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.

$$ZnO_2^{2-} + 2H_2O \leftrightharpoons Zn^{2+} + 4OH^- \tag{1}$$

$$HZnO_2^- + H_2O \leftrightharpoons Zn^{2+} + 3OH^- \tag{2}$$

$$Zn^{2+} + S^{2-} \rightarrow ZnS\downarrow \tag{3}$$

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:

$$ZnO_2^{2-} + 2H_2O \leftrightharpoons Zn^{2+} + 4OH^- \tag{4}$$

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

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

2.3 High-sulphur Bauxite Method

In the high-sulphur bauxite method for zinc removal, the pyrite present in bauxite is used to remove zinc through sulphur. Since the amount of free Zn^{2+} in the Bayer liquor is very low, an excess of sulphur is required to remove zinc from the sodium aluminate liquor. During the bauxite digestion process, if high-sulphur bauxite containing pyrite is added, the pyrite reacts with soda under high temperature and high pressure, releasing a large amount of sulphur into the liquor. In the liquor, sulphur mainly exists in the form of S^{2-}. The main reaction takes place as per Equation (6) [5].

$$30NaOH + 8FeS_2 \rightarrow 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O \tag{6}$$

Sodium sulphide then reacts with zinc in the alkaline solution to form ZnS precipitates (see Equation (3)). ZnS is subsequently adsorbed by bauxite residue and removed together with it.

2.4 Improved Filtration Method

Currently, most zinc removal technologies both domestically and internationally adopt the sulphide precipitation method, which inevitably leads to the introduction of sulphur impurities. Using filtration devices to remove zinc can effectively address this issue. The principle relies on the adsorption effect of Fe_2O_3 on impurities such as zinc. The filtration device shown in Figure 1 was designed by Paulj et al. [7]. The sodium aluminate liquor enters through inlet 8 and flows into filter layer 5, which is packed with Fe_2O_3, with an Fe_2O_3 content of at least 10 %, and ideally a in a 40–100 % range. The iron oxide particle size ranges from 100–400 microns, and the filter layer must also meet certain height requirements, with a minimum of 38 cm. The filtered sodium aluminate liquor exits through outlet 12, while impurities such as Zn and Cu are removed in the filter layer. Through this filtration device, the zinc content in the sodium aluminate liquor is reduced from 24 to 5–9 mg/L. However, because the filter layer requires regular cleaning and replacement, and the equipment is prone to corrosion by acids and soda, periodic replacement is necessary. This increases the operational complexity and cost of alumina refineries.

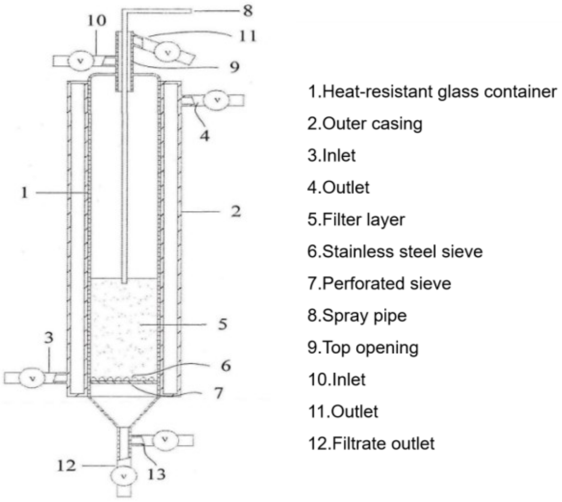


Figure 1. Schematic diagram of the filtration device [7].

2.5 Dilution Desilication Method

In the dilution desilication stage (90–100 °C) of the Bayer process alumina production, the addition of zinc removal agents (such as sodium sulphide) can effectively remove zinc. The reaction forming the insoluble ZnS precipitate was shown previously, see equation (3). The ZnS precipitate is settled and separated together with bauxite residue, thus being removed from the process.

Compared to the high-temperature digestion stage, the lower temperature environment in the dilution stage is more favourable for the complete sulphidation reaction, avoiding the precipitation or reverse reaction of zinc sulphide caused by high temperature.

