Effects of vacuum conditions on activation of high-alumina fly ash roasted using conventional and microwave heating

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Abstract
In this study, Na₂CO₃ was used as activator to roast and activate high-alumina fly ash (HAFA), and the vacuum roasting technology was used to enhance the activation process of HAFA. The effects of the vacuum conditions on the activation of HAFA roasted using conventional and microwave heating were investigated. It was determined that the reaction time was shortened and the activation effect of HAFA was improved under vacuum conditions; however, the effect of the vacuum conditions on the roasting temperature was negligible. The activation process of HAFA-Na₂CO₃ mixtures (HAFA/Na₂CO₃ mass ratio of 1:1) was promoted by conducting conventional and microwave heating experiments under vacuum (−0.04 MPa). The leaching rate of aluminium of 93.00% was reached at the roasting temperature of 900 °C after only 20 min when the HAFA-Na₂CO₃ mixture was subjected to conventional heating under vacuum, and after 60 min when conventional heating occurred under normal atmospheric pressure. Moreover, the leaching rate of aluminium of 96.00% was reached at the roasting temperature of 700 °C after only 20 min when the HAFA-Na₂CO₃ mixture underwent microwave heating under vacuum, and after 30 min when microwave heating occurred under normal atmospheric pressure.

1. Introduction

Coal fly ash (CFA), a by-product of the coal-fired industry, is mainly generated via coal combustion. Owing to the developments in the electric power industry, the amount of CFA discharge from coal-fired power plants has been increasing annually, and CFA became the largest single source of industrial solid waste in China. The annual emissions of CFA in China since 2014 exceeded 600 million tons [1, 2]. This markedly increased the dichotomy between the accumulation of large quantities of CFA and the occupation of land in China. Fine particles and heavy metals in CFA can cause significant environmental disruption [3–5]. Long-term CFA storage could result in wasting land resources and could significantly damage the environment, which could cause significant harm to human health, pose safety concerns, and could hinder the long-term global development goals.

Aluminium plays an important role in the national economic construction and defence industry, and its consumption is second only to steel [6]. At present, bauxite is the main raw material for alumina production. Large amounts of bauxite are imported yearly to meet the industrial demands in China. It was determined that alumina contains abundant amounts of CFA, and the alumina content of CFA with 30% total emission in China exceeds 30% [7, 8]. This CFA presents great application prospects and is known as high-alumina fly ash (HAFA).
High-alumina fly ash can be used as substitute for bauxite to produce alumina, alleviate the shortage of bauxite resources in China, and reduce the environmental pollution caused by the accumulation of CFA.

The mineral composition of HFA is very complex, and its degree of polymerisation is very high. Of the minerals comprising HFA, silica and alumina are mainly present in mullite (Al₆Si₂O₁₃) and quartz phase, respectively, which hinder the direct extraction of alumina. Therefore, stimulating the activity of mullite in HFA, breaking the Al–Si bond, and allowing elemental aluminium to be effectively released and recovered are key research topics.

The most common activation methods used nowadays are physical and chemical [9–13]. Physical activation involves the mechanical grinding of HFA, whereas chemical activation requires the addition of chemical additives to HFA and the calcination of the resulting mixture at high temperatures. Both methods were designed to destroy the mullite phase in HFA, and the chemical activation method using Na₂CO₃ as activator presented the best activation effect on HFA. Guo et al [12] studied the direct activation of HFA as well as that after pre-desilication, using Na₂CO₃. Their results indicated that by adding Na₂CO₃ to HFA after pre-desilication for 2 h at 850 °C, the extraction rate of alumina reached 87%, while the consumption of Na₂CO₃ could be greatly reduced. Matjie et al [13] mixed CFA with fine coal and lime at the weight ratio of 1:0.8:0.2 and sintered the mixture in the temperature range of 1000–1200 °C. Afterwards, 85 wt% aluminium was leached using a H₂SO₄ solution [13].

