

Effect of Organic Impurity on Seed Precipitation in Sodium Aluminate Solution

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Abstract

Organics are important impurity in Bayer alumina production process. Organics has the greatest impact on particle size and strength of product. The impact of organic impurity on sodium aluminate solution was studied from three aspects in this paper: (1) Analysis of distribution of organics in sodium aluminate solution, and the distribution of organics were quantified in different units. (2) Comparative experiments with different single Low Molar Weight organics were finished, and the impacts of each organic matter on precipitation indexes was quantitatively discussed. (3) Comparative tests of two sodium aluminate solution, pregnant liquor from plant containing organic impurity and pure pregnant liquor, were done with different temperature schedules, and precipitation yield and particle size were quantified. The distribution of organics in the sodium aluminate solution was initially mastered, and the impact of LMW organics was quantified. Meanwhile, an optimized temperature schedule was identified for the sodium aluminate solution containing organics.

Keywords

Organics • Influence effect • Precipitation yield
Particle size • Sodium aluminate solution

Introduction

Seed precipitation, which dominates the efficiency of Bayer alumina production and quality of product [1], is a key unit in Bayer alumina production process. The precipitation

process aims at producing good quality aluminum hydroxide. However, the structure and properties of supersaturated solution significantly change for different concentrations, molar ratio and temperature conditions [2], which make the precipitation complicated. Besides, the different impurity in sodium aluminate solution has various influences on precipitation.

Organic impurity exists in Bayer liquor, There are deleterious outcomes to both product quality and quantity because of accumulation of organic in Bayer process system [3]. Organics enters the Bayer process during digestion of bauxite ore and into the concentrated sodium hydroxide solution while temperature increases. The impact of organic impurity in Bayer alumina plants is potentially serious. Organic impurity in the liquor can decrease precipitation yield considerably. The reduction of precipitation rates, in the presence of organic compounds, is attributed to the poisoning of seed surface [4]. The action of poisoning generally appears to be caused by the elevation of the equilibrium aluminate concentration and is related to adsorption of impurity on the gibbsite surface.

Organic carbon, in Bayer liquor, totally exists in forms of oxalate, not extracted organic and organic acid. The organic acid includes: LMW organic acid, humate, aromatics and others organic acid. The oxalate and organic acid are dissolved by caustic soda into Bayer liquor for circulation, but not extracted organic are discharged with red mud. The high molecular weight organic biopolymers (lignin, cellulose, and humic substances) are quickly degraded to LMW organic during digestion of the bauxite ore, and decomposition products for both aliphatic and aromatic carboxylates are formate, acetate, oxalate, succinate and lactate and other compounds [5]. LMW organics, which take more than 50% of total organic, is the most important organics in Bayer liquor. Formate, acetate acid, propionate have inhibitory effects on the agglomeration (8 h), and the lower the temperature is, the stronger the inhibitory action is. They can make second nucleation happen and then the particle size of gibbsite product decreases [6].

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Precipitation test with LMW organics for long time (40 h) were finished in order to quantify the effect of organic on precipitation yield and particle size distribution, and comparative analysis were also completed between pure pregnant liquor and pregnant liquor of plant.

Experimental

Materials

Experimental materials were supplied by a Bayer alumina refinery in China, including spent liquor, pregnant liquor, aluminum hydroxide and additives.

The pregnant liquor containing organic impurity was made of spent liquor and industrial aluminum hydroxide in an autoclave at the temperature of 145 °C. And the liquor was finally diluted to that α_K was 1.43 and the concentration of Al_2O_3 was 166.9 g/L. Organic pure solution was prepared with industrial sodium hydroxide, industrial aluminum hydroxide, under the same condition of preparation of the former liquor. The content of pure pregnant liquor (number 1) and plant pregnant liquor (number 2) is shown in Table 1.

Methods

Organic carbon was quantified by an NC3100 analysis instrument made in Germany.

