.6	1.44	14.7	79.2
	ASC	399.0	219.27	386.0	13.0	0.91	3.3	

BSC= Before super concentration ASC= After super concentration

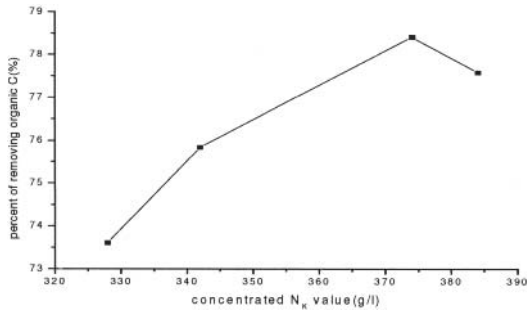


Figure 4: Relation of concentrated N_k value and organics removal percent (3)

3.3 Effect of crystal seed addition on organic carbon removal percent

The crystal seed addition test is carried out under the conditions No.3 and No.4 specified in table 2. The results indicates that the crystal seed addition can increase the settlement percent ($\Delta C_{organics}$) of caustic sodium oxalate a littlebit and also is good for improving the settlement and filtration performance. The effect of crystal seed addition on the sodium oxalate precipitation refers to the following table (table 4).

Table 4: Effect of crystal seed addition on organic carbon percent

No	Original conditions	Crystal seed coefficient (added $Na_2C_2O_4$ liquor / $Na_2C_2O_4$ in the liquor) %			
		0	0.5	1	1.2
		$\Delta C_{organics}$ %	$\Delta C_{organics}$ %	$\Delta C_{organics}$ %	$\Delta C_{organics}$ %
1	No.3 in table 2	81.3	81.8	82.1	81.5
2	No.4 in table2	79.2	81.9	82.3	82.1

3.4 Causticization test

3.4.1 One-section causticization

The No. 3 liquor (main components: N_T 160.4g/l; Al_2O_3 82.9g/l; N_K 136.8 g/l; N_C 23.6 g/l; $C_{organics}$ 1.44 g/l) in table 2 is concentrated to 364g/l, and then the slurry after concentration is treated by the one-section causticization and the control conditions (such as causticization green liquor N_c , molar ratio $[CaO/Na_2O_c]$, temperature, reaction time etc.) of the causticization reaction are adjusted. The chemical components of the precipitated liquor and solid are respectively analyzed, and the sodium carbonate casuticization percent and the organics removal percent are shown as follows:

Table 5: Sodium carbonate causticization percent and organics removal percent of one-section causticization

Test No	Factors			Sodium carbonate causticization percent (%)	$\Delta C_{organics}$ (%)	
	N_c (%)	$\frac{[CaO]}{[Na_2O_c]}$	Temperature			Time
1	10	1.2	55	2	86.73	62.1
2	10	1.3	75	3	91.21	61.8
3	10	1.4	95	4	94.81	67.8
4	12	1.2	75	4	94.52	69.3
5	12	1.3	95	2	96.12	64.7
6	12	1.4	55	3	93.67	62.9
7	14	1.2	95	3	93.98	76.45
8	14	1.3	55	4	90.64	75.36
9	14	1.4	75	2	93.90	72.68

According to the test results, the maximum difference in organics removal is shown after concentrated slag causticization is carried out. This shows the order of the effect of factors on the organics removal percent are: $N_c > \text{time} > \text{temperature} > [CaO/Na_2O_c]$; the optimum caustic conditions of the organics removal are: N_c -14%, time-3 hours, temperature-95 °C, $[CaO/Na_2O_c]$ -1.2. These conditions are also the optimum conditions for carbonate removal.

3.4.2 Two-section causticization

The causticization slurry No.7 to No.9 in table 5 is cooled to 50-70°C and added the lime $\frac{[CaO]}{[Na_2C_2O_4]} = 0.5 - 1.0$ for two-section causticization, then we can get the results shown in table 6.

Table 6: Two-section causticization organics removal percent and total organics removal percent (%)

$\Delta C_{organics}$ (%)	Super concentration $\Delta C_{organics}$ (%)	One-section $\Delta C_{organics}$ (%)	Two-section $\Delta C_{organics}$ (%)	Total $\Delta C_{organics}$ (%)
No.				
1	75.3	76.12	87.63	$75.3 \times 87.63 = 66.0\%$

The results show that the two-section causticization treatment based on the one-section causticization can increase the organic carbon removal percent in the concentrated slag by about 10%. The total removal percent of the organics in the liquor after super concentration, one-section causticization and two-section causticization is about 66.0%.