Both HFA and Na₂CO₃ are solid powders, which will not melt during roasting. The mass-transfer efficiency of solid–solid reactions is low [14]. Consequently, during the conventional heating method (CHM), when HFA is activated using Na₂CO₃, the reactants should be maintained at high temperature for extended times, which leads to considerable energy consumption. As a novel, green, and efficient heating method, the microwave heating method (MHM) presents incomparable advantages in terms of heating characteristics and heat transfer efficiency of materials [15]. Microwaves act on materials with fully enclosed power, causing the microwave-absorbing material of the HFA activation system to become the preferential heat source for the process. The absorbent would subsequently transfer heat to the other non-absorbent materials to achieve overall rapid heating of all materials. Microwave heating contributes to the breaking of the SiO₂–Al₂O₃ bond, which causes structural changes in the materials and evolutionary reactions to improve the activation efficiency of the process [16]. Liu et al [17] used Na₂CO₃ as activator for CFA, and the CFA-Na₂CO₃ mixture was activated using both conventional and microwave heating. The effects of different roasting factors on the activation of CFA were studied, and it was determined that the MHM could significantly improve the parameters of the CFA activation process. The time and temperature required to achieve the leaching rate of aluminium of 95% were 60 min and 900 °C, respectively, when conventional heating was used compared with only 20 min and 700 °C, respectively, for microwave heating.

Zhou et al [18] studied the phase transformation mechanism of Na₂CO₃-activated CFA using the CHM, and analysed the reactions that occurred during the activation process. They determined that most reactions that occurred during the activation process generated CO₂; this was the compatibilisation reaction. The rate of the compatibilisation reaction could be increased under vacuum conditions [19].

In this study, we roasted HFA-Na₂CO₃ mixtures using conventional heating under vacuum, and analysed the influence of the vacuum conditions on the activation of HFA. Subsequently, to analyse the influence of the vacuum conditions on various factors, we compared the results with those obtained when conventional heating under normal atmospheric pressure was used. Then, the microwave-vacuum synergistic enhanced roasting of HFA-Na₂CO₃ mixtures was performed, and the results were compared with those of the microwave heating roasting experiment under normal atmospheric pressure. The enhancing effect of various factors on the activation of HFA under vacuum conditions was analysed. Microwaves and vacuum conditions were used during the activation of HFA-Na₂CO₃ mixtures to enhance the activation process, promote the reaction, shorten the activation reaction time, and ultimately reduce the energy consumption associated with the process.

2. Experimental

2.1. Materials

The chemical composition of HFA was determined using chemical element analysis (table 1). The main chemical compounds in pulverised HFA were SiO₂ and Al₂O₃; the Al₂O₃, SiO₂, and total SiO₂ and Al₂O₃ contents of HFA were 49.68, 41.82, and 91.5 wt%, respectively, while the content of Fe, Ca, Mg, Ti, and other elements was very low. The mineralogical phases of HFA were characterised using x-ray diffraction (XRD), and the results are presented in figure 1. The dominant mineral phases of HFA were Al₆Si₂O₁₃, Al₂SiO₅, Al₂O₃, and SiO₂.
2.2. Experimental method
A muffle furnace with the highest roasting temperature of 1350 °C was used for the conventional heating experiments and a microwave box furnace with the highest power of 6400 W and the highest roasting temperature of 1600 °C was used for the microwave heating experiments. The heating equipment was fitted with an air pump able to pump out the gas from the chamber to achieve vacuum conditions.

Equal amounts of raw HAFA and Na₂CO₃ were weighed, and then the materials were stirred and mixed evenly in a crucible. The mixture was roasted to activate it using either the muffle furnace or the microwave box furnace. After the material was cooled, it was weighed, grinded, and characterised. Next, 10 g activated material was added to a flask. Condensation tubes were placed above the flask and the circulating cooling water was turned on. A certain amount of HCl solution was extracted in the flask. The filtrate volume was determined by stirring and leaching at a set temperature. The schematic diagram of the experimental process is depicted in figure 2. The Al³⁺ content in the filtrate was determined using inductively coupled plasma atomic emission spectroscopy, and the leaching rate of aluminium could be calculated as follows:

\[ \eta = \frac{V_c C_x}{M W_a} \times 100\% \]

where \( M (g) \) is the quantity of raw HAFA material, \( W_x (\text{wt}\%) \) is the mass fraction of aluminium in the raw HAFA material, \( C_x (\text{g} \cdot \text{L}^{-1}) \) is the mass concentration of Al³⁺ ions in the acid leaching solution, and \( V_c (\text{L}) \) is the volume of the prepared acid leaching solution.