Gas chromatography was used to analyze the species of LMW organic, and it was the basis of a variety of methods for the investigation of organic compounds in Bayer liquors. The type of the gas chromatography used was Agilent 7890A GC. Its performance parameters were as follow: the column was DB quartz capillary column with the specification of 30 m \times 0.25 mm \times 0.25 mm; carrier gas was high-purity nitrogen (99.999%); column flow rate was 1 mL/min; split ratio was 1:40; inlet temperature was 200 °C; injection volume was 1 μ L; temperature program was: column temperature is 60 °C (1 min), then temperature is raising to 250 °C (3 min) at 10 °C/min.

Preparation of sodium aluminate solution: First, 10 mL sodium aluminate solution was pipetted into a beaker. Then 1:1 hydrochloric acid was slowly added to the beaker with

the solution being stirred constantly. During this process, large amounts of precipitation came out at first and then disappeared when pH was less than 1. Next 10 mL n-butanol was respectively added. Finally the extract was analyzed by gas chromatography. The standard curve method for different sodium aluminate solution was mainly used to analyze small molecule organic acids qualitatively and quantitatively. Pharmacy was added directly and dissolved in butanol, of which the volume was 10 mL.

Dissolution of aluminum hydroxide: (1) Alkali dissolution: 5 g aluminum hydroxide was dissolved in 100 g/L sodium hydroxide solution under the heating and stirring condition. After aluminum hydroxide completely dissolved, 1:1 hydrochloric acid was added. And then 10 mL n-butyl alcohol, as extraction, was added, the extract constant volume was 10 mL. (2) Acid dissolution: 5 g aluminum hydroxide was dissolved in the phosphoric acid under the heating and stirring condition. After aluminum hydroxide completely dissolved, sodium hydroxide was added to adjust pH value to 1–2. Then 10 mL butanol was added, the constant extract volume was 10 mL. (3) Dissolved directly with butanol: 5 g aluminum hydroxide was directly dissolved in butanol and the volume was 10 mL.

Precipitation test equipment was used for comparative tests, which was a set of stainless steel tanks. Each tank had an agitator and volume of 1 L. Temperature profile was achieved by water bath and the temperature ranged from 25 to 100 °C. After being added a certain amount of seed, pregnant liquor was started to be stirred, and the decomposing test was conducted in accordance with a temperature schedule. After stirring, the slurry were sampled and analyzed to obtain alkali and alumina concentration of the liquor at every certain time, and the particle size of aluminum hydroxide was also analyzed. Meanwhile, the precipitation yield could be calculated according to the molar ratio of solution obtained before and after decomposition. The calculation formula is as follow:

$$\eta_A = \left(1 - \frac{\alpha_{kPregnantLiquor}}{\alpha_{kSpentLiquor}} \right) \times 100\%$$

η_A —precipitation yield of alumina,%;

$\alpha_{kPregnantLiquor}$ —molar ratio of pregnant liquor;

$\alpha_{kSpentLiquor}$ —molar ratio of spent liquor.

Table 1 Ingredient of pregnant liquor

Temperature (°C)	No.	N_K (g/L)	N_T (g/L)	Al_2O_3 (g/L)	Molar ratio
64–53–48	1 [#]	166.5	190.0	192.2	1.43
	2 [#]	166.5	190.7	192.4	1.42
62–51–46	1 [#]	167.6	176.7	196.3	1.41
	2 [#]	166.8	187.7	195.3	1.41
62–49–46	1 [#]	168.9	194.8	196.7	1.41
	2 [#]	163.7	184.3	192.7	1.40

Results and Discussion

Analysis of Organics in Sodium Aluminate Solution

Organic carbon in pregnant liquor and its corresponding spent liquor was detected. The results are listed in Table 2.

Table 2 shows that organic carbon in pregnant liquor and spent liquor are 2.45 and 2.31 g/L, respectively. The concentration of organic carbon in spent liquor is lower than that in pregnant liquor, which indicates part of organic carbon was removed with aluminum hydroxide.

The type and content of LMW organics was confirmed by gas chromatography, through comparing with standard gas chromatography of butanol. The results of LMW organics are listed in Table 3.

