Calcification Transformation Process of High-Iron Red Mud for Sustainable Alumina Production

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Abstract

The Bayer process is the predominant process for global alumina production, resulting in the generation of a significant volume of highly alkaline red mud. The absence of cost-effective treatment techniques has led to the stockpiling of most red mud, which poses a serious ecological threat due to its high alkalinity. This paper addresses the global challenge of red mud generated from alumina production by proposing a novel approach for its low-cost and large-scale utilization, focusing on mineral phase reconstruction and high-value end products. A new technology, the "calcification-transformation" process, has been developed based on the leaching characteristics of the Bayer process and the mineral structure of red mud. This process can effectively utilize red mud and facilitate the synergistic extraction of valuable elements contained within it. A comprehensive investigation has been conducted to examine how various parameters of the calcification-transformation process influence its effectiveness. Utilizing X-ray fluorescence (XRF), X-ray diffraction (XRD), and scanning electron microscopy (SEM), the chemical compositions, phase compositions, and microstructures of red mud and the slag produced at each stage of the calcification-transformation process were analyzed. The results indicate that temperature and the calcium-to-silicon ratio significantly affect the calcification process. Specifically, at a calcination temperature of 260 °C, with a calcium-to-silicon ratio of 2, a caustic soda concentration of 230 g/L, a molecular ratio of sodium aluminate solution, a liquid-to-solid ratio of 4:1, and a reaction time of 60 minutes, the Na_2O and A/S in the calcined slag were found to be 0.61 % and 1, respectively. The transformed slag can be utilized to produce iron-making pellets, providing high-quality raw materials for the steel industry. This process not only reduces the demand for iron ore mining but also promotes the comprehensive utilization of red mud. This technology is essential for alleviating existing red mud stockpiles and fostering sustainable alumina production within the industry.

Keywords: Environmentally friendly, Red mud, Calcification transformation, Complete treatment, Mine phase reconstruction.

1. Introduction

Red mud (also called bauxite residue) is a highly alkaline solid waste produced during the alumina extraction process [1, 2]. The quantity of red mud generated varies based on the source, grade, and processing methods of bauxite, typically ranging from 1.5 to 2.5 tonnes per tonne of alumina produced [3]. In recent years, the rapid expansion of the alumina industry has led to an increase in the volume of red mud discharged [4]. Currently, the global stockpile of red mud exceeds 4 Gt and continues to grow at a rate of 180 Mt annually. Notably, China's red mud stockpile has surpassed 600 Mt. The global average utilization rate of red mud stands at 15 %, while in China, this rate is only 4 % [5]. At present, red mud is primarily managed through the dry stacking method, which not only causes infiltration and pollution of surface and groundwater but also contaminates the air and soil, posing significant hazards to the surrounding environment and wildlife, and creating safety risks [1, 6, 7]. The 2010 collapse of the red mud dam at the Ajka alumina plant in Hungary resulted in ten fatalities include three missing persons, with the highly alkaline red mud severely impacting several European countries along the Danube River. This incident served as a wake-up call for the alumina industry worldwide [8].

Red mud can be categorized based on the production process into three types: sintering process red mud, Bayer process red mud, and combined process red mud [9]. The Bayer process accounts for over 90 % of global alumina production [10]. The primary chemical components found in red mud include Al_2O_3, SiO_2, Fe_2O_3, CaO, TiO_2, Na_2O, and MgO, along with trace elements such as K, Ga, Mn, Ni, V, and rare earth elements [11]. The concentration of these main chemical components varies among different types of red mud, influenced by the alumina production processes and the raw materials sourced from bauxite ore [12]. Table 1 below illustrates the composition of red mud derived from various processes and origins. Notably, red mud produced by the Bayer process exhibits higher concentrations of Na_2O, Al_2O_3, and Fe_2O_3 when compared to that from the sintering or combined processes. In contrast, red mud from the sintering or combined processes typically shows elevated levels of SiO_2 and CaO relative to the Bayer process.

