

Preparation of Mineral Silica-Potash Fertilizer from Calcified-Potash Alkaline Treated Red Mud

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Abstract

As a significant bulk solid waste, the emission and accumulation of red mud have been increasing annually, severely damaging the ecological environment and posing safety hazards. With the growing scarcity of high-quality aluminum resources, red mud has gradually attracted attention due to its richness in various valuable metals such as aluminum (Al) and iron (Fe). In response to the challenges posed by the scale of Bayer red mud disposal and the potassium deficiency in China's soil, the Northeastern University Special Metallurgy Innovation Team has proposed a novel process for preparing mineral silica-potassium fertilizer through a one-step hydrothermal leaching of red mud within a calcareous-potassium alkali system. This process involves leaching red mud with potassium hydroxide (KOH), which not only extracts alumina but also replaces the harmful sodium element in red mud. Consequently, hydrated sodium silicoaluminate in red mud is transformed into potassium silicoaluminate. The resulting transformed slag can be utilized to produce mineral silica-potassium fertilizer, thereby promoting crop growth. This paper aims to achieve sustainable red mud production through KOH hydrothermal leaching by investigating the effects of mixed solutions with varying sodium and potassium ratios on the preparation of silica-potassium mineral fertilizers, facilitating synergistic sodium removal and aluminum extraction. This research provides a new reference for the realization of cross-boundary resource recycling in the context of "Aluminum-Agriculture," addressing the issues of red mud accumulation and alleviating the pressure on the scarcity of aluminum resources and potash fertilizers, thereby enhancing the core competitiveness of China's alumina enterprises.

Keywords: Red mud, Hydrothermal leaching, Total quantitative elimination, Mineral silica-potash fertilizer.

1. Introduction

Currently, the industrial production of alumina predominantly uses the Bayer method and the sintering method, as illustrated in Figure 1 below. The Bayer method is optimal for high-grade bauxite ores with an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio ranging from 7 to 10, whereas the sintering process is applicable to bauxite ores with an $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio between 3 and 6. Notably, the energy consumption of the sintering process is significantly higher, requiring approximately 30 GJ to produce one tonne of alumina, which is 2.5 times greater than that of the Bayer process [1]. Furthermore, the Bayer method accounts for over 90 % of global alumina production [2]. In 2022, China's alumina production capacity exceeded 99.5 million tonnes, with an actual output reaching

79.76 million tonnes, representing 58.2 % of the total global output, thereby establishing it as a pillar industry within China's metallurgical sector.

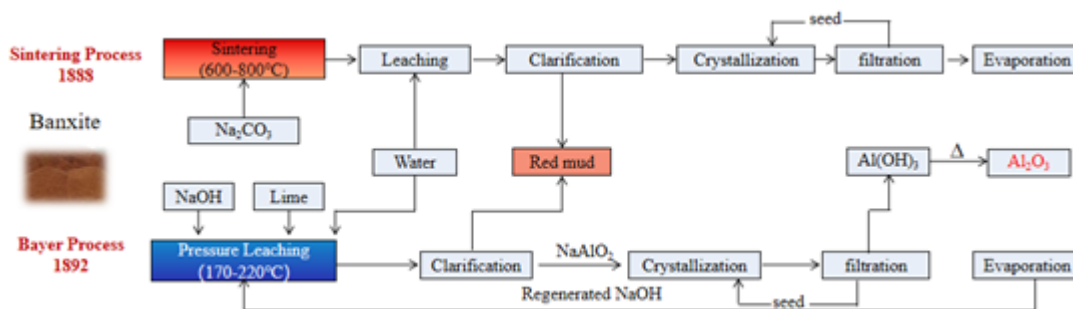


Figure 1. Bayer's and sintering process flow sheet [1].