3.5 Anti-solution test of causticization slag

The resolution test shall be respectively done for the causticization slag from the test No.7 in table 4 and the causticization slag of this test slurry after two-section causticization. The 2 kinds of test results are almost consistent with the resolution law: the alumina concentration during washing has only a small effect on the resolution percent of $C_{organics}$, and the temperature has a big effect

on it. The resolution test result of organic carbon in causticization slag is shown in table 7.

Table 7: Resolution of organic carbon in causticization carbon

No.	N _k (g/L)	A _o (g/L)	Temperature (□)	Resolution C _{organics} (%)
1	4.0	4.8	70	2.9
2	4.0	4.8	70	3.1
3	4.0	4.8	80	5.1
4	4.0	4.8	95	7.5
5	6.0	7.2	60	3.4
6	6.0	7.2	70	4.2
7	6.0	7.2	80	7.6
8	6.0	7.2	95	10.8
9	8.0	9.6	60	3.6
10	8.0	9.6	70	7.1
11	8.0	9.6	80	11.5
12	8.0	9.6	95	15.2

4. Conclusion

The organic carbon removal percent has the direct relation with the initial organic carbon content; it is increased along with the increase of the initial organic carbon content.

When the initial organic carbon content reaches a certain level, the organics removal percent is increased first by the linearity along with the increase of the concentrated caustic soda concentration; however, the organic carbon removal percent is reduced along with the increase of the high concentrated caustic soda concentration after the concentrated caustic soda concentration reaches the maximum value 360g/l.

The crystal seed addition can slightly improve the settlement percent of the causticization sodium oxalate product.

The reaction percent of the oxalate crystallization after one-section causticization is 62.1%-72.68%.

The two-section causticization treatment based on one-section causticization can increase the total organic carbon removal percent in the concentrated slag by about 10%.

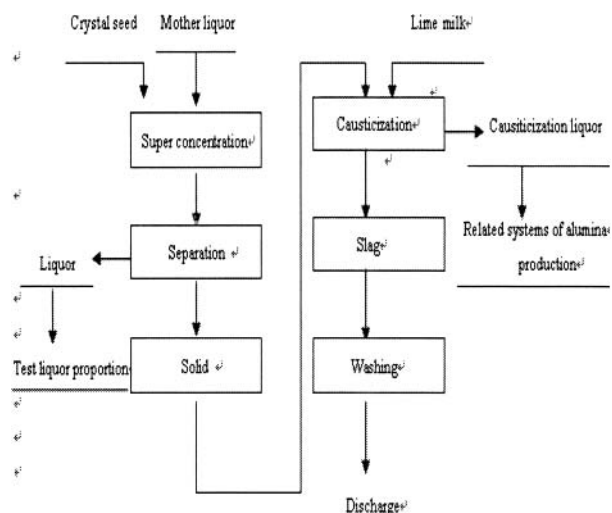
The alumina concentration has a small effect on the resolution percent of C_{organics}, and the temperature has a big effect on it.

This method can not only effectively remove the oxalate, but also has a relatively good carbonate removal effect.

5. Process flow of super concentrated causticization

The mother liquor in the alumina system is sent to the general evaporators for preliminary concentration, and the concentrated mother liquor is sent to the super-concentrated evaporators for super concentration, then the super-concentrated slurry is sent to

the salt settlers for concentration and to the downstream separators for separation. After separation, the solid after solution is sent to one-section causticization tank with lime milk addition, the one-section causticization slurry is obtained by heating the reaction and is sent to a two-section causticization tank after it is cooled. The two-section causticization slurry is obtained and sent to separation washing machines, and then the washing liquor is sent to the alumina production system, the slag is sent to the alumina red mud washing system and is discharged after washing along with the red mud.



References

- Center-south University, Guiyang Aluminum Magnesium Design & Research Institute. "Study report on organics removal of alumina production with bauxite by Bayer process". 2009.
- Chen Wengu, Tang Jiaming, Zhang Li. "Study on sodium oxalate in the Bayer Process". Light Metal 2005, 5: 11-15.
- B Gnyra and G Lever. "Review of Byer Organics-Oxalate Control Processes". Light Metals 1979, 151-161.
- W Arnswald et al. "Removal of Organic Carbon from Liquor by Wet Oxidation in Tjbe Digesters". Light Metals 1991, 23-27.
- G M Bell. "Osidation of Organic Substances in the Bayer Process". Light Metals 1981, 117-128.
- P Atkins and S C Grocott. "The Liquid Anion Exchange Process for Organics Removal". Light Metals 1993, 151-157.