Table 1. Comparison of main components of typical Bayer process red mud, sintering process red mud, and combined process red mud (wt%).

Method	Bayer process			Sintering method			Combined process	
Location	Gui Zhou	Guang Xi	Queensland	Gui Zhou	Shan Dong	Shan Xi	He Nan	Shan Xi
Na_2O	4.0	4.0	4–10	3.1	2.8	2.60	2.58–3.68	2.6–3.4
Al_2O_3	32.0	17.47	15–20	8.5	6.4	8.22	5.96–8	8.2–12.8
SiO_2	12.8	11.93	24–29	25.9	22.00	21.43	18.9–20.7	21.4–23
CaO	22.0	14.13	0.5–4	38.4	41.90	46.80	39–43.3	37.7–46.8
Fe_2O_3	3.4	32.47	21–36	5.0	9.02	8.12	10–12.6	5.4–8.1
MgO	3.9	-	0.5–1	1.5	1.70	2.03	2.15–2.6	2.0–2.9
K_2O	0.2	1.0	-	0.2	0.30	0.20	0.47–0.59	0.2–1.5
TiO_2	6.5	5.45	-	4.4	3.20	2.90	6.13–6.7	2.2–2.9
LOI	10.7	9.46	7–12	11.1	11.70	8.00	6.5–8.15	8.0–12.8
Others	4.5	4.09	-	1.9	0.98	-	-	-

The iron content in red mud generated from the Bayer process for alumina production is typically high, with some samples exceeding 30 % total iron content. The combined content of Fe_2O_3 and Al_2O_3 can reach as high as 50 %, positioning red mud as a valuable secondary resource for iron and aluminum [13]. The recovery and utilization of valuable metals, such as iron and aluminum, represent significant pathways for the resource utilization of high-iron red mud [12]. Extensive research has been conducted both domestically and internationally on the recovery of iron from high-iron red mud, primarily utilizing physical separation methods [14], hydrometallurgical recovery [15], and pyrometallurgical recovery [16]. While physical separation methods are straightforward and easy to operate, they yield a low iron recovery rate and produce iron concentrates of low grade （TFe < 50%） [17]. The impurities present in red mud consume substantial amounts of acid during the hydrometallurgical recovery process, which not only increases the cost of iron extraction but also contributes to secondary pollution through the generation of considerable waste liquid [18]. Pyrometallurgical recovery of iron involves the

4. Conclusions

Addressing the challenge of limited low-cost and large-scale disposal methods for high-iron red mud, primarily due to its elevated alkali content, this study introduces a novel high-temperature calcification process that leverages mineral phase reconstruction. This innovative approach not only facilitates the efficient recovery of sodium oxide and alumina but also ensures the complete disposal of red mud. The dissolution of undissolved boehmite in red mud can be improved during the calcification transformation process. Under the specified conditions of a reaction temperature of 260 °C, a calcium to silicon molar ratio of 2, a liquid to solid ratio of 4:1, a stirring speed of 300 rpm, a sodium oxide concentration of 210 g/L, and a reaction time of 60 minutes, the sodium oxide content in the calcification slag was found to be 0.61 %, while the alumina recovery rate reached 67.31 %. These findings indicate that the calcification transformation process yielded favorable results.

During the calcification transformation process of high-iron red mud treatment, the sodium-containing phase (sodalite) in the slag, gradually converts into an alkali-free hydrogarnet phase under low-temperature conditions. In contrast, the iron-containing phase in the red mud persists in the calcification transformation slag as hematite.

As a result of its low alkalinity, the calcification-transformed red mud is a particularly valuable iron containing resource. By incorporating 35 % calcification slag and following a suitable batching and pelletizing process, the resulting pellets exhibit impurity composition and strength properties that comply with the standards for ironmaking pellets.

5. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

6. Data Availability

Data will be made available on request.

7. Acknowledgments

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