The production of 1 tonne of alumina via the Bayer method generates between 0.6 and 2.0 tonnes of red mud, resulting in a global stockpile of red mud that has surpassed 5 billion tonnes and continues to increase at an alarming rate of nearly 200 million tonnes per year. In China alone, the red mud stockpile has exceeded 1.2 billion tonnes [3]. Due to its complex composition, large specific surface area, and strong alkalinity, finding large-scale applications for red mud has proven to be challenging [4]. Current utilization of red mud can be categorized into several areas, as illustrated in Figure 2: (1) construction materials, including the preparation of cement, ceramics, or road base materials [5–7]; (2) metal recycling, focusing on the recovery of iron, titanium, aluminum, or rare earth elements [1, 8]; (3) the production of environmentally friendly chemical materials, such as modified adsorbents, desulfurizers, or molecular sieves [9]; and (4) agricultural applications, particularly in the formulation of soil conditioners. However, due to the high alkalinity of red mud and issues related to the stability of heavy metals, most of these processes remain in the experimental research phase. The global comprehensive utilization rate of bauxite slag is approximately 15 %, while in China, it is less than 5 %.

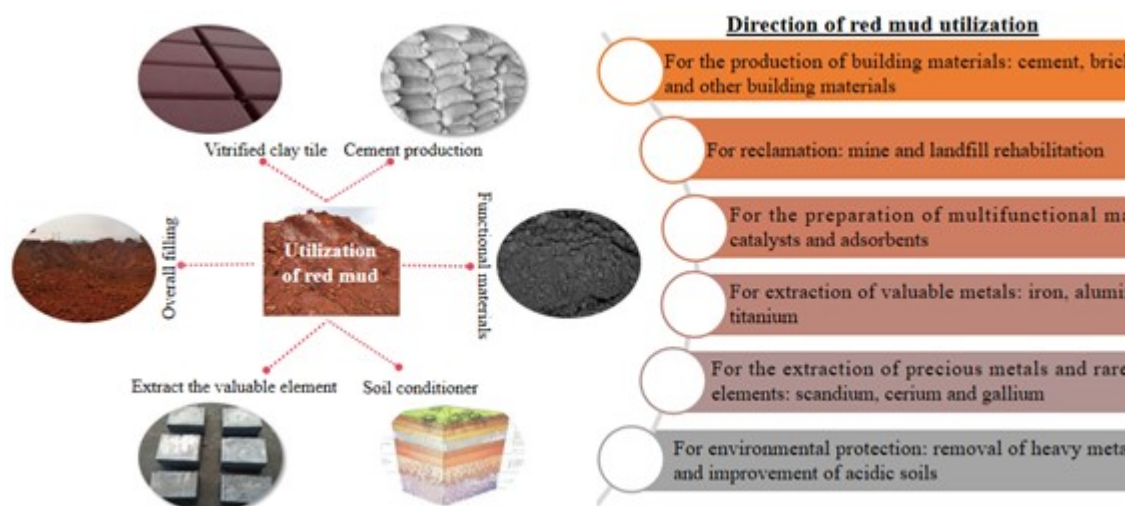


Figure 2. Summary of existing methods and routes for utilizing red mud.

Currently, the predominant method for treating red mud remains stacking and damming, which not only increases costs but also creates significant environmental safety hazards. Red mud pollutants have the potential to seep into both surface water and groundwater,

while fine particles can be easily dispersed by wind, leading to water and air pollution. Moreover, the storage of large quantities of red mud presents a serious safety risk. A notable incident occurred in 2010 when a dam at the Ajka red mud disposal area in Hungary collapsed, resulting in 10 fatalities, numerous severe injuries, and the catastrophic loss of approximately 40 kilometers of agricultural land [10]. Consequently, the discharge of red mud poses a substantial threat to the ecological environment and safe production, significantly hindering the sustainable development of the alumina industry [11]. Therefore, the harmless treatment and resource utilization of red mud are urgently needed.