3. Optimization Suggestions for Zinc Removal

Based on the five main zinc removal methods described above and considering the actual conditions of the alumina production process, this paper proposes an optimized solution.

3.1 Optimization of Bauxite Blending

The zinc removal performance can be enhanced by adding high-sulphur bauxite through bauxite blending and the initial zinc concentration can be reduced. Zhenglin Zhang et al. [8] added high-sulphur bauxite during material preparation. After mixing the two types of bauxites with lime and spent liquor, zinc was removed using the high-sulphur bauxite method during the digestion process. The results showed that, compared to the case without adding high-sulphur bauxite, the Zn concentration in the pregnant liquor gradually decreased as the amount of high-sulphur bauxite increased (see Figure 2). When calculating the zinc removal rate relative to the scenario without high-sulphur bauxite, the removal rate rose from 4.92 % to 43.15 % as the sulphur content in the blended bauxite increased from 0.2 % to 0.5 % (see Figure 3). Properly incorporating high-sulphur bauxite during production can help achieve zinc removal to a certain extent.

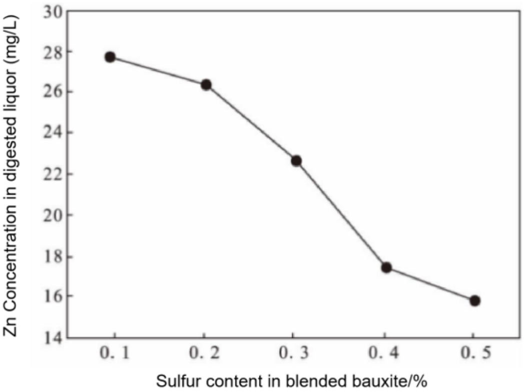


Figure 2. Effect of high-sulphur bauxite addition on Zn concentration in digested liquor (Nk = 210 g/L) [8].

Wenlei Chen, Bing Jiang, et al. [9] added pyrite for zinc removal during the digestion process. When the addition amount of pyrite reached 4 mg/L, the zinc content in the digested liquor decreased from 70 mg/L to 10 mg/L.

Xiaolian Hu, Wenmi Chen, et al. [10] blended high-sulphur bauxite for zinc removal during the digestion process. When the high-sulphur bauxite accounted for 10–20 % of the total bauxite, the zinc removal effect was significant, reducing the zinc content in the digested liquor to below

15 mg/L. It was also proved that adding high-sulphur bauxite had no impact on the digestion of alumina.

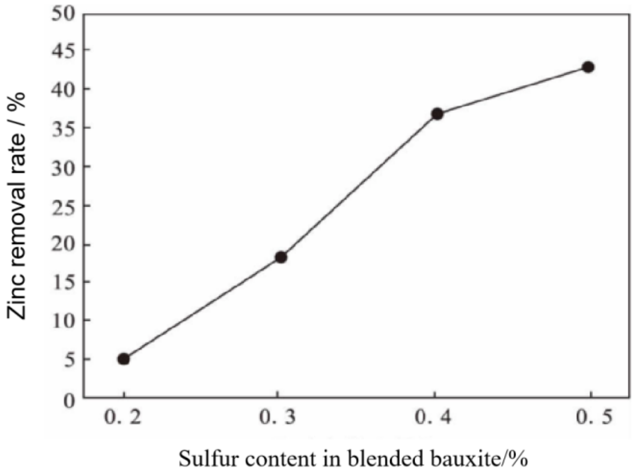


Figure 3. Effect of high-sulphur bauxite addition on Zinc Removal Rate [8].

Properly blending high-sulphur bauxite during production can achieve a certain degree of zinc removal. However, attention must be paid to the addition method and the amount of high-sulphur bauxite added. In actual operation, if high-sulphur bauxite is added continuously for zinc removal, and the concentration of sodium sulphate in the liquor exceeds 8 g/L, issues such as excessive turbidity and scaling may occur [5]. After adding high-sulphur bauxite, the sulphur content in the blended bauxite in the form of pyrite should not exceed 0.5 % to prevent sulphur from forming soluble FeS [11], which could increase the Fe content in the liquor and likely lead to secondary contamination of the alumina product.

