Industrial Application of Sodium Nitrate Oxidation Treatment Technology for High-Sulphur Bauxite

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Abstract

With the rapid development of China's alumina industry, its alumina output in 2024 already accounted for 56 % of the world's total. However, as domestic high-quality bauxite resources are increasingly depleted, a large amount of high-sulphur bauxite cannot be directly used in alumina production due to its severe impacts on product quality and equipment corrosion during the Bayer process, becoming a bottleneck restricting the sustainable development of the industry. To address this technical challenge, this paper analyses the oxidation mechanism of sulphur during the digestion of the Bayer process and conducts experimental research on oxidative desulphurization using sodium nitrate ($NaNO_3$). After 12 months of continuous operation verification in a 1-Mtpa alumina production line, the results demonstrate that when the sulphur content in bauxite does not exceed 0.5 %, adding sodium nitrate during the bauxite blending process can effectively eliminate the influence of low-valence sulphur, ensuring the iron content in alumina products remains within the first-grade standard. This technology is simple, technically feasible, economically reasonable, and can be promoted in industrial production using high-sulphur bauxite.

Keywords: High-sulphur bauxite, Bayer process, Sodium nitrate, Oxidative desulphurization.

1. Introduction

With the rapid development of China's alumina industry, its alumina output in 2024 already accounted for 56 % of the world's total. However, domestic bauxite-based alumina refineries generally face an increasingly acute shortage of high-quality bauxite resources, while simultaneously sitting on massive reserves of high-sulphur, high-carbon bauxite that cannot be directly processed via the Bayer process. According to statistics, China has proven reserves of high-sulphur, high-carbon bauxite amounting to hundreds of millions of tonnes. During high-temperature and high-pressure digestion, sulphur (mainly in low-valence forms) and organic carbon extensively dissolve into the solution, leading to increased viscosity, reduced precipitation efficiency, difficulties in evaporation and salt removal, elevated iron content in aluminium hydroxide products, and diminished whiteness. Additionally, these issues cause severe equipment corrosion and tank leakage problems.

To address the negative impact of sulphur in high-sulphur bauxite on alumina production, flotation desulphurization is applied at the front end of the process, while roasting-based pyrometallurgical desulphurization and wet oxidation desulphurization are primarily employed during alumina production. Other methods, such as electrolytic desulphurization, are also under research [1, 2]. Both flotation desulphurization and roasting desulphurization require the construction of large-scale production units in industrial applications, with investments exceeding hundreds of millions of RMB and high operational costs. Additionally, flotation desulphurization introduces significant amounts of attached water and flotation reagents into the bauxite concentrate, while roasting desulphurization suffers from relatively high energy consumption.

Regarding this technical challenge, this paper analyses the oxidation mechanism of sulphur during the digestion of the Bayer process. Experimental studies were conducted by adding sodium nitrate as an oxidant. After 12 months of industrial application in a 1-Mtpa alumina production line, the results demonstrate that when the sulphur content in bauxite does not exceed 0.5 %, the addition of sodium nitrate during bauxite blending can eliminate the impact of low-valence sulphur, ensuring the iron content in the alumina product remains within the premium-grade range. This technology does not require the construction of large-scale treatment facilities, as sodium nitrate can be directly mixed into the raw materials. It is simple, effective, and suitable for widespread adoption in alumina refineries utilizing high-sulphur bauxite.

2. Oxidation Mechanism of Sulphur in Digestion of Bayer Process

The high-sulphur and high-carbon bauxite in China is primarily of the diaspore type, where the sulphur-bearing minerals are mainly pyrite, and the organic carbon consists largely of humic acid and similar compounds. Xiaobin Li, Wankun Chen, Guozhi Lv, et al. [3, 5] conducted a systematic study on the reaction behaviour of pyrite and the behaviour of sulphur in Bayer liquor. Under high-temperature digestion conditions at 260–270 °C, pyrite reacts with caustic soda in sodium aluminate solution, with sulphur primarily entering the solution as S^{2-}, while the remainder exists as S_2^{2-}, $S_2O_3^{2-}$, SO_3^{2-}, and SO_4^{2-}. Most of the organic carbon in the bauxite enters the sodium aluminate solution in the form of high-molecular-chain compounds such as humic acid, which can easily accumulate to high concentrations, darkening the colour of the sodium aluminate solution, sometimes even turning it a dark soy-sauce black. The main reaction between pyrite and sodium hydroxide during the digestion of high-sulphur bauxite is as follows:

$$8FeS_2 + 30NaOH = 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O \quad (1)$$

$$6FeS_2 + 22NaOH = Fe_2O_4 + 10Na_2S + Na_2S_2O_3 + 11H_2O \quad (2)$$

$$3FeS_2 + 8NaOH = Fe_2O_4 + 3Na_2S + Na_2S_2 + 4H_2O \quad (3)$$

With the increase in temperature, the stability of sodium thiosulphate decreases, leading to its decomposition during the high-temperature digestion process.

$$3Na_2S_2O_3 + 6NaOH = 2Na_2S + 4Na_2SO_3 + 3H_2O \quad (4)$$

$$Na_2S_2O_3 + 2NaOH = Na_2S + Na_2SO_4 + H_2O \quad (5)$$

Under conditions where no oxygen or other oxidizing agents are added, reactions (1)–(3) dominate, while further oxidation to higher-valence sulphur (SO_4^{2-}) becomes considerably more challenging. Reactions (4) and (5) represent the secondary oxidation of intermediate sulphur species generated during the reaction between pyrite and caustic soda, requiring higher temperatures and prolonged durations. Notably, reaction (5) is even more unfavourable than (4).

Wenmi Chen et al. [6, 10], conducted laboratory studies on the oxidation of low-valence sulphur and organics in solutions under different temperature conditions, employing atmospheric and high-pressure wet processes with the addition of oxidants such as oxygen, hydrogen peroxide, and metal oxides. All methods achieved favourable oxidation results. In reactions involving oxygen, the primary oxidation process proceeds as follows:

$$2Na_2S + 2O_2 + H_2O = Na_2S_2O_3 + 2NaOH \quad (6)$$

$$Na_2S_2O_3 + 2O_2 + 2NaOH = 2Na_2SO_4 + H_2O \quad (7)$$

absorbance. As shown in the figure above, under industrial testing conditions without excess sodium nitrate addition, the absorbance trend curves of the test group and the blank group largely overlap, indicating a minimal oxidation effect. The statistical average shows only a 1.3 % reduction, demonstrating that organics are hardly oxidized by sodium nitrate under actual industrial production conditions. To enhance the oxidation of organics, a significant excess of sodium nitrate would be required. However, excessive NO_3^- would enter the bauxite residue in the form of double salts, increasing losses and raising costs. Therefore, alternative methods for organic removal must be explored.

4. Conclusions and Recommendations

The use of high-sulphur bauxite for alumina production can be effectively and simply controlled by adding sodium nitrate during the bauxite blending process to mitigate the adverse effects of sulphur. During the oxidation process, S^{2-} in the slurry is first oxidized to $S_2O_3^{2-}$, then further oxidized to SO_3^{2-} and SO_4^{2-}. Increasing the dosage of sodium nitrate, raising the reaction temperature, and prolonging the reaction time help enhance the oxidation degree of sulphur and improve the oxidation effects. The oxidation of S^{2-} in the solution reduces the formation of sodium hydroxythioferrate, thereby decreasing the dissolved iron content in the solution. Additionally, NaOH is generated as a byproduct in the oxidation reaction involving $NaNO_3$, which can partially compensate for soda consumption. According to industrial test results, when the sulphur content in bauxite does not exceed 0.5 %, the adverse effects of sulphur on alumina production can be effectively controlled by adding sodium nitrate to oxidize low-valence sulphur. This method proves to be a simple and effective solution for alumina refineries that process bauxite containing minor high-sulphur bauxite or intentionally blend small amounts of high-sulphur bauxite to compensate for raw material shortages. With this technology, the S^{2-} concentration in pregnant liquor can be maintained within safe limits, the iron oxide content in final products meets quality standards, and the additional cost remains acceptable. This technique is recommended for promotion and application by domestic high-temperature Bayer refineries utilizing high-sulphur bauxite.

5. References

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