

AA20 - The Behavior and Removal of Bauxite Zinc in the Bayer Process

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Abstract



Bayer liquor impurities are an important factor affecting Al_2O_3 quality. With the grade of Chinese domestic bauxite decreasing, its impurity composition has become more complex, and impurities' negative effects on product quality have become more obvious. High zinc content in alumina products of Guangxi Pingguo Aluminum results from the high zinc in its bauxite. High zinc in metallurgical alumina has a negative impact on the current efficiency of aluminum electrolysis and the properties of aluminum metal and alloys. The occurrence of zinc in bauxite, the behavior of zinc in the Bayer process and its removal methods are summarized, while different removal methods were analyzed, and the future development direction for zinc removal technology in alumina production is discussed.

Keywords: Bauxite bearing-zinc, current efficiency, removal zinc.

1. Introduction

Chemical impurities in metallurgical alumina can have a large effect on aluminum metal quality. With the degrading quality of bauxite in China, higher impurity content and the impact on aluminum quality have become more obvious. The global quality specification for electrolytic aluminum has become increasingly strict, where the impurity content of the highest quality primary aluminum should not exceed 0.015%.

The zinc content in alumina should not exceed 0.01 %, and to reach this value, the zinc content in Bayer liquor must be controlled to below 15 mg/L [1,2]. In China, the content of zinc in Guangxi bauxite is relatively high (0.025 % as ZnO), and consequently ZnO in alumina in this region is relatively high (>0.015 %), which seriously impacts product quality, and the competitiveness of these refineries. Although zinc has some benefits seeded precipitation (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 [3] points out that an increase of the Zn ion content in the electrolysis bath by 0.01 % reduces current efficiency by 0.13 %, and the material properties of alloys are affected. For example, aluminum profiles with high zinc content are more brittle and have poor ductility.

A large amount of research on the behavior and removal method of zinc in the process of alumina production have been conducted both in China and globally.

2. Occurrence of Zinc in Bauxite

Zinc is one of the secondary mineral elements occurring in bauxite, where the zinc content can reach up to 0.75 % [3]. ZnO contents of some bauxites in China and globally are shown in Table 1. As shown in Table 1, ZnO contents are a little higher in Karst bauxites, such as those from China, Montenegro, Bosnia Herzegovina, and Russia. Lateritic bauxites such as those from Australia, Guinea and Brazil are generally lower in ZnO by up to an order of magnitude lower than karst bauxites. The zinc content in bauxites from different mining areas of the same country can also be different, like that from North Ural and Komi Republic of Russia. Scavnicar [4] analyzed ZnO content in forty-seven bauxite samples from Montenegro, of which a concentration of 0.012-0.025% was found in forty samples, 0.037 % in four samples and 0.05 % in one sample.

Table 1. ZnO content of some bauxites.

Origin	Australia	Guinea	Brazil	China	Jamaica	Montenegro	Bosnia and Herzegovina	Kazakhstan	Russia	
	Weipa	Boke	Trombetas	Pingguo	All deposits	Niksic	Milici	Krasnookya brskoye	North Ural	Timan
ZnO, %	<0.005	0.0012	0.0067	0.025	0.040	0.035	0.014	0.014	0.019	0.06

Numerous studies of zinc occurrence in bauxites have shown the wide differences between different areas. Bárdossy [5] found ZnS in Hungarian bauxites, in which he reported that the zinc mineral's particle size is 20-30 μm . Feret, See et al [6] found a new mineral bearing manganese and zinc, and from its X-ray diffraction pattern, it was deduced that its structure was like limonite, and the bauxite's zinc content increases with the MnO_2 content. By systematic analysis of 340 samples from different regions, it was concluded that zinc in bauxite is unlikely to replace iron in goethite or hematite. The lithium content measured by ICP was very low. Due to the difference in ion radius, zinc cannot replace lithium or aluminum. Further analysis by X-Ray Diffraction shows that the new mineral containing zinc and manganese was zinc pyrolusite, whose formula is $\text{Al}(\text{Zn}_x\text{Mn}_{1-x})\text{O}_2(\text{OH})_2$, where X may vary from 0.02 to 0.24.