3.2 Improvement of the Digestion Process

In the digestion process, optimizing the amount of sulphides added and the reaction temperature can significantly enhance zinc removal efficiency. Hrishikesam et al. [12] added Na_2S during digestion for zinc removal. With only 0.18 g/L of Na_2S, the zinc content in the digested liquor was reduced from 24 to 10 mg/L. After subsequent bauxite residue filtration, the zinc content further decreased from 10 to only 6 mg/L.

However, in actual operation, the required addition amount of sodium sulphide is much higher than the theoretical amount. Introducing excessive sulphide ions increases the sulphur content in the Bayer cycle system. These sulphur impurities will be gradually oxidized to form sodium sulphate, which can adversely affect alumina production. The ZnS precipitates formed by the reaction between Na_2S and Zn impurities in the Bayer liquor have very small particle sizes and tend to form colloids that are difficult to remove by filtration. As a result, some ZnS will bypass the zinc removal stage and carry over into subsequent processes, ultimately reducing the overall zinc removal efficiency.

To address some of the issues associated with the sulphide method, Zhenglin Zhang and Xiaotao Lu [8] studied the effect of different digestion temperatures on zinc removal by sodium sulphide, aiming to mitigate the negative impact of sulphur introduction (see Figures 4 and 5). As illustrated, when the digestion temperature was increased from 260 to 275 °C, the zinc concentration in the digested liquor gradually decreased, while the zinc removal rate gradually increased. With a sodium sulphide dosage of 0.7 g/L, the zinc concentration in the digested liquor decreased from 19.42 to 6.70 mg/L, and the zinc removal rate rose from 16.08 to 74.36 %. Similarly, with a sodium sulphide dosage of 0.9 g/L, the zinc concentration in the digested liquor further dropped from 14.86 to 4.93 mg/L, and the zinc removal rate increased from 35.78 to 81.15 %. Raising the digestion temperature accelerates the reaction between S^{2-} and Zn^{2+} to form the ZnS precipitates, thereby enhancing zinc removal efficiency. Therefore, in the initial operation stage of the digestion trains, maintaining a higher digestion temperature can improve the zinc removal efficiency and reduce equipment corrosion by sulphur, thus achieving better overall results.

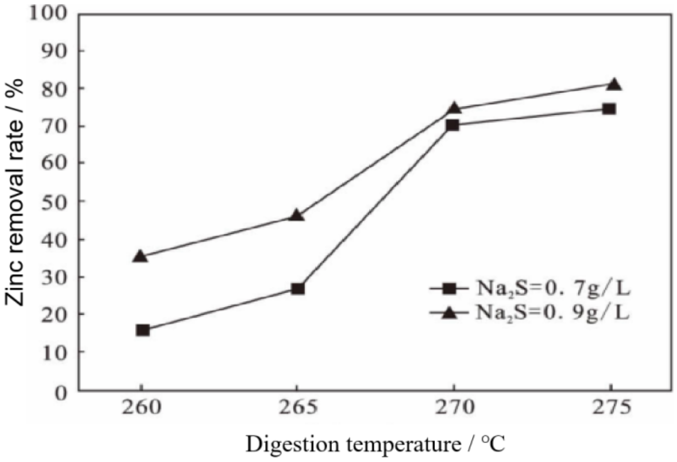


Figure 4. Effect of digestion temperature on zinc removal rate [8].