Table 1. Chemical composition of high-alumina fly ash.

| Component | \( \text{Al}_2\text{O}_3 \) | \( \text{SiO}_2 \) | \( \text{Fe}_2\text{O}_3 \) | \( \text{CaO} \) | \( \text{MgO} \) | \( \text{TiO}_2 \) |
|-----------|----------------|----------------|----------------|-------------|-------------|-------------|
| Content (%) | 49.68 | 41.82 | 2.68 | 1.21 | 0.29 | 1.77 |

Figure 1. X-ray diffraction pattern of high-alumina fly ash.

Figure 2. Schematic diagram of experimental process; here XRD is x-ray diffraction.
3. Results and discussion

3.1. Roasting of HAFA-Na$_2$CO$_3$ using conventional heating under vacuum

3.1.1. Effect of vacuum degree on activation of HAFA

The experimental roasting conditions for the CHM were as follows: roasting temperature of 900 °C, roasting time of 60 min, and HAFA/Na$_2$CO$_3$ mass ratio of 1:1. Vacuum degrees of 0, $-0.02$, $-0.04$, and $-0.06$ MPa were used to investigate the effect of the vacuum conditions on the activation of HAFA, and the results are illustrated in figure 3.

It was determined that as the vacuum degree increased, the activation of HAFA was promoted to a certain extent, and the leaching rate of aluminium was also improved. The leaching rate of aluminium under normal atmospheric pressure was 93.10% and increased under vacuum conditions. When the vacuum degree was $-0.04$ MPa, the leaching rate of aluminium reached 95.59%. However, the leaching rate of aluminium did not increase significantly as the vacuum degree continued to increase. This indicated that at the vacuum degree of $-0.04$ MPa, the reaction between HAFA and Na$_2$CO$_3$ could be considered complete. Therefore, activating HAFA under vacuum conditions was beneficial, and the leaching rate of aluminium at different roasting temperatures and times will be further investigated at the vacuum degree of $-0.04$ MPa.

3.1.2. Effect of roasting temperature on activation of HAFA

The experimental roasting conditions for the CHM were as follows: roasting temperature of 900 °C and HAFA/Na$_2$CO$_3$ mass ratio of 1:1. The leaching rate of aluminium was measured at different temperatures in the 600–1000 °C range. The vacuum degree of $-0.04$ MPa was used to compare the effects of different roasting temperatures in the 600–900 °C range on the activation of HAFA during conventional heating experiments. The effect of the roasting temperature under vacuum conditions on the activation of HAFA was the same as that observed during conventional heating under normal atmospheric pressure (figure 4).

As the temperature increased, the leaching rate of aluminium increased. The leaching rate of aluminium reached 95.59% at 900 °C, which was considered to be the optimum roasting temperature. However, given the same temperature, the leaching rate of aluminium was markedly higher when the conventional heating experiment was conducted under vacuum than when it was performed under normal atmospheric pressure. The most significant increase in the leaching rate of aluminium (11.66%) was observed at 700 °C; from 44.52% under normal atmospheric pressure to 56.18% under vacuum conditions. It was concluded that the activation effect of HAFA was improved under vacuum conditions, but the roasting temperature was not decreased.