It can be seen from Table 3 that the LMW contains oxalate, acetate, formate, malonate, succinate and dimethylacetone [7]. The content of LMW organics in pregnant liquor is obviously higher than that in spent liquor. This can be explained that the LMW organics were discharged with occluded soda and aluminium hydroxide. Among these LMW organics, oxalate has the highest initial concentration, 2.55 g/L, in pregnant liquor and decreases the most obviously, from that to 0.51 g/L in spent liquor. It indicates that

most of oxalate is discharged with aluminum hydroxide during seed precipitation (Table 4).

The behavior of oxalate is a result of the adsorption of organics on the surfaces of crystals. And the most important single factor that determines the shapes of the agglomerates appears to be supersaturation, which depends on the presence of organics impurity. Oxalate supersaturation may be defined as the highest concentration of oxalate that can be achieved in a given solution before spontaneous nucleation of sodium oxalate occurs. When the concentration is higher than equilibrium concentration of oxalate, oxalate begins to crystallize with aluminum hydroxide [8].

Influence of LMW Organics on Precipitation

It is known that LMW organics mainly contains oxalate, acetate and formate from above. The influence of each single organics (oxalate, acetate, formate) [9] on precipitation was studied.

Precipitation temperature schedule is 58–47–45 °C with the first period 23 h and the second period 22 h. The seed addition is 700 g/L. And the ingredient of pregnant liquor is shown in Table 5.

The content of organics is as follow: oxalate is 5 g/L, acetate is 1.5 g/L and formate is 1.5 g/L.

Table 2 Organic carbon in Bayer system

Liquor type	Unit	C _{total}	C _{Inorganic}	C _{Organic}
Pregnant liquor	g/L	8.44	5.99	2.45
Spent liquor	g/L	8.85	6.54	2.31

Table 3 Organics in sodium aluminate solution (g/L)

Type	Pregnant liquor	Spent liquor
Oxalate	2.55	0.51
Acetate	1.24	0.93
Formate	1.45	0.3
Malonate	1.08	0.2
Succinate	0.77	0.33
Dimethylacetone	1.06	0.94

Table 4 Organics in aluminium hydroxide (g/L)

Organics	Oxalate	Acetate	Formate	Malonate
Content	2.29	0.50	0.43	0.81

Table 5 Ingredient of pregnant liquor

Organics	N _K (g/L)	Al ₂ O ₃ (g/L)	Molar ratio
Blank	166.8	192.0	1.43
Formate	166.8	192.0	1.43
Acetate	166.8	192.0	1.43
Oxalate	166.8	192.0	1.43

Table 6 Results of spent liquor with different organics

Organics	N _K (g/L)	Al ₂ O ₃ (g/L)	Molar ratio	Yield (%)
Blank	170.5	103.7	2.71	47.15
Formate	173.6	107.0	2.67	46.42
Acetate	167.4	103.8	2.65	46.09
Oxalate	176.1	110.9	2.61	45.27

The results of influence of oxalate, acetate and formate on precipitation yield are shown in Table 6.

The precipitation yield decreased 0.73, 1.06 and 1.88% respectively compared with the blank test when formate, acetate and oxalate alone existed.

Organic carbon was detected and the result is shown in Table 7.

It indicates that oxalate has the highest influence to precipitation yield and the influence of acetate and formate is lower than oxalate.

The influence of oxalate, acetate and formate on particle size is shown in Table 8 (Fig. 1).

It can be seen that formate has the highest influence to particle size and the influence of acetate and oxalate is lower than formate.

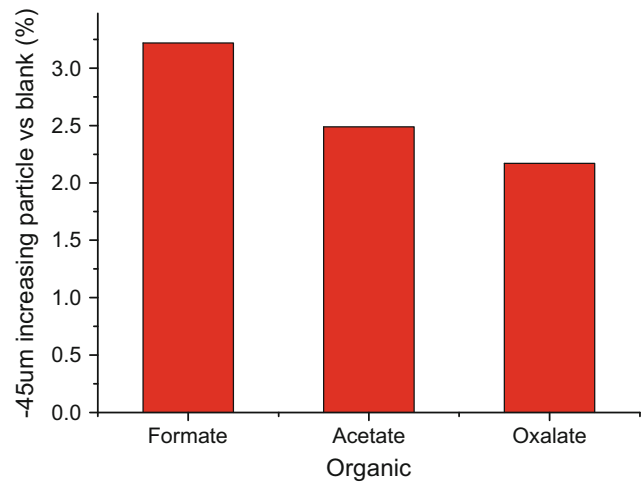
LMW organics shows significant adsorption [10]. Accordingly, the presence of simple organics appears to have aggregate effect on the ionic strength of the liquor. Organic acid have been reported to have significant effects on yield and particle size distribution of product under conditions of unseeded precipitation, apparently due to effects on the induction period [11]. And it also has been found in Bayer process liquor of low concentrations [12]. Systematic studies of this class of compounds have shown