The optimal solution for the disposal of red mud lies in the development of technologies that facilitate its economic utilization, particularly in sectors such as cement and other building materials [12]. However, as the real estate sector becomes saturated, there is an urgent need to explore new avenues for the comprehensive utilization of red mud. Agricultural fertilizers emerge as a promising option, as red mud contains a variety of elements essential for plant growth. After disodiumization treatment, it can be processed into mineral silica-potassium fertilizers. Given that China is a major agricultural producer, potassium is one of the crucial nutrients necessary for crop growth. It not only enhances photosynthesis, thereby promoting crop development, but also improves crops' disease resistance and resilience to adverse conditions, ultimately leading to increased agricultural yields [13]. Potassium fertilizers hold an irreplaceable position in efficient agricultural production. Currently, China's arable land is severely deficient in potassium, leading to a substantial demand for potash fertilizers. However, the reserves of soluble potassium salt resources in China are relatively limited, resulting in a high degree of foreign dependence. The market proportions of nitrogen fertilizers, phosphorus fertilizers, and potash fertilizers in China are significantly imbalanced, with over 40% of potash fertilizers being imported annually, which severely restricts the rapid development of Chinese agriculture [14]. Silicon, the second most abundant element in soil, has a low effective content that can be absorbed by plants, which decreases over time with prolonged planting. Elemental silicon can enhance photosynthesis in crops and improve their resistance to collapse and drought. As arable land diminishes and soil fertility declines, the demand for fertilizers continues to rise. However, the extensive use of chemical fertilizers poses significant threats to both the environment and food safety, transforming agriculture from a green industry into one characterized by high energy consumption and pollution [15]. In light of this critical situation, it is imperative to develop multi-element mineral fertilizers to reduce the reliance on chemical fertilizers while simultaneously restoring soil health to alleviate environmental pressures.

To address the evolving landscape of bauxite resource management and to expedite the elimination of aluminum and silicon solid waste while mitigating soil deficiency issues in China, our team conducted extensive experiments on the calcification and potassium alkali dissolution of red mud. The findings indicate that under conditions of K₂O concentration at 360 g/L and a leaching temperature of 240 °C, the dissolution of monohydrate stibnite-type red mud can reduce the Na₂O content in the dissolution product to 0.5 %. Furthermore, the conversion residue indices align with the market demands for inorganic compound fertilizers, allowing for further processing into mineral silica-potassium fertilizers, which exhibit significant market potential [16]. Building upon these results, this paper focuses on the Bayer method applied to low-iron red mud as a

research subject. We employed a calcification-potassium alkali process to simulate the cyclical processing of alumina plant mother liquor, investigating the influence of sodium-potassium mixed mother liquor on the desoduming of red mud and the composition of transformation products. The flowchart is illustrated in Figure 3. Our study examines the synergistic effects of varying sodium-potassium ratios in solution on the desoduming process and the enhancement of alumina extraction, ultimately leading to the preparation of silica-potassium mineral fertilizers from red mud. The transformed residue resulting from this process can be further refined to produce mineral silicon-potassium fertilizers to promote crop growth. This methodology not only facilitates the removal of deleterious sodium elements from red mud and the recovery of alumina but also achieves an economically viable and sustainable recycling of mother liquor, thereby providing a novel reference framework for the large-scale utilization of red mud and the clean production of alumina.

