AA19 - The Behaviour of Zinc in the Bayer Process

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Abstract

High zinc in metallurgical alumina has a negative impact on the current efficiency of aluminum electrolysis and the properties of aluminum metal and alloys. In this study, the behaviour of zinc in bauxite in the Bayer process was studied. The effects of digestion conditions on the extraction rates of zinc in digestion, and that of the caustic concentration on the precipitation rate of zinc in a seeded precipitation process were investigated. With the increase in leaching temperature, digestion time and lime addition, the digestion efficiency of zinc increased at first and then decreased. From the material balance, it can be seen that in digestion process, about two-thirds of the zinc in bauxite is extracted into the Bayer liquor, and the rest into red mud. At precipitation conditions where temperatures are between 60 °C and 48 °C, a precipitation time of 45 hours, first tank seed solids content of 800 g/L and caustic concentration (N_k) of 165~175 g/L (as Na_2O), 40～60 % of zinc in green liquor enters aluminum hydroxide product during seeded precipitation. Reducing the caustic concentration is conducive to the precipitation of zinc during seeded precipitation.

Keywords: Bauxite bearing-zinc, digestion, seeded precipitation.

1. Introduction

The zinc content in Guangxi bauxite is high (about 0.025 % as ZnO), and consequently the alumina produced in this region is relatively high in ZnO (>0.015 %), which seriously impacts product quality, and the competitiveness of these refineries. Although zinc provides some benefits in the Bayer precipitation process, such as contributing to the crystal growth rate and characteristics of the gibbsite crystal, its high concentration in product alumina will affect the current efficiency of aluminum electrolysis, purity of aluminum ingots and metal and alloy material properties. Suss et al points out that the current efficiency decreases by 0.13 % for every 0.01 % increase in zinc content, and the material properties of alloys are also affected. For example, aluminum profiles with high zinc content are more brittle and have poor ductility [3].
In this study, the behaviour of zinc in the Bayer process was investigated. The effects of digestion conditions on the extent of zinc extraction from bauxite, and the effect of the liquor caustic concentration on the precipitation of zinc during Bayer seeded precipitation were examined. Besides analyzing the test results, a material balance for zinc in different process areas of an alumina refinery was conducted, which could help clarify the distribution and behaviour of zinc though the process, and provide a mathematical basis for the control of zinc in alumina product.

2. Raw Materials and Methods

2.1 Raw Materials

2.1.1 Bauxite

The bauxite used in this test was provided by the Guangxi Branch of the Aluminum Corporation of China Limited. All the bauxite was crushed and ground to the particle size specification for the Guangxi Branch refinery. Following milling, it was homogenised, divided, bagged and sealed for use. The particle size of the bauxite sample is shown in Table 1.

Table1. Particle size distribution of test bauxite sample (%).

+60 mesh	-60~+100 mesh	-100~+230 mesh	-230 mesh
0.30	6.35	18.15	75.20

Following bauxite sample preparation, its chemical composition was analyzed. The chemical and phase composition of the high-zinc bauxite are shown in Tables 2 and 3 respectively. The X-ray diffraction pattern is shown in Figure 1.

Table 2. Chemical composition of test bauxite (%).

Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO	ZnO	A/S	LOI
52.48	4.96	23.00	2.98	0.12	0.055	0.45	0.15	0.014	10.58	14.21

Table 3. Mineral phase composition of test bauxite (%).

diaspore	gibbsite	goethite	hematite	illite	kaolinite	anatase	rutile	calcite	dolomite
54.5	3.0	20.8	5.0	2.0	9.0	2.6	0.4	0.7	0.3

