Zinc Removal in Bayer Process Alumina Production – Current Status and Optimization Suggestions

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Abstract

In the Bayer process alumina production, zinc, which enters the sodium aluminate liquor along with other bauxite soluble components, can significantly affect the purity of alumina, thereby influencing the quality of electrolytic aluminium. This paper reviews the sources, behaviours, and removal methods of zinc in the Bayer process. Based on the latest research progress at home and abroad, the paper focuses on the physical and chemical behaviours of zinc during key steps such as bauxite blending, digestion, and precipitation. It proposes optimization suggestions, including improvements to bauxite blending, digestion process, and precipitation control, with the aim of providing theoretical basis and technical support for zinc removal in alumina production.

Keywords: Bayer process, Zinc removal, Review, Impurity control.

Introduction

The Bayer process is the primary method for the industrial production of metallurgical grade alumina. The process involves extracting alumina through steps such as bauxite blending, digestion, and precipitation. However, bauxite often contains impurities like zinc, which can enter the alumina product during the Bayer process, affecting its purity and the quality of subsequent electrolytic aluminium. Zinc, being more electropositive than aluminium, will be preferentially formed during the electrolysis process, leading to a decline in the quality of aluminium ingots. Therefore, it is of great significance to study the behaviour of soluble zinc species and their removal methods during the Bayer process.

1. Sources, Morphology, and Behaviours of Zinc in Sodium Aluminate Solution

Among bauxites at home and abroad, those from mines in Bosnia and Herzegovina contain approximately 0.012–0.025 % of ZnO; for instance the ZnO content in bauxites from the Podgorica and Niksic mines in Montenegro is about 0.035 % and 0.044 %, respectively. In comparison, in some Chinese domestic bauxite deposits, the ZnO content reaches around 0.02 % [1, 2]. During the Bayer process, most zinc impurities in the produced alumina are introduced by the bauxite. In the digestion process, zinc-bearing minerals dissolve in the strong alkali solution and ultimately form ZnO_2^{2-} in the sodium aluminate liquor. While a portion of the zinc impurities is adsorbed by bauxite residue during settling, the majority remains in the liquor. In the subsequent seeded precipitation process, zinc is further adsorbed onto aluminium hydroxide $Al(OH)_3$, also called alumina trihydrate, $Al_2O_3 \cdot 3H_2O$ (ATH)) and thus becomes incorporated into the alumina product. Eventually, it enters the aluminium metal during electrolysis, thereby reducing the purity of the aluminium product [2].

Internationally, there are strict requirements for the purity of electrolytic aluminium. The total impurity content in the highest-grade primary aluminium must not exceed 0.015 %, and the zinc content in alumina must not exceed 0.01 % [3], both expressed as ZnO. To meet this standard, the zinc content in the Bayer liquor must be controlled to below 15 mg/L during alumina production [4]. Therefore, adopting effective technical measures to remove zinc impurities and reduce their content in alumina products can enhance the efficiency of aluminium electrolysis and lay a solid foundation for producing high-purity aluminium.

2. Main Methods for Zinc Removal

In the alumina production process, commonly used zinc removal technologies include the sodium sulphide method, dithiocarbamate method, high-sulphur bauxite method, improved filtration method, and dilution desilication method. This section provides a brief introduction to these five methods.

2.1 Sulphide Method

The sulphide method is currently the most widely used method for zinc removal. By adding sodium sulphide (Na_2S), zinc ions react with sulphide ions to form insoluble ZnS precipitates. In the Bayer liquor, zinc mainly exists in the form of ZnO_2^{2-}. In strong alkaline solutions, a small portion exists in the forms of Zn^{2+} and $HZnO_2^-$, with the following hydrolysis reactions predominantly occurring [5]. When sodium sulphide is added, Zn^{2+} reacts with S^{2-} to form ZnS. The solubility product constant of ZnS is very small, only 2×10^{-24}, making it almost insoluble in the Bayer liquor.

$$ZnO_2^{2-} + 2H_2O \leftrightharpoons Zn^{2+} + 4OH^- \quad (1)$$

$$HZnO_2^- + H_2O \leftrightharpoons Zn^{2+} + 3OH^- \quad (2)$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS\downarrow \quad (3)$$

2.2 Dithiocarbamate Method

The dithiocarbamate method is efficient for zinc removal. Dithiocarbamates act as heavy metal chelating agents capable of effectively removing various heavy metal ions. The reaction principle is that the sulphur atoms in the polar dithio groups of dithiocarbamates possess lone pairs of electrons that are easily polarized to generate a negative electric field. According to the ligand field theory, the dithiocarbamate groups can capture cations and tend to form bonds, coordinating with divalent heavy metal ions (Cu and Zn) into planar square or regular tetrahedral configurations. The ligands chelated to the same metal ion come from different dithiocarbamate molecules, resulting in highly cross-linked three-dimensional structures. These stable and cross-linked networking heavy metal ion chelates ultimately precipitate, removing heavy metal impurities [6].