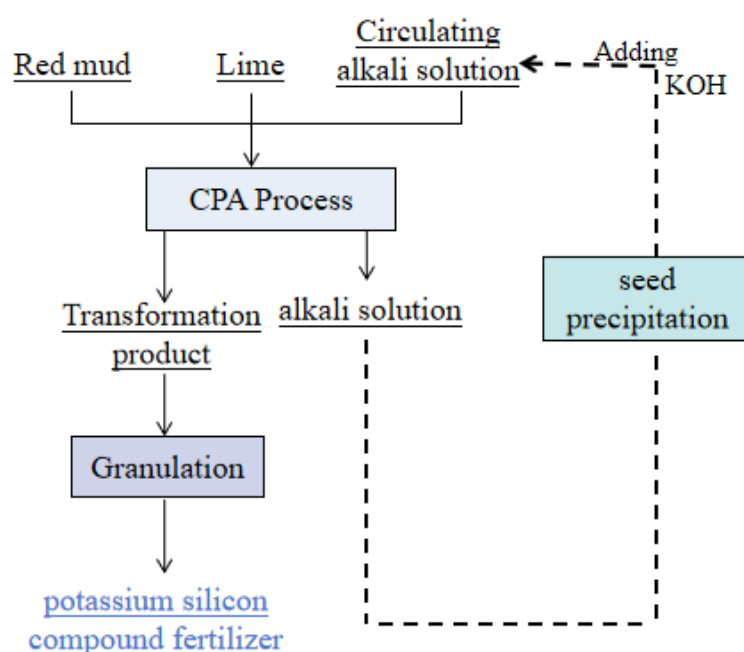


Figure 3. Flow chart for the preparation of silica-potassium mineral fertilizer from red mud treated with sodium-potassium recycling mother liquor under calcification-potash process.

2. Experimental Research Methods

2.1 Raw Materials

The reagents used in the experiment, including KOH, CaO, and NaOH, were of analytical grade and sourced from China National Pharmaceutical Chemical Reagent Co., Ltd. The red mud raw materials were obtained from an alumina plant in Shanxi, China, via the Bayer method for the dissolution. Prior to the leaching experiment, the red mud was placed in an oven at 100 °C for 24 hours. Following drying, the bauxite was crushed using a rod mill, followed by vibration and sieving. The chemical composition and physical phase analysis were conducted using X-ray fluorescence (XRF) and X-ray diffraction (XRD). Additionally, the solutions utilized in the experiments were prepared or diluted with deionized water.

2.2 Experimental Method

The experiment employed a mixture of KOH and NaOH to investigate the impact of the sodium-potassium molar ratio on the dissolution effect of red mud. Following the concentration settings for the required mass of KOH and NaOH analytical reagents in a 2L PTFE beaker, deionized water was added and stirred until clarified. Subsequently, red mud, lime, and the mixed lye were added to a steel bomb after slurry mixing, adhering to a liquid-solid ratio of 5:1. A specified number of nickel beads were introduced into the bomb for further agitation, which was then sealed and placed in a salt bath furnace (model HF-TGC-300-24-8, Wenzhou, China) that utilized molten nitrate (sourced from Anqiu, China) as the heating medium for rotary heating. After the reaction, the bomb was removed from the tank and quickly cooled in water. At the conclusion of the reaction, the slurry was centrifuged to obtain the supernatant, and the remaining product was repeatedly washed with deionized water until a pH of 7 to 8 was achieved. Vacuum filtration was then performed to facilitate liquid-solid separation, and the solids were dried in an oven (Model DHG-914385-III, Shanghai, China) at 100 °C for 24 hours. The solid powder was collected for subsequent characterization of the reaction.

During the hydrothermal leaching of red mud, almost all of the silicon oxide enters into the solid-phase product, so the dissolution rate of alumina from red mud was calculated using silicon oxide as an internal standard, as shown in Equation (1).

$$\eta_a = \frac{(A/S)_O - (A/S)_R}{(A/S)_O} \times 100 \% \quad (1)$$

where:

η_a Actual extraction rate of Al₂O₃, %

$(A/S)_O$ Al₂O₃ to SiO₂ mass ratio in the red mud

$(A/S)_R$ Al₂O₃ to SiO₂ mass ratio in the transformation product.