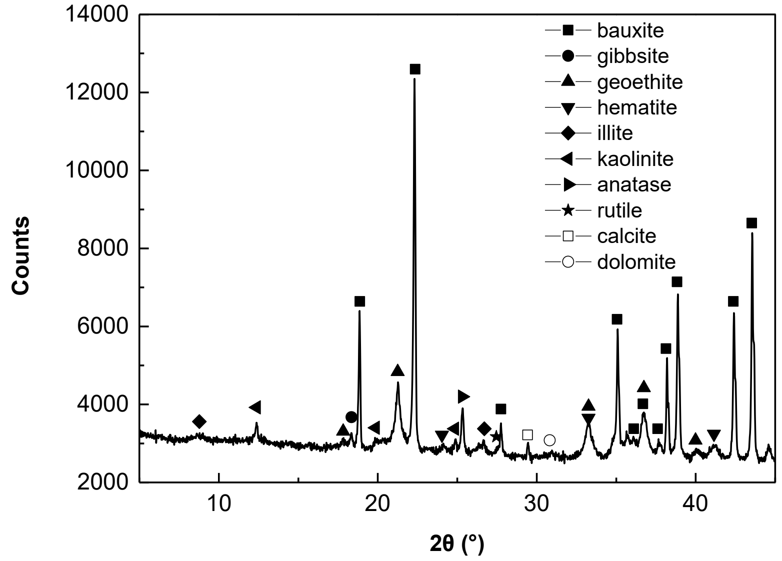

Figure 1. X-ray diffraction pattern of test bauxite.

As shown in Table 2, the largest chemical components of this bauxite are Al_2O_3 and Fe_2O_3, at 52.48 % and 23.00 % respectively. These are followed in concentration by SiO_2 and TiO_2, at 4.96 % and 2.98 % respectively, with an A/S of 10.58, and zinc content of 0.014 % (as ZnO).

Table 3 shows that the available alumina in this bauxite occurs as a mixture of diaspore and gibbsite. The main silicon-bearing minerals are kaolinite and illite, with contents of 9 % and 2 %, respectively; while the main iron-bearing minerals are goethite and hematite, with contents of 20.8 % and 5 %, respectively. The main titanium-bearing mineral is anatase (2.6 %) with a minor rutile content of 0.4 %. The main calcium-bearing minerals are calcite and dolomite, with contents of 0.7 % and 0.3 % respectively.

2.1.2 Lime

Lime used in the test was provided by Aluminum Corporation of China Limited Guangxi Branch, ground to pass a 100-mesh sieve, bagged and sealed for use. Its chemical composition is displayed in Table 4.

Table 4. Chemical composition of lime (%).

Al_2O_3	SiO_2	CaO_T	MgO	CaO_f
0.63	0.71	84.42	2.26	80.30

Table 4 shows that CaO_T content in this lime is 84.42 %, where CaO_f is 80.30 %.

2.1.3 Sodium Aluminate Liquor

Sodium aluminate liquor used in the test was provided by Aluminum Corporation of China Limited Guangxi Branch. The chemical composition is shown in Table 5.

Table 5. Chemical composition of test liquor.

Na_2O_T(g/L)	Al_2O_3(g/L)	Na_2O_k(g/L)	α_k	SiO_2(g/L)	Zn^{2+}(mg/L)
259.79	130.60	243.00	3.06	1.02	5.85

2.2 Experimental and Analytical Method

Digestion experiments were conducted using steel bombs heated in molten salt. The extraction rate of zinc oxide from bauxite was calculated according to the zinc-iron ratio of bauxite and red mud, as detailed in the calculation below:

$$\eta_{Zn} = \frac{(Zn/F)_B - (Zn/F)_R}{(Zn/F)_B} \times 100\% \qquad (1)$$

where:

$(Zn/F)_B$	mass ratio of ZnO to Fe_2O_3 in the bauxite
$(Zn/F)_R$	mass ratio of ZnO to Fe_2O_3 in the red mud

Based on the change of zinc in Bayer liquor before and after zinc removal, zinc removal rate during digestion process was calculated, using the calculation as detailed below:

$$\eta_{Zn} = \frac{C_{Zn-blank} - C_{Zn-liquor}}{C_{Zn-blank}} \times 100\% \qquad (2)$$

where:

$C_{Zn\text{-}blank}$	Zinc content in liquor of blank test, in mg/L;
$C_{Zn\text{-}liquor}$	Zinc content in liquor before and after zinc removal, in mg/L.

Zinc in liquor was analyzed using ICP, while that in red mud was analyzed using XRF.