Suss et al [3] propose that the zinc content in the Nordic and Ural karst bauxites of Russia is related to the existence of oolitic chlorite ($\text{Fe}^{2+} \cdot 1.5\text{AlFe}^{3+} \cdot 0.2\text{Mg} \cdot 0.2\text{Si} \cdot 1.1\text{Ag} \cdot 0.9\text{O}_5 \cdot (\text{OH})_2$). Further analysis by Rietveld-X diffraction, suggested the new mineral bearing zinc and manganese was "zinc hard manganese ore", whose chemical formula is $\text{Al}(\text{Zn}_x \cdot \text{Mn}_{1-x}) \cdot \text{O}_2 \cdot (\text{OH})_2$, in which x can vary between 0.02 and 0.24. Suss et al [3] thought the zinc content in the Nordic and Russian Ural Karst bauxites is as chlorite ($\text{Fe}^{2+} \cdot 1.5\text{AlFe}^{3+} \cdot 0.2\text{Mg} \cdot 0.2\text{Si} \cdot 1.1\text{Ag} \cdot 0.9\text{O}_5 \cdot (\text{OH})_2$). Chinese researchers [1] believe that zinc in Pingguo bauxite exists in the form of sphalerite and smithsonite.

3. Behavior of Zinc in the Bayer Process

3.1 Behavior of Zinc Occurring in Bauxite in the Bayer Digestion Process

The behavior of zinc in bauxite in Bayer digestion is related to its occurrence (concentration and mineral phase), and the dissolution rate mainly depends on its mineral occurrence and digestion conditions. Consequently, the dissolution rate of zinc is different for different digestion conditions and different bauxites. The zinc ore ZnCO_3 can be fully reacted with caustic liquor at a lower temperature, while the zinblende (ZnS) is very stable and does not react with sodium aluminate liquor below 240 $^\circ\text{C}$ [7].

The results of Ostap [8] show that the dissolution of ZnO is low (10-20 %) at low temperature (about 143 $^\circ\text{C}$). He reported that aluminous goethite is dissolved at high temperature with a large

4.2 Physical Methods

To avoid the disadvantages of Bayer liquor contamination by sodium sulfide due to its excessive addition, Paul [29] reported a method to filter out copper and zinc from Bayer process liquors. This method uses high-silica / high-iron bauxite ($A/S = 4.53$) as the raw material, in which the ZnO and CuO content are 0.05 and 0.012 % (in alumina products) respectively. The overflow from settling digestion slurry after the high-pressure digestion (230 °C) was used as a test stock solution, in which the ZnO and CuO contents were 0.025 g/L and 0.015 g/L, respectively. The raw liquid was passed through a cylindrical sand bed filter containing an Fe₂O₃ filter media. The content of Fe₂O₃ in the sand bed should be at least 10%, preferably 40 % to 100 %, the particle size of Fe₂O₃ is 100 to 400 µm, and the thickness of Fe₂O₃ sand bed is at least 38 cm. In addition to Fe₂O₃, the sand bed contains SiO₂, TiO₂, Al₂O₃ and other components. The results show that the zinc removal increases with the height of the sand bed and decreases with the volume of liquor passing through the bed. The stock liquor was passed through the 38.1 cm and 69.1 cm sand beds, and the ZnO content of the alumina product decreased from 0.05 % to 0.033 % and 0.012 % respectively. At the same sand bed height, when the sand bed is coated with a layer of saturated zinc sulfide, the ZnO content in the alumina product can be reduced to 0.006 %. Rinsing the filter bed with 1.0 N hydrochloric acid or dilute sulfuric acid 5 times at room temperature made the sand bed reusable.

The physical (adsorption) method provides good removal, and avoids the adverse effects of the inorganic and organic chemical processes. Unfortunately, the filter layer needs to be periodically cleaned and replaced, so the operation is complicated, the additional operating cost is high, and it is difficult to industrialize.

5. Conclusions

Excessive zinc in alumina products has become a restriction on the development of alumina refineries using Guangxi bauxite as a raw material. Where this bauxite is used for alumina production, zinc removal has therefore become a difficult and urgent topic. It is recommended that, first of all, the mineral forms in which zinc occurs in high-zinc bauxites and their behavior in the Bayer process should be further studied to allow optimisation of the digestion conditions for these bauxites, to inhibit the dissolution of zinc. The objective would be to have a large proportion of bauxite zinc leaving the process with red mud, reducing that accumulating in the process liquor. The development of an organic, environmentally friendly zinc removal technology is recommended as the future zinc control technology development direction. The technology should not only effectively reduce the zinc content in the product, but also avoid the negative impacts on the production process that other methods presently suffer from.

6. References

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