The extraction rate of Na₂O from red mud during hydrothermal leaching of red mud was calculated according to Equation (2):

$$\eta_s = \frac{1 - m_1 \cdot n_1}{m \cdot n} \times 100 \% \quad (2)$$

where:

η_s Na₂O removal rate, %

m quantity of raw material before the reaction, g

m_1 Quantity of the transformation slag after the reaction, g

n mass fraction of Si₂O in raw material, %

n_1 mass fraction of Na₂O in the transformed slag after reaction, %

2.3 Analysis Methods

Raw materials and products were analyzed by XRD (D8 Advance, Bruker, Germany, Cu target, scanning step of 0.0095°, diffraction angle range 10° < 2θ < 90°) for detection and characterization. The chemical composition was analyzed by XRF (ZSX Primus IV, Rigaku, Japan) after sample preparation by melting with a melt sampler (Haina HNJC-T4, Luoyang, China). The supernatant of the slurry obtained from the reaction was centrifuged in a centrifuge and then tested for caustic concentration alumina concentration by acid-base titration, and the

solid samples obtained from the filtration and drying were analyzed for effective K and Na content in the solids using ICP-OES (720 ES, Agilent, USA) after digestion with inorganic acids.

3. Results and Discussion

3.1 Characterization of Materials

The results of the red mud's XRF quantitative analysis and XRD physical phase detection are shown in Table 1 and Figure 7. The mass fractions of Na₂O, Al₂O₃, and SiO₂ in the red mud composition were 4.66 %, 19.85 %, and 23.75 %, respectively, and its A/S ratio was about 0.84. The XRD patterns showed that the main crystalline phases of the experimental raw materials were hydrated garnet, water and sodium silicate-aluminate, and kaolinite with part of iron oxide.

Table 1. Chemical composition of red mud raw materials (mass fraction %).

Component	K ₂ O	Na ₂ O	Fe ₂ O ₃	CaO	Al ₂ O ₃	SiO ₂	TiO ₂	L.O.I	A/S	N/S
Content	2.26	5.28	10.26	15.49	23.46	19.89	3.57	17.92	1.18	0.26

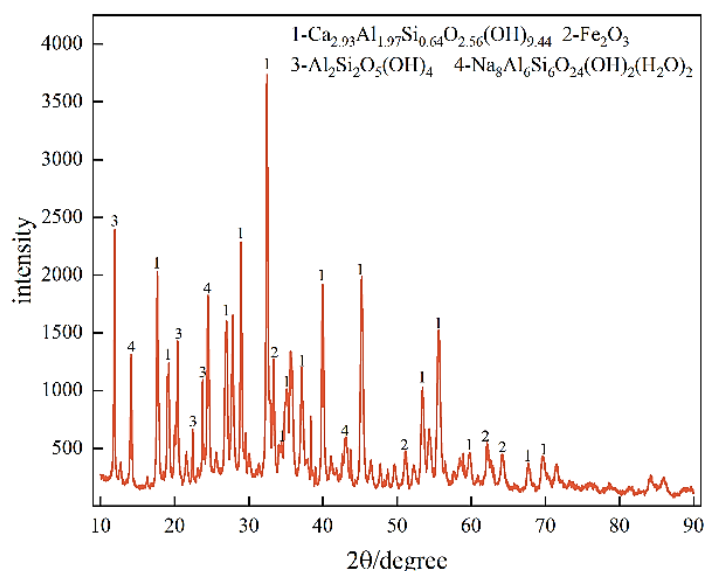
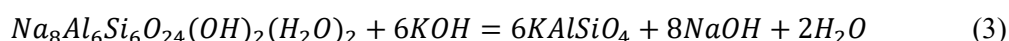


Figure 4. XRD results of red mud raw materials.

3.2 Influence of Reaction Parameters on Leaching Effect

The essence of the red mud calcification-potassium-base transition process lies in the sodium-potassium replacement mechanism, whereby hydrated sodium silica-aluminate is converted into potassium silica-aluminate. The overall reaction can be represented by Equation (3).