Table 7 Organic carbon of spent liquor

Organics	C _{organics} (g/l)	Residual C _{organics} (g/l)
Formate	0.21	0.53
Acetate	0.68	1.40
Oxalate	Trace	Trace

Table 8 Particle size of aluminum hydroxide

Organics	-45 μm (%)
Blank	13.30
Formate	16.52
acetate	15.79
Oxalate	15.47

**Fig. 1** Particle size of Al(OH)₃ with different organic carbon

that they generally inhibit precipitation. The acid group generally enhances the inhibition effect [13]. All of those organic acid groups were found to adsorb to the gibbsite surface and to be precipitation inhibitors. At the same time, the former appears to be associated with direct interactions with aluminum ion, either in growth units or directly on the surface of them, resulting in inhibiting effect of growth sites. On the other hand, the presence of organic acid groups alone appears to result in the formation of an increased number of secondary nucleus that do not adhere to the growth surface, causing an increasing of fine particles and hence a greater overall surface area for precipitation.

Influence on Precipitation of Plant Pregnant Liquor

Comparing test are done with plant pregnant liquor and pure pregnant liquor prepared in laboratory. The pure pregnant liquor is named number 1 and the plant pregnant liquor with organic impurity is named number 2.

Precipitation temperature schedule are 64–53–48, 62–51–46 and 62–49–46 °C. Total precipitation time is 40 h with

Table 9 Ak in different temperature rule

Time (h)	64–53–48 °C		62–51–46 °C		62–49–46 °C	
	1 [#]	2 [#]	1 [#]	2 [#]	1 [#]	2 [#]
2	1.70	1.71	1.73	1.65	1.65	1.63
4	1.85	1.82	1.89	1.82	1.83	1.78
6	1.95	1.93	1.97	1.88	1.94	1.91
11.5	2.14	2.09	2.11	2.02	2.11	2.04
13.5	2.15	2.14	2.14	2.13	2.20	2.09
15.5	2.20	2.15	2.26	2.25	2.21	2.14
36	2.40	2.34	2.44	2.42	2.42	2.35
38	2.41	2.35	2.46	2.45	2.50	2.40
40	2.53	2.38	2.50	2.47	2.51	2.41

the first stage 13.5 h and the second stage 26.5 h. The industrial seed is added at 630 g/L.

Precipitation yield of pure pregnant liquor (number 1) and plant pregnant liquor (number 2) is shown in Table 9 (Fig. 2).

It can be seen that precipitation yield of pure pregnant liquor is higher than pregnant liquor of plant, it indicates that there is organics of negative effect in system, which makes precipitation yield decrease 1.5% or even higher. It is benefit for precipitation yield to decrease initial precipitation temperature with the same final temperature. The influence of organics is obvious in higher precipitation temperature schedule. It indicates that the effect of organics to yield can be obviously controlled by temperature schedule.

There are two main ways in which organics affects precipitation. Firstly, the presence of organic acid anions requires an equivalent amount of cations, particularly sodium ions, to maintain charge balance, which reduces the number of sodium ions available to balance hydroxide and aluminate ions. Secondly, organic compounds may adsorb to seed surfaces and affect the kinetics of gibbsite precipitation, which reduces the precipitation yield. Adsorption effect and the influence of crystallization of solid sodium oxalate can have a major effect on the size distribution of the precipitated gibbsite. In order to maintain an acceptable particle size distribution, some measures are usually taken, which have an indirect effect on precipitation yield. There is no single correlation between adsorption strength and the degree of inhibition, but the adsorption can lead to either inhibition or enhancement of precipitation yield.