3. Results and Discussion

3.1 Behavior of Zinc in the Digestion Process

3.1.1 The Effects of Digestion Temperature

Pre-desilication of the bauxite was performed at a temperature of 100 °C, residence time of 10 hours, liquor caustic concentration (Na_2O_k) of 243 g/L, and Lime was added at a C/S ([CaO]/[Na_2O]) of 1.2 %. Pre-desilication was followed by a digestion time of 60 minutes. The effects of digestion temperature on the extraction rates of Al_2O_3 and ZnO were examined, with test results as shown in Figure 2:

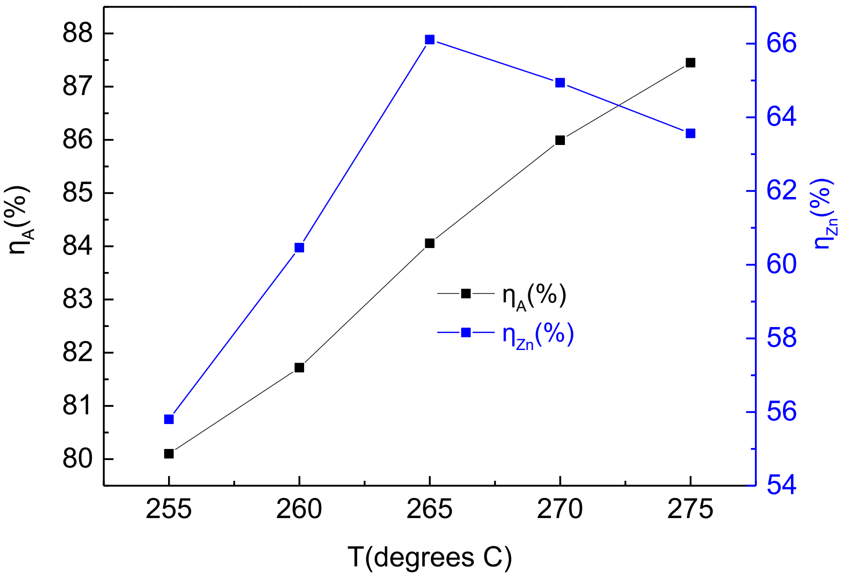

Figure 2. The effect of digestion temperature on the extraction rates of Al_2O_3 and ZnO.

As shown in Figure 2, under the same test conditions, with increasing temperature, the zinc in liquor, as indicated by $\eta_{zn,}$ first increases and then decreases above 265 °C, while that of Al_2O_3 (as indicated by η_A) increases. The digestion of zinc reaches its maximum value at a digestion temperature (T_d) of 265 °C, while if T_d >265 °C, zinc reduces with increasing T_d, where majority of zinc enters into Bayer liquor and minority enters into red mud. This result relates dissolution of zinc in the digestion process to its mineral occurrence in the bauxite and the digestion conditions. Therefore, increasing the digestion temperature not only enhances the extraction rate of Al_2O_3, but also lowers ZnO dissolution.

3.1.2 The Effects of Digestion Time

Pre-desilication of the bauxite was performed at the same conditions as the digestion temperature test; a temperature of 100 °C, residence time of 10 hours, liquor caustic concentration (Na_2O_k) of

243 g/L, and Lime was added at a C/S ([CaO]/[Na_2O) of 1.2 %. A digestion test followed at a digestion temperature of 265 °C, and the effects of digestion time on the extraction rates of Al_2O_3 and ZnO were recorded, with test results shown in Figure 3.

Figure 3 shows that under the same test conditions, with increasing digestion time, the concentration of zinc in liquor first increases and then reduces, while the liquor concentration of Al_2O_3 continues to increase. The concentration of zinc reaches its maximum value at a digestion time (Θ_d) of 60 minutes, while if $\Theta_d > 60$ min, the concentration of zinc reduces with increasing Θ_d. An explanation for zinc's behaviour may be that it is dissolved as sodium zincate in the caustic liquor and adsorbed onto red mud. As time goes on, adsorption of zincate onto red mud will reduce the concentration of zinc in liquor. A suitably longer digestion time, therefore, not only enhances the dissolution of Al_2O_3, but can also lower the liquor ZnO concentration.