The reaction can be primarily divided into two processes: the decomposition of hydrated sodium silicate and the generation of potassium aluminum silicate. In this study, we explore the effects of varying the calcium-silica ratio and the sodium-potassium molar ratio on the dissolution of red mud, the alumina extraction rate of the transformation product, and the efficiency of alumina demineralization at a liquid-solid ratio of 5:1, a temperature of 260 °C, and a K₂O concentration of 320 g/L, as illustrated in the accompanying figure. It is observed that as the Na₂O/K₂O molar ratio increases, the alumina dissolution rate also gradually increases (Figure 5, left). This

phenomenon is presumed to occur because sodium ions, being smaller than potassium ions, more readily react with the hydrated silica-aluminate present in red mud under identical conditions, thereby promoting alumina dissolution. Conversely, when the calcium-silica ratio increases, the alumina extraction rate at a Na₂O/K₂O molar ratio of 0.241 gradually decreases with rising calcium-silica ratios. This decline can be attributed to the higher concentration of free alkali, which enhances the decomposition of hydrated silica-aluminate in red mud. As the calcium-silica ratio increases, free calcium ions compete with potassium ions for crystallization, altering the specific components of the product and resulting in a reduced Al/Si ratio, which in turn diminishes the alumina extraction rate. At lower sodium-potassium molar ratios, the alumina extraction rate initially increases and then decreases with the calcium-silica ratio. This is likely due to the dissolution of calcium oxide producing OH⁻ ions, which facilitates the dissolution of silica-aluminate. However, as the calcium-silica ratio continues to increase, the competitive crystallization of potassium and calcium leads to a decrease in the alumina dissolution rate. The effects of sodium removal and alumina extraction rate exhibit an inverse relationship (Figure 5, right). It is evident that as the sodium-potassium molar ratio increases, the sodium removal rate from red mud significantly decreases. For instance, at a calcium-silica ratio of 0.83, when the sodium-potassium molar ratio increases from 0.186 to 0.241, the sodium removal rate declines from 93 % to 14.4 %. This indicates that the sodium-potassium ratio significantly influences sodium removal effectiveness. Furthermore, when the sodium and potassium ratios are excessively high, an increase in the calcium-silica ratio promotes the transformation of hydrated sodium silicoaluminate into hydrated garnet in red mud, subsequently reducing the sodium oxide content in the product, as depicted in the specific reaction shown in Equation 4.

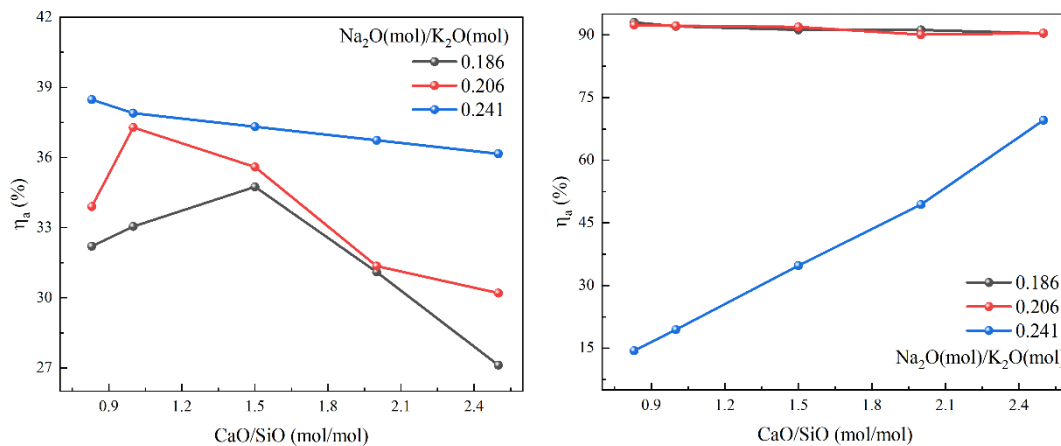
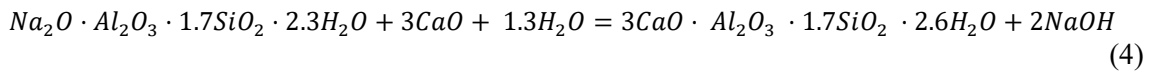


Figure 5. Variation of alumina extraction rate (Left) and desodiumization rate (Right) of red mud with calcium-silicon ratio at different Na₂O/K₂O molar ratios.