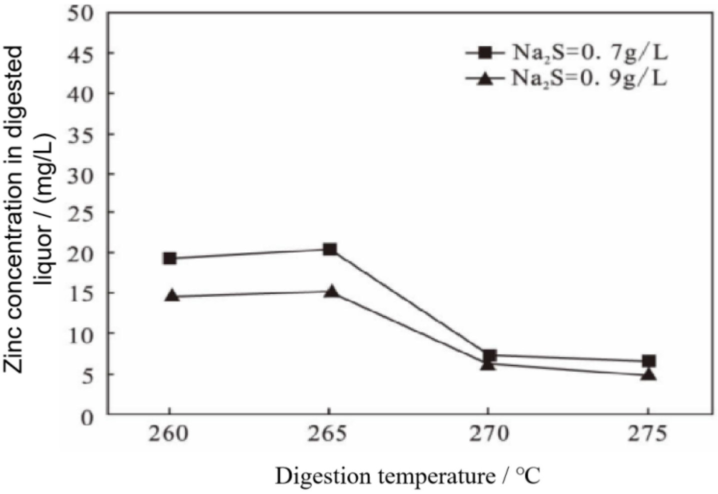


Figure 5. Effect of digestion temperature on zinc concentration in pregnant liquor (Nk = 210 g/L) [8].

Yingjie Shi [6] proposed the Na_2S-flocculation method. Under the conditions that the dosage of Na_2S is 0.5 g/L, the flocculant is added at 0.1 %, the reaction temperature is 60 °C, and the reaction time is 2 hours, the zinc concentration can be reduced from 70 to 10 mg/L. The principle is that after adding the flocculant, colloidal particles aggregate into larger particles. When ZnS colloidal particles continuously coagulate, the zinc removal reaction proceeds more rapidly, and the utilization rate of S^{2-} is greatly improved, effectively addressing the problems of slow settling and low zinc removal efficiency.

3.3 Control of Precipitation Process

After Zn is digested, it enters the seed precipitation stage with the solution and becomes absorbed onto the surface of ATH, which adversely affects both the morphology and precipitation rate of ATH.

Lei Xu et al. [13] conducted an in-depth study on the mechanism by which zinc ions affect the precipitation process of sodium aluminate solution, shown in Figure 6. A zinc-containing simulated liquor was prepared and the zinc-containing ATH seeds were characterized using infrared spectroscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM), as shown in Figures 7–9. From the infrared spectrum in Figure 7, it can be seen that the intensity of the Zn-O bond at 453 cm^{-1} increases with rising zinc concentration in the liquor, indicating that Zn (II) can enter the ATH. The XRD spectrum in Figure 8 shows that Zn (II) interacts with the crystal planes of α-ATH, affecting its crystal growth, while it has little effect on the crystal planes of β-ATH. Notably, no ZnO crystals appear, indicating that Zn mainly enters the α-ATH crystals and may affect their formation. As seen in Figure 9(b), many fine particles adhere to the surface of ATH as the Zn concentration increases to 1000 mg/g. These small particles act as "binders", leading to an increase in the particle size of the ATH seeds.

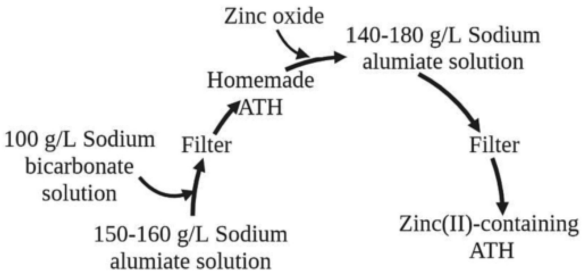


Figure 6. Schematic flow diagram of the preparation of simulated zinc-containing sodium aluminate solution and seed precipitation test [13].

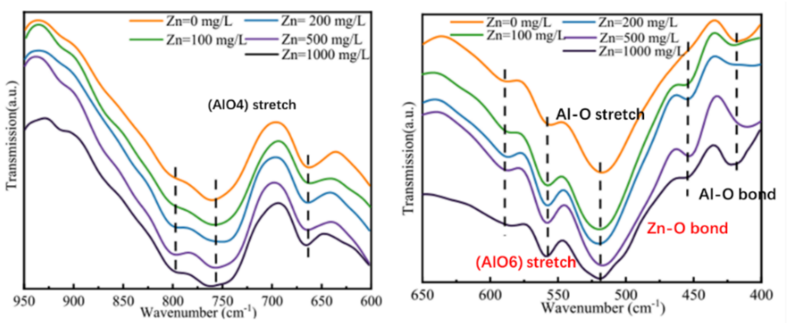


Figure 7. Infrared spectrogram of ATH seeds obtained by precipitation from zinc-containing sodium aluminate solution with Nk value of 177 g/L [13].