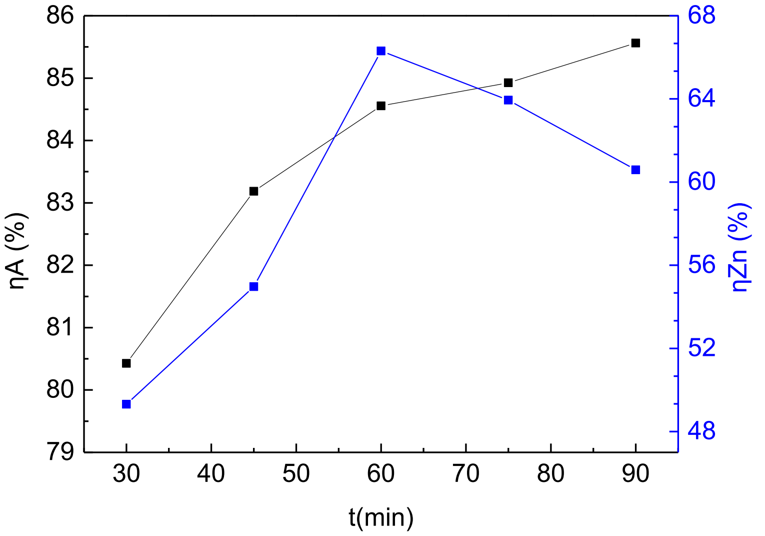

Figure 3. The effect of digestion time on the extraction rates of Al_2O_3 and ZnO.

3.1.3 The effect of Lime Addition

Pre-desilication conditions were the same as for previous tests, but without lime addition. Following pre-desilication, a digestion test was performed at a temperature of 265 °C and duration of 60 min. The effect of lime addition on the extraction rates of Al_2O_3 and ZnO were recorded. Test results as shown in Figure 4.

Figure 4 shows that under the same test conditions, with lime addition increasing, the extraction rate of zinc in liquor first increases and then reduces. The extraction rate of zinc reaches its maximum with C/S of 1.2, while if C/S > 1.2, the extraction rate of zinc reduces gradually with increasing C/S. An explanation for this effect could be that zinc exists in the form of $Zn(OH)_4^{2-}$ in a strong alkali system [4]. Excess calcium hydroxide then reacts with $Zn(OH)_4^{2-}$ in the Na_2O-ZnO-H_2O system to form a calcium zincate precipitate that is insoluble under these solution conditions, and as a result, the concentration of zinc in the solution drops. The reaction equation proposed is as follows [5, 6]:

$$2Zn(OH)_4{}^{2-} + Ca(OH)_2 + H_2O = Ca(OH)_2 \cdot Zn(OH)_2 \cdot 2H_2O \downarrow + 4OH^- \quad (3)$$

While the extraction rate of alumina first increases, its concentration flattens and starts to trend downwards. The extraction rate of Al_2O_3 reaches its maximum value with a C/S of 1.4, while if

C/S >1.4, there is a downward trend with increasing C/S. Excess lime reacts with alumina to form calcium aluminate compounds such as hydrogarnet, leading to a loss of alumina from the liquor.

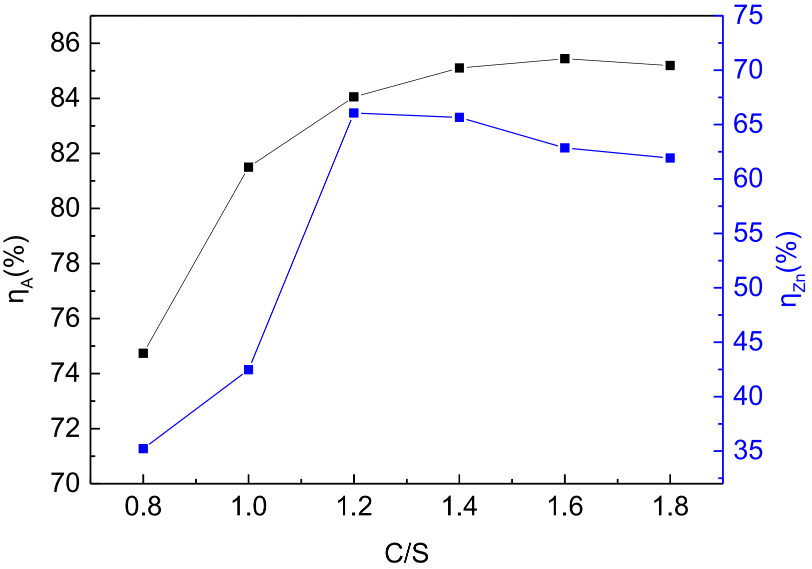

Figure 4. The effect of lime addition on the extraction rates of Al_2O_3 and ZnO.

3.2 The Behavior of Zinc in a Precipitation Circuit

The industrial precipitation test conditions used for this study were as follows: residence time is 45 hours, solid content of seed in the first tank is 800 g/L. Under these conditions, the effects of caustic concentration (N_k) on the precipitation of zinc during precipitation circuit were investigated, with 3 months of liquor zinc analytical results averaged. The results of the industrial test are shown in Figures 5 and 6.