It is presumed that in the leaching reaction, sodium in red mud preferentially undergoes a replacement reaction with potassium until the sodium and potassium ions in the liquid phase reach equilibrium solubility. As illustrated in Figure 6, with an increase in CaO content, there is no significant change in Na₂O content at a sodium-potassium ratio of 0.206. This suggests that the replacement reaction between K and Na ions has reached equilibrium at this molar ratio. Under the condition of a calcium-silicon ratio of 0.83, the Na₂O content in the solid-phase product is only 0.4 %. When the sodium-potassium molar ratio is increased to 0.241, the Na₂O content in the leaching product is merely 4.48 % under the same calcium-silicon ratio of 0.83. This indicates that the concentration of sodium ions in the liquid phase is approaching saturation, thereby inhibiting the decomposition of sodium silicate-aluminate hydrate in red mud. Further addition of

calcium oxide can react with sodium, thereby enhancing the efficiency of sodium removal. However, the addition of calcium oxide results in a decrease in the contents of Al_2O_3 , K_2O , and SiO_2 in the product. A high content of calcium oxide in the transformation product is detrimental to the preparation of subsequent silica-potassium fertilizer. Therefore, the sodium/potassium molar ratio in the circulating lye of the red mud leaching process should not be excessively high, with a ratio of $n(\text{Na}_2\text{O})/n(\text{K}_2\text{O})$ of 0.206 being more suitable.

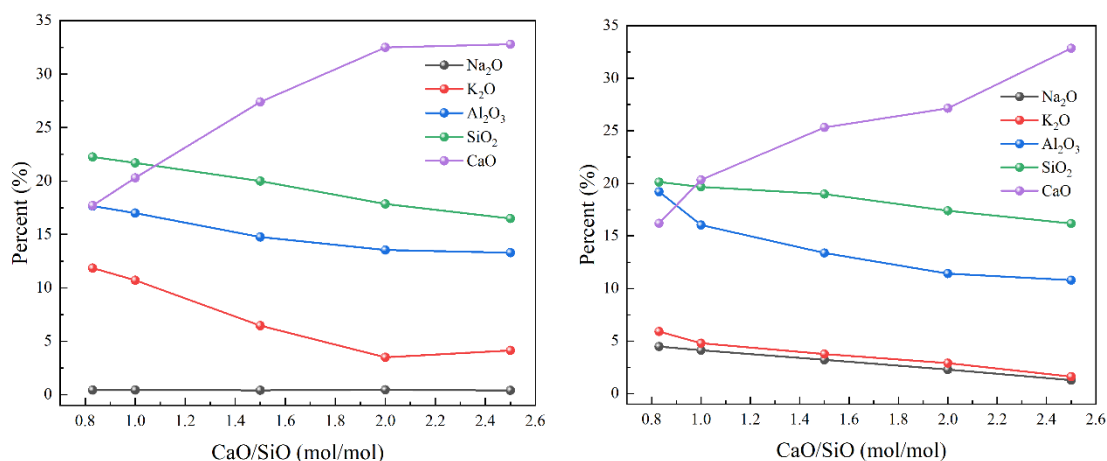


Figure 6. XRF results of transformation products at different Ca/Si ratios.
Left: $\text{Na}_2\text{O}/\text{K}_2\text{O}$ molar ratio = 0.206, Right: $\text{Na}_2\text{O}/\text{K}_2\text{O}$ molar ratio = 0.241.