Zinc mainly exists in the form of ZnO_2^{2-} in the Bayer liquor. In the Bayer liquor, ZnO_2^{2-} undergoes hydrolysis equilibrium:

$$ZnO_2^{2-} + 2H_2O \leftrightharpoons Zn^{2+} + 4OH^- \quad (4)$$

When sodium dimethyldithiocarbamate is added, the dimethyldithiocarbamate molecules react with zinc ions in the Bayer liquor to form zinc dimethyldithiocarbamate chelates, thereby removing zinc.

$$2(CH_3)_2NCSS^- + Zn^{2+} \rightarrow ((CH_3)_2NCSS)_2Zn \quad (5)$$

Therefore, it is necessary to adapt to local conditions. In regions rich in high-sulphur bauxite, adding a certain proportion of high-sulphur bauxite during the bauxite blending stage is a simple process that does not require additional equipment or processes, and has certain cost advantages. In the digestion stage, the sodium sulphide method for zinc removal is not suitable for long-term continuous use. However, properly controlling the dosing cycle and increasing the digestion temperature can still achieve effective zinc removal. In the precipitation stage, adding crystallization aids can help remove zinc and improve the precipitation rate, but it is important to enhance the selectivity of crystallization aids to reduce alumina loss.

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6. References

1. Oljača, Đurđa et al., Removal of zinc from Bayer liquor using aluminium hydroxide with specific structural properties as a crystallizing agent, *Proceedings of the 12th Conference of Chemists*, *Technologists and Environmentalists of the Republic of Srpska*, (2018), 155–158.
2. Qingxiang Zhang, et al., Existence forms and removal of zinc in alumina production process, *Journal of Central South University of Technology*, Vol. 30, Issue 6, (1999), 589–591 (in Chinese).
3. Hrishikesan K G, Kane J F, Teas E B et al., Treatment of digested slurry by Bayer process, *U.S. Patent 3,469,935*, filed on September 30, 1969.
4. Bing Jiang, Study on zinc removal by sulphides in the Bayer process, Hunan Province: Central South University, 2006 (in Chinese).
5. Junfu Li, et al., Research status on removal of zinc impurities in alumina production by Bayer process, *Mining and Metallurgy*, Vol. 26, Issue 2, (2017), 59–63 (in Chinese).
6. Yingjie Shi, et al., Application of dithiocarbamates in zinc removal from Bayer liquor, *Modern Chemical Industry*, Vol. 37, Issue 6, (2017), 72–74 (in Chinese).
7. Paulj, Removal of copper and zinc species from Bayer process liquor by filtration, *U.S. Patent 4,414,115*, filed on November 8, 1983.
8. Zhenglin Zhang, Xiaotao Lu, Study on zinc removal technology in alumina production by Bayer process, *Light Metals*, Issue 11, (2021), 20–25 (in Chinese).
9. Wenmi Chen, et al., Zinc removal by adding pyrite during bauxite digestion, *Light Metals*, Issue 10, (2006), 21–24 (in Chinese).
10. Xiaolian Hu, Wenmi Chen, Daojin Cao, Phase study of sulphur in high-sulphur bauxite and its application in zinc removal during bauxite digestion, *Journal of Hunan University of Science and Technology (Natural Science Edition)*, Vol. 24, Issue 2, (2009), 79–83 (in Chinese).
11. Baowei Liu, et al., A method for removing impurity zinc oxide from industrial sodium aluminate solution, *Chinese Patent 101,913,631 A*, filed on August 9, 2010 (in Chinese).
12. Hrishikesan K. G., Removal of Zinc, *U.S. Patent US 3,445,186*, filed on May 20, 1969.
13. Xu, Lei, et al., Effect of zinc (ii) and caustic soda content on the precipitation of sodium aluminate liquor and its relevance to the Bayer process, *Hydrometallurgy*, Vol. 225, (2024), 106287 (in Chinese).
14. Guipeng Diao, Analysis on the necessity of upgrading and renovating the digestion system of Jamaica Alpart Alumina Refinery, *China Chemical Trade*, Issue 2, (2021), 226–229 (in Chinese).