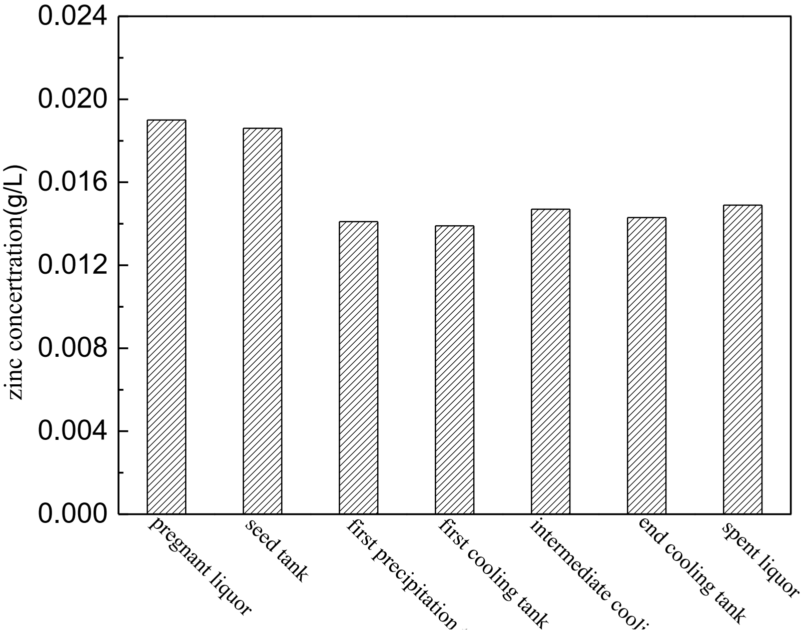

Figure 5. Variation of Zn in seeded precipitation process (N_k: 172.9g/L).

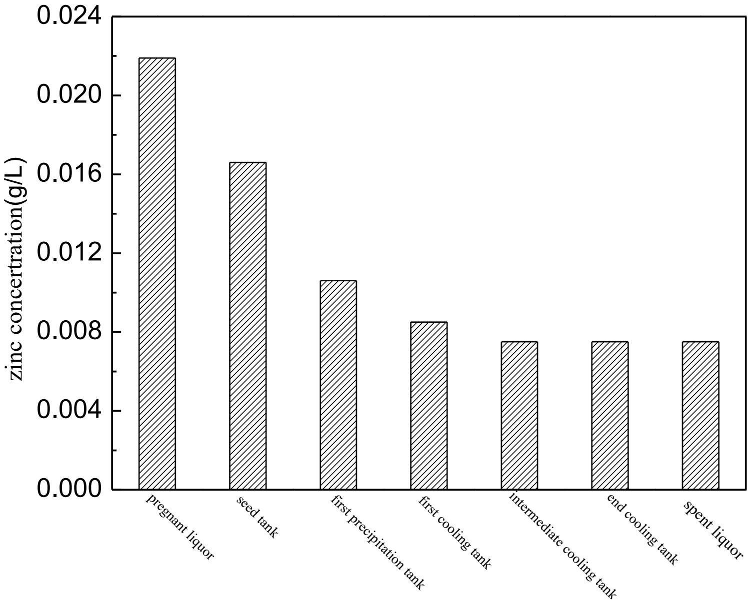

Figure 6. Variation in Zn in seeded precipitation process (N_k: 165g/L).

Figures 5 and 6 show that the liquor zinc showed a decline in the early precipitation tanks, and then tended to be stable through the rest of the precipitation process. Under the same precipitation conditions, the percentage of liquor zinc precipitated is 61.75 % at an N_k of 165 g/L, while only 41.16 % precipitates at an N_k of 172.9 g/L. It can therefore be concluded that liquor N_k has a significant influence on the precipitation of zinc in the precipitation circuit, with the lower N_k being more conducive to the precipitation of liquor zinc.

3.3 The Distribution and Trends of Zinc in the Alumina Production Process

Based on the test results and on-site process conditions, the material balance in the production process of 1000 kg of bauxite was calculated, with results shown in Table 6.