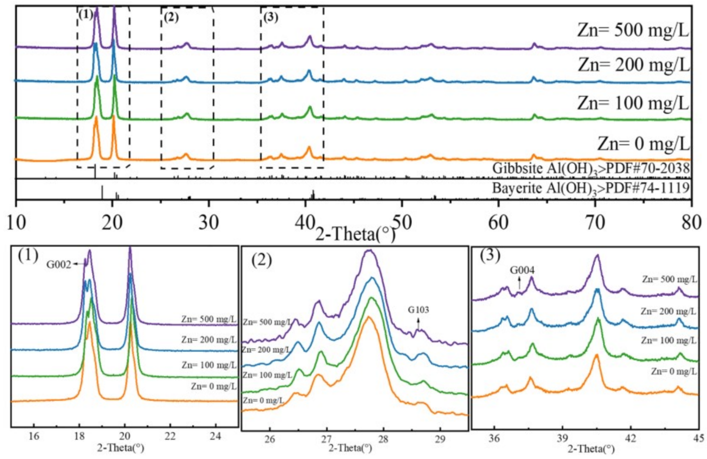
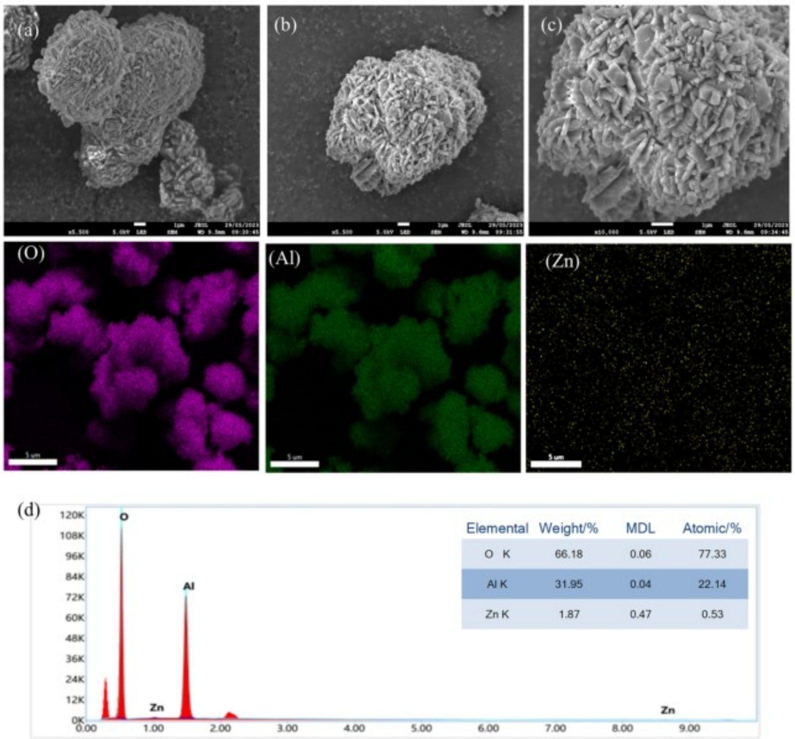


Figure 8. XRD spectrum of ATH seeds obtained by precipitation from zinc-containing sodium aluminate solution with Nk value of 177 g/L [13].



Elemental	Weight/%	MDL	Atomic/%
O K	66.18	0.06	77.33
Al K	31.95	0.04	22.14
Zn K	1.87	0.47	0.53

Figure 9. Morphology of ATH after precipitation from zinc-containing sodium aluminate solution: (a) Zn(II) = 0 g/L, Nk = 177 g/L; (b) and (c) Zn(II) = 1000 mg/L, Nk = 177 g/L; (d) Element distribution in ATH seed particles [13].

Based on the infrared, XRD and SEM-EDX characterizations, it can be concluded that morphological and structural analyses indicate that Zn(II) may form new complexation relationships with $Al(OH)_6$ octahedra in the alkaline solution, as shown in Figure 10. These interactions affect the precipitation behaviour of the sodium aluminate solution and promote the agglomeration of fine seeds.