The particle size and percentage of -45 μ m of aluminum hydroxide produced from pure pregnant liquor (number 1) and pregnant liquor of plant (number 2) are shown in Table 10 (Fig. 3).

It can be seen that the presence of organics affects not only the precipitate on yield, but also the particle size of

product. Besides, the particle size of aluminum hydroxide is also influenced obviously by temperature. Aluminum hydroxide product was thinned when slurry was quickly cooled at early stage, although with the same precipitation time. The negative influence of organics on particle size of product is greater when the initial temperature of precipitation is higher. Fine particle is much less when the initial temperature is lower and decreases slowly in initial stage of precipitation.

For pure solutions at high supersaturation, precipitation yield is high and the growth of crystallization is mainly by the birth and spreading of grains on the basal face. Sodium ions are associated with aluminate ions and clusters and adsorbed on the gibbsite surface.

Effect Mechanism of Organics in Bayer Liquor

The negative effect of organic impurity acts on both precipitation yield and particle size in sodium aluminate solution. Inhibition of precipitation yield is influenced by the active surface areas of gibbsite seed [13–15]. The actions of poisons highlight the importance of surface chemical reactions in the crystallization of gibbsite. Adsorption is a key step in crystallization inhibition. It may independently be a key step in sodium incorporation. Compounds that strongly adsorb not only reduce precipitation yield, but also incorporate into the gibbsite lattice. Organic impurity decreases yields significantly. And their relative degrees of inhibition are determined by the strength of adsorption at growth sites on the gibbsite surface.

Gibbsite grown from sodium hydroxide solutions may display a variety of shapes and sizes. The resultant shape and size distributions are relatively insensitive to crystallization conditions and impurity, and therefore are a result of properties inherent in the crystallization process itself. It has been