Under varying calcium-silicon ratios, the leaching products at a $\text{Na}_2\text{O}/\text{K}_2\text{O}$ molar ratio of 0.206 were analyzed using X-ray diffraction (XRD), with the results illustrated in Figure 7. The findings indicate that the kaolinite diffraction peaks in the red mud completely disappeared and were transformed into KAlSiO_4 and hydrated garnet diffraction peaks. As the calcium-silicon ratio increased, the silicon saturation coefficient of the hydrated garnet also increased, leading to a rise in the intensity of the diffraction peaks. Conversely, the intensity of the potassium silicate-aluminate diffraction peaks gradually decreased. This aligns with the hypothesis of potassium-calcium competitive crystallization. To ensure the subsequent preparation of mineral silicon and potassium fertilizers, it is crucial that the calcium-silicon ratio does not exceed a certain threshold. Therefore, a ratio of 0.83 is deemed more appropriate. At this ratio, the main phases of the product are KAlSiO_4 and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 1.25\text{SiO}_2\cdot 3.5\text{H}_2\text{O}$, with the product contents of Na_2O , K_2O , and SiO_2 measured at 0.44 %, 11.86 %, and 22.26 %, respectively.

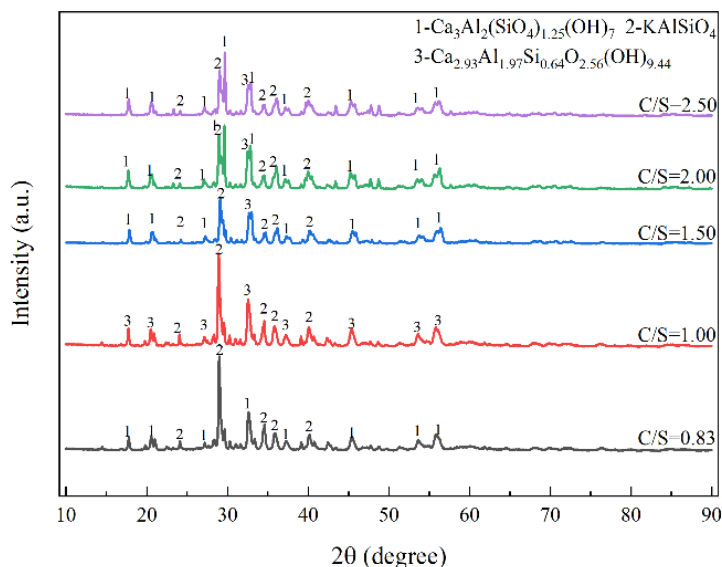


Figure 7. XRD results of transformation products with different Ca-Si ratios at $\text{Na}_2\text{O}/\text{K}_2\text{O}$ molar ratio = 0.206.

4. Conclusion

To achieve sustainable production of silica-potassium mineral fertilizer through hydrothermal leaching of red mud with KOH, it is essential to recycle the leaching solution. This study investigates the impact of mixed solutions with varying sodium-potassium ratios on the synergistic desodiumization and alumina extraction from red mud for the preparation of silica-potassium mineral fertilizer. The findings indicate that sodium atoms in the slag phase of the hydrothermal leaching process are released into the KOH solution as Na^+ , with the sodium content in the leachate being a critical factor affecting recycling efficiency. When the molar ratio of Na_2O to K_2O in the sodium-potassium mixed solution is 0.206, the mass fraction of Na_2O in the transformed slag obtained from hydrothermal leaching of red mud at 260 °C for 1 hour is 0.44 %. The primary equilibrium mineral phase of the product shifts from hydrated sodium silica-aluminate to potassium silica-aluminate and partially hydrated garnet, with Na_2O , K_2O , and SiO_2 contents recorded at 0.44 %, 11.86 %, and 22.26 %, respectively. Furthermore, the mineral-based silicon and potassium fertilizer can be enhanced with organic matter to meet plant growth requirements. This process does not produce secondary pollution, offering a novel reference scheme for addressing the red mud accumulation issue and promoting sustainable clean alumina production.

5. Acknowledgments

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