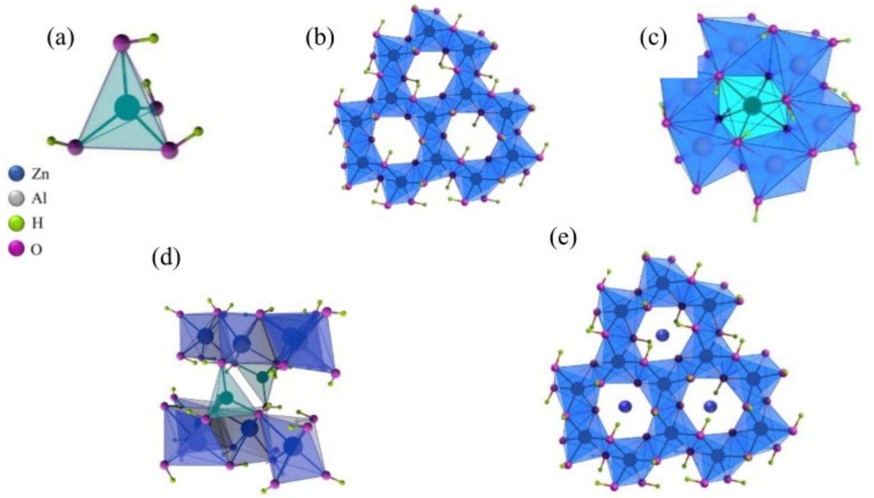


Figure 10. Schematic diagrams of the structures of $Zn(OH)_4$ and $Al(OH)_6$ and possible mechanisms. Images are 4D renderings generated with Diamond and Cinema: (a) $Zn(OH)_4^{2-}$; (b) $Al(OH)_6$; (c) Octahedral structure with $Zn(OH)_4^{2-}$ aggregated at the center, similar to $Al(OH)_6$ units and hydrotalcite; (d) Co-precipitation resembling $ZnAl_2O_4^-$-ATH; (e) Zn^{2+} ions enter ATH seeds and occupy vacancies, which may promote precipitation and fine particles aggregation [13].

The research group also investigated the effect of different pregnant liquor Nk values on the seed precipitation rate. As shown in Figure 11, the results indicate that Nk plays a critical role in modulating the influence of Zn(II) on the precipitation of sodium aluminate liquor, which can be summarized as follows.

- At lower Zn(II) concentrations of 100 and 200 mg/L, change in ATH zinc content during precipitation at various Nk values is negligible.
- At Zn(II) concentrations of 500 and 1000 mg/L, with an Nk value of 141 g/L, the ATH zinc content decreases slightly as precipitation time extends.
- The higher the Zn(II) concentration, the more pronounced this decrease becomes (Figure 11(a)).
- For an Nk of 160 g/L, the ATH zinc content increases slightly at longer precipitation times.
- For an Nk of 177 g/L, the ATH zinc content increases gradually with at longer precipitation times and this increase in zinc content becomes more significant with the increase of Zn(II) concentration (Figure 11(c)).

These studies therefore suggest a potential correlation between increased ATH zinc content and larger particle sizes.

This present study elucidated the mechanism by which zinc ions influence the precipitation process of ATH and proposed regulating the alkali concentration of the pregnant liquor as an effective approach to improve the quality of ATH products and control the particle size of ATH. In addition, by adding crystallization aids and controlling the Na_2O/Al_2O_3 ratio, zinc in the sodium aluminate liquor can be removed along with bauxite residue, thereby ensuring the purity of the alumina product.