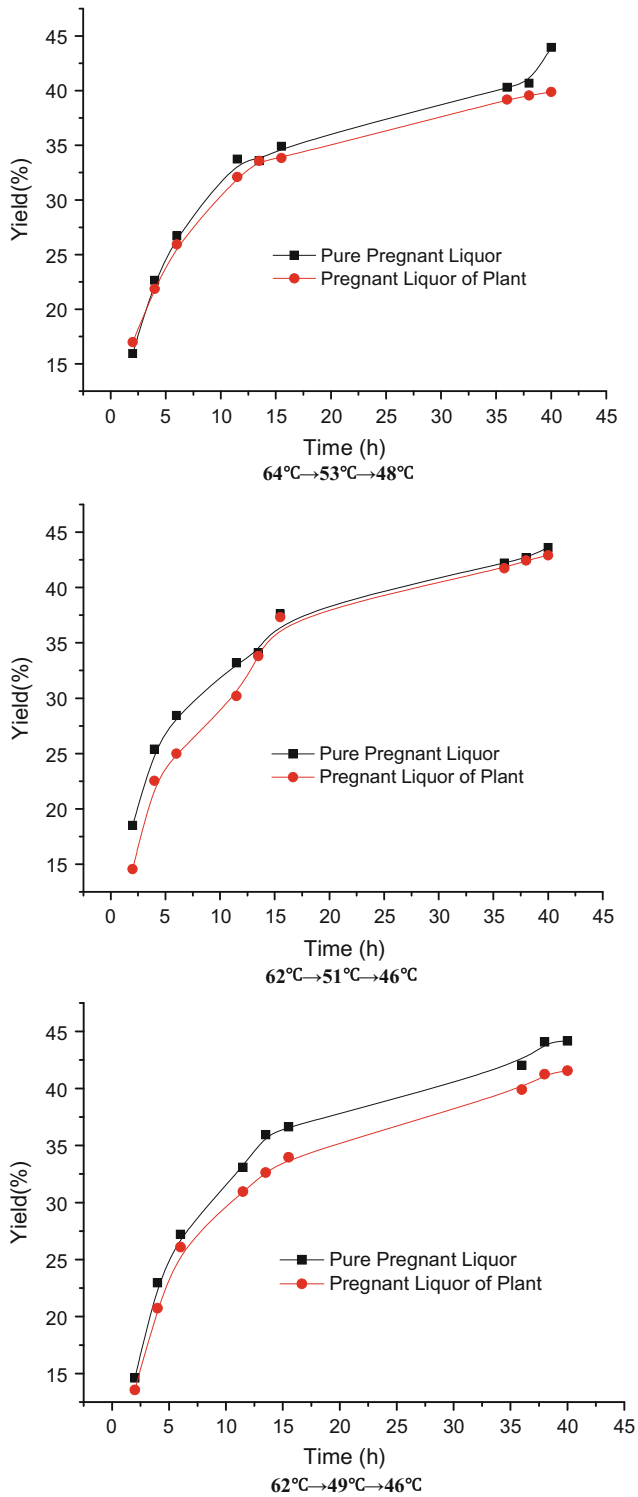


Fig. 2 Precipitation yield of sodium aluminate solution at different temperature

shown that the effects which dominate in the production of this diversity include crystal twinning at the nucleation stage, accumulation of surface defects and the continuous formation of nuclei during growth [16]. Dispersion between

Table 10 Particle size of aluminum hydroxide on different temperature schedule

Temperature	No.	-45 μm (weight g)	+45 μm (weight g)
64–53–48 °C	1 [#]	5.99	42.29
	2 [#]	6.47	41.99
62–51–46 °C	1 [#]	5.89	42.94
	2 [#]	5.98	42.75
62–49–46 °C	1 [#]	7.17	42.08
	2 [#]	7.24	41.73

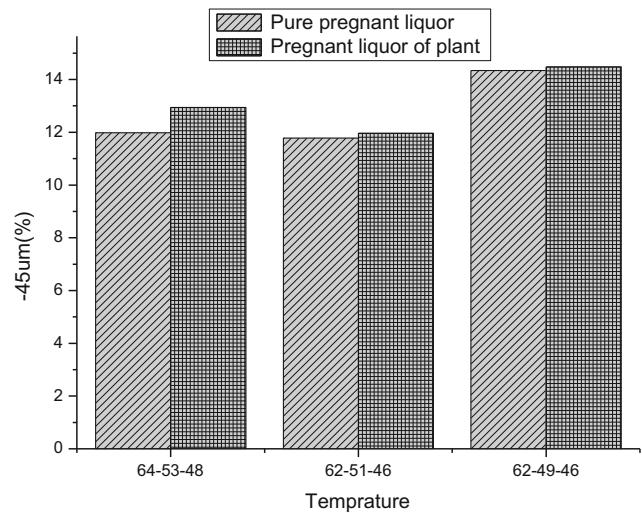


Fig. 3 Particle size of aluminum hydroxide on different temperature schedule

crystal facets in the final shape of each crystal is a key determining factor of the precipitation yield [17].

Conclusion

- (1) Organics are one of very important impurity in Bayer alumina production process. Organic carbon in pregnant liquor and spent liquor is 2.45 and 2.31 g/L. Through quantitative analysis of sodium aluminate solution in an alumina refinery. Parts of organics are taken away by adsorption on the surface of aluminum hydroxide or co-crystallization with aluminum hydroxide.
- (2) Effect on precipitation yield, oxalate has greater than other LMW organics, such as acetate and formate. Then the effect on particle size, formate has much greater than acetate and oxalate.
- (3) Organics has negative effect on precipitation yield, which can be reduced more than 1.5% for organics.

Lower initial precipitation temperature schedule is benefit for precipitation yield. The effect of organics to precipitation yield can be obviously controlled by a reasonable temperature schedule.

- (4) Particle size of aluminum hydroxide is influenced obviously by organic impurity. The particle size of aluminum hydroxide is finer when organic impurity exists. Aluminum hydroxide is thinned when slurry was quickly cooled at early stage with the same precipitation time, the maximum difference of percentage of $-45 \mu\text{m}$, in different temperature schedules, is over 2%.

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