The material balance calculation shows that bauxite is the main zinc input to the process, while about 2/3 of the zinc in bauxite enters the liquor, the rest is discharged with red mud. The distribution of zinc through the Bayer process (1000kg bauxite) is presented in Table 7 and Figure 7.

Table 6. Material balance per 1000kg bauxite.

Material	Zinc content in liquor (g)	Zinc content in solid (g)
bauxite	—	106.73
liquor	36.46	—
predesilication bauxite slurry	36.45	106.51
digestion slurry	107.60	35.08
red mud	—	34.95
green liquor	107.20	0.46
pregnant liquor	106.74	—
spent liquor for evaporation	53.01	—
aluminum hydrate	—	53.72

Table 7. The distribution of zinc in Bayer process materials (per 1000 kg bauxite).

Item	Bauxite	Liquor	Red mud	Product	Spent liquor for evaporation	Others
Zn(g)	106.73	36.46	34.95	53.72	53.01	1.50

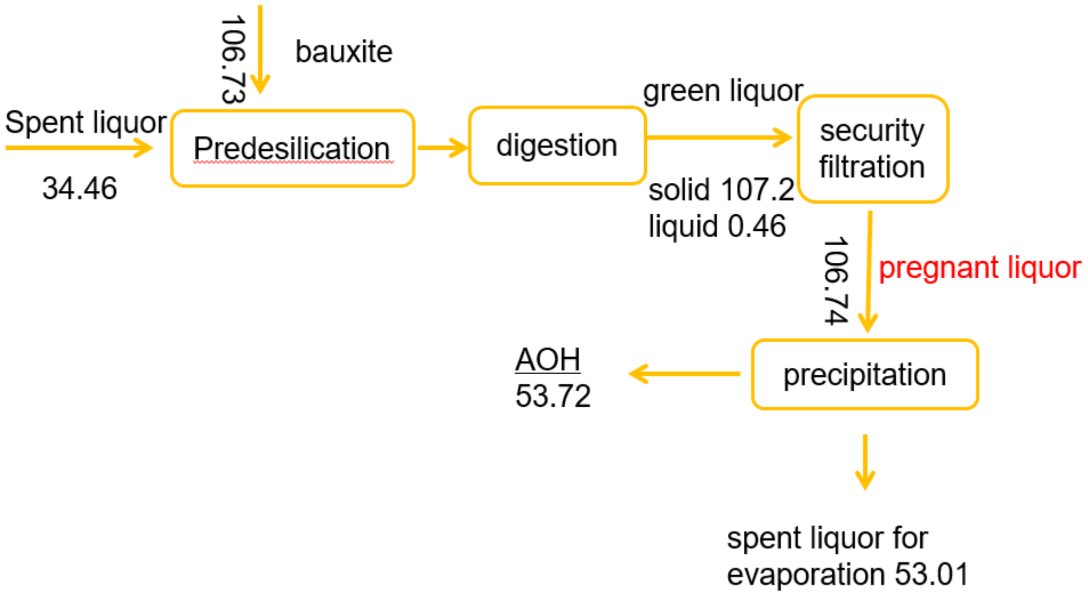

Figure 7. Distribution of zinc in process materials as grams of zinc/ton of bauxite feed.

Zinc in product can be predicted through the liquor zinc content coupled with the results of material balance calculations. This provides a useful basis for assessing options for controlling zinc in alumina product. For example, when the ZnO content in alumina product needs to be reduced from 0.0164 % to 0.0075 %, we can calculate that the removal rate of zinc from the pregnant liquor is greater than 42.87 % by the above calculation, which indicates the process condition changes required to control the zinc in product to the target.

4. Conclusions

1. Under the same digestion conditions, with increasing digestion temperature, duration, and lime addition, the dissolution of zinc into liquor firstly increase then reduces. From the results of material balance calculation, we can see that about 2/3 zinc in the bauxite is extracted into liquor, while the rest is contained in red mud.

2. Under the precipitation conditions of a temperature of 60～48 °C, solid content of seed in the first tank of 800 g/L, and liquor caustic concentration of 165～175 g/L, about 40～65 % of zinc in pregnant liquor enters aluminum hydrate during seeded precipitation process, and reducing caustic concentration may be conducive to the precipitation of zinc during seeded precipitation process.

3. The distribution and behaviour of zinc in the Bayer process can be demonstrated using material balance calculations, which provide a mathematical basis for evaluating options for controlling zinc content in alumina product.

5. References

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