3.1.3. Effect of roasting time on activation of HAFA

The results of the above-mentioned experiments indicated that the improvement in the activation effect of HAFA when the conventional heating experiments were performed under vacuum was not reflected in a decrease in the reaction temperature. Therefore the effect of the vacuum conditions on the roasting time should be investigated. The experimental roasting conditions for the CHM were as follows: roasting temperature of 900 °C and HAFA/Na$_2$CO$_3$ mass ratio of 1:1. The leaching rate of aluminium at different times in the 20–120 min range was measured under these conditions. The vacuum degree of $-0.04$ MPa was used to
compare the effects of different roasting times in the 20–60 min range on the activation of HAFA using the CHM, and the results are depicted in figure 5.

When the experiments were performed under vacuum conditions, the time required to reach a high leaching rate of aluminum was shorter compared with that of the experiments performed under normal atmospheric pressure. When the roasting time was 20 min, the leaching rate of aluminum reached 93.09% under vacuum conditions, which was 12.51% higher than the rate obtained after 20 min of conventional heating under normal atmospheric pressure. This indicated that performing the reaction under vacuum conditions greatly shortened the time required by HAFA and Na$_2$CO$_3$ to react. As the roasting time was extended, the leaching rate of aluminum still increased. The same activation effect was obtained when roasting was conducted for 60 min under vacuum conditions or after 120 min of conventional heating under normal atmospheric pressure. These results indicated that performing the experiment under vacuum conditions greatly promoted the reaction of HAFA and Na$_2$CO$_3$, and thus better activation effect was achieved in a shorter time.

The optimum roasting conditions for the CHM under vacuum conditions were as follows: vacuum degree of $-0.04$ MPa, HAFA to Na$_2$CO$_3$ mass ratio of 1:1, roasting temperature of 900 °C, and roasting time of 20 min. Under these conditions, the leaching rate of aluminum was 93.02%.

Figure 4. Effect of roasting temperature on leaching rate of aluminium (vacuum degree of $-0.04$ Mpa).

Figure 5. Effect of roasting time on leaching rate of aluminium.
3.1.4. XRD analysis

Figure 6 compares the XRD patterns of HAFA-Na₂CO₃ mixtures roasted via conventional heating (900 °C, HAFA/Na₂CO₃ 1:1 (g/g), 20 min; 900 °C, HAFA/Na₂CO₃ 1:1 (g/g), 60 min) and under vacuum conditions (−0.04 MPa, 900 °C, HAFA/Na₂CO₃ 1:1 (g/g), 20 min). The distinct diffraction peaks of mullite and Na₂CO₃ can be observed in the spectra of the materials roasted for 30 min using the CHM. However, these phases disappeared from the spectra of the materials roasted under vacuum conditions for 20 min and characteristic peaks of the \((\text{Na}_2\text{O})_{0.33}\text{NaAlSiO}_4, \text{Na}_{1.75}\text{Al}_{1.75}\text{Si}_{0.25}\text{O}_4\), and Na₂SiO₃ phases were observed instead. These peaks were similar to those identified in the XRD spectra of the materials roasted for 60 min using the CHM. This indicated that the reaction time was shortened and the activation effect of HAFA was improved under vacuum conditions.

3.2. Combined microwave–vacuum enhanced roasting experiment of HAFA-Na₂CO₃

From the above experiments, it was determined that the vacuum conditions exhibited a certain promoting effect on the activation of HAFA. In addition, the roasting time and roasting temperature of activation of HAFA could be remarkably reduced using microwave heating.

Therefore, in this study, the cooperative microwave–vacuum enhanced roasting of HAFA-Na₂CO₃ was performed, and the effects of various factors, namely the vacuum degree and roasting time, on the activation effect of HAFA were investigated by comparing the results with those obtained using the MHM. The above-mentioned experimental results indicated that the vacuum degree exhibited little effect on temperature, and therefore, it was not examined in this experiment.