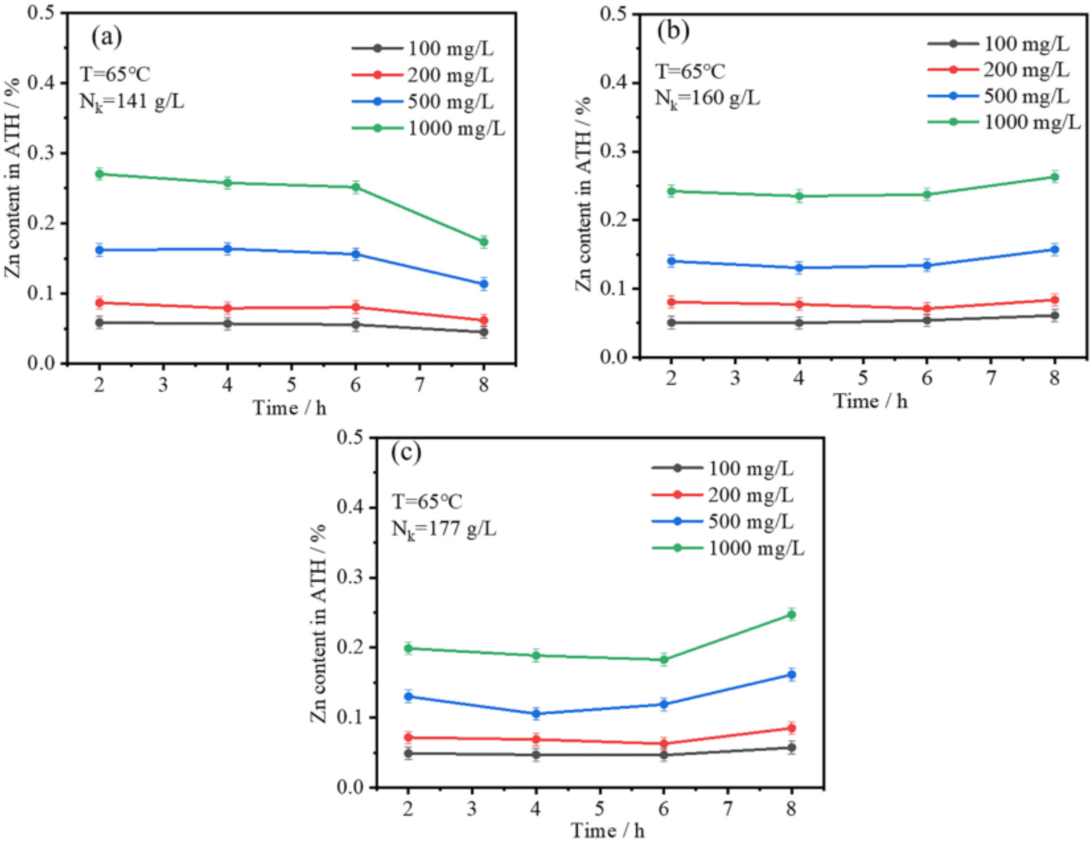


Figure 11. Trends in Zn(II) incorporation (%) in ATH at Nk values of (a) 141 g/L, (b) 160 g/L, and (c) 177 g/L [13].

Durda et al. [1] removed Zn from sodium aluminate liquor by adding fine ATH seeds with a special structure. The results showed that at 50 °C, when the concentration of these specially structured fine ATH seeds exceeded 15 g/m^3, the Zn content in the sodium aluminate liquor decreased from 66 to 11 mg/L within 2 hours, achieving a zinc removal rate of 80 %. However, while removing zinc, this method also led to 20 % alumina losses. In addition, this crystallization aid could only be used at most twice. Therefore, it is necessary to modify the structure of the crystallization aid to extend its service life and further reduce costs.

4. Conclusions and Prospects

Zinc removal is a key technical challenge in the production of alumina by the Bayer process. The zinc impurity content can be effectively reduced and the quality of alumina products can be improved by optimizing bauxite blending, improving the digestion process, and controlling the precipitation process.

Based on the general Bayer process, production data from some alumina refineries [14] illustrate that the zinc impurity content can be controlled through three processes. In the digestion process, when the digestion temperature is controlled at 270 °C and 0.9 g/L sodium sulphide is added, the zinc removal rate reaches 81.15 %. In the dilution stage, adding 0.5 g/L sodium sulphide yields an even higher and more efficient zinc removal rate of 90.23 %. In the digestion stage, when high-sulphur bauxite is added and the sulphur content in the blended bauxite is 0.4 %, the zinc removal rate is 36.92 %. This method is more economical but less efficient.

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.

5. Acknowledgements

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