3.2.1. Effect of vacuum degree on activation of HAFA

The roasting conditions for the microwave heating experiment were as follows: roasting temperature of 700 °C, roasting time of 30 min, and HAFA/Na₂CO₃ mass ratio of 1:1. Different vacuum degrees (0, −0.02, −0.04, and −0.06 MPa) were used to investigate the effect of the vacuum conditions on the activation of HAFA. As presented in Figure 7, the leaching rate of aluminium under normal atmospheric pressure was 95.96%. When the
vacuum degree was $-0.06$ MPa, the leaching rate of aluminium increased to 96.72%, which was not a significant improvement. It was presumed that the leaching rate of aluminium during microwave heating approached the experimental peak value and it was unable to further increase. This indicated that performing the experiment under vacuum conditions did not effectively improve the leaching rate of aluminium. Therefore, further studies should be conducted to investigate whether performing the experiments under vacuum conditions could reduce the reaction time; the vacuum degree of $-0.04$ MPa was selected for this investigation.

3.2.2. Effect of roasting time on activation of HAFA

The roasting condition for the microwave heating experiment were as follows: roasting temperature of 900 °C and HAFA/Na$_2$CO$_3$ mass ratio of 1:1. The leaching rate of aluminium was measured at different times in the 10–50 min range. The vacuum degree of $-0.04$ MPa was used to compare the effects of different roasting times in the 10–30 min range on the activation of HAFA during the microwave heating experiments, and the results are illustrated in figure 8. Under the same roasting conditions, the leaching rate of aluminium obtained using the combined microwave-vacuum enhancing method was higher than that obtained for the microwave heating experiment under normal atmospheric pressure. After 10 min, the leaching rates of aluminium obtained using the MHM and combined microwave–vacuum enhanced method were 89.37% and 93.22%, respectively. As the roasting time was prolonged, the leaching rate of aluminium increased. In addition, the leaching rate of aluminium reached 96.00% after 30 min of microwave heating, and after only 20 min of combined microwave–
vacuum enhanced heating. This indicated that the combined microwave–vacuum enhanced method significantly shortened the roasting time.

Therefore, the activation reaction of HFA was further promoted by the combined microwave–vacuum enhanced method, which effectively reduced the roasting time.

3.2.3. XRD analysis
The XRD patterns of HFA-Na2CO3 mixtures roasted using the MHM (700 °C, HFA/Na2CO3 1:1 (g/g), 30 min; 900 °C, HFA/Na2CO3 1:1 (g/g), 30 min) and the combined microwave–vacuum enhanced method (−0.04 MPa, 700 °C, HFA/Na2CO3 1:1 (g/g), 20 min) are compared in figure 9. The two XRD patterns of the HFA-Na2CO3 mixtures were very similar. This indicated that the combined microwave–vacuum enhanced roasting of HFA-Na2CO3 achieved the same activation effect in less time (20 min, compared with 30 min of roasting required for the MHM). Under vacuum conditions, the reaction time was shortened and the activation effect of HFA was effectively improved.

4. Conclusion
In this study, Na2CO3 was used as activator to roast and activate HFA. The vacuum roasting technology was used to enhance the activation of HFA, and the effects of the vacuum conditions on the activation of HFA roasted via conventional and microwave heating were investigated. The main conclusions were as follows:

(1) The reaction time was shortened and the activation effect of HFA was improved under vacuum conditions; however, the effect of the vacuum conditions on the roasting temperature was negligible.

(2) The activation process of HFA-Na2CO3 mixtures (HFA/Na2CO3 mass ratio of 1:1) was promoted by performing the experiments under vacuum conditions (−0.04 MPa). Moreover, the leaching rate of aluminium of 93.00% was attained in only 20 min when conventional heating was performed at 900 °C,

Figure 9. X-ray diffraction patterns of high-alumina fly ash-Na2CO3 mixture roasted under different conditions.
under vacuum conditions; the same leaching rate of aluminium was reached after 60 min during the conventional heating experiment conducted at 900 °C under normal atmospheric pressure.

(3) The activation of HFA-Na2CO3 mixtures (HFA/Na2CO3 mass ratio of 1:1) was promoted when the microwave heating experiment was performed under the vacuum degree of −0.04 Mpa at 700 °C. The leaching rate of aluminium of 96.00% was reached after only 20 min under vacuum conditions and after 30 min when the microwave heating experiment was performed under normal atmospheric pressure.

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