Spinel Ferrite Transformation for an Efficient Fe Removal from Circulating Fluidized Bed Fly Ash by Carbothermal Reduction at a Low Temperature

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ABSTRACT: Alumina (Al₂O₃) extraction from circulating fluidized bed (CFB) fly ash (CFBFA) is one of the most important pathways for value-added utilization. However, in CFBFA, impurity iron (Fe) normally coexists, resulting in complicated separation processes, low Al₂O₃ extraction efficiency, and substandard Al₂O₃-based products. How to remove Fe impurity effectively from CFBFA has become an important issue. For an effective Fe removal from CFBFA, spinel ferrite transformation by carbothermal reduction at a low temperature was discussed in the paper. The effects of the reduction temperature and reduction time on the removal efficiency of Fe and the recovery of aluminum (Al) as well as the removal of other metals were systematically investigated, and the transformation mechanisms of Fe-containing phases were investigated by X-ray diffraction, X-ray photoelectron spectroscopy, and a scanning electron microscope−energy dispersive spectrometer. The results showed that Fe in CFBFA was present in the form of weakly magnetic α-Fe₂O₃, leading to a Fe removal of about 17.1% after magnetic separation; however, the recovery efficiency of Al reached 97.4%. Weakly magnetic hematite (α-Fe₂O₃) could be converted to strongly magnetic spinel-type ferrite (MFe₂O₄) after carbothermal reduction at 700 °C for 60 min, and the Fe removal efficiency could reach 62.8% after magnetic separation; however, the recovery of Al was 81.2%, which was decreased compared to the recovery of Al under the condition without carbothermal reduction treatment. However, the carbothermal reduction−magnetic separation process did not have a major effect on the existing form and leaching behavior of Al, Li, and Ga. Simultaneously, it could be observed that some transition metal elements such as Mn, Cr, and so forth could be enriched in spinel-type MFe₂O₄ and removed after magnetic separation, which also provided a way for transition metal enrichment and extraction of transition metals from other tailings.

1. INTRODUCTION

Considering both the lower SO₂, NOₓ emissions, and energy conservation, the circulating fluidized bed (CFB) combustion technology has been greatly developed and widely popularized as a highly efficient clean fuel combustion technology for use in coal combustion.¹,² Furthermore, some significant advantages such as good fuel adaptability and the high efficiency of desulfurization can facilitate utilization of the low reactivity coals, such as coal gangue and high-sulfur fuels.³⁻⁵ Therefore, more than 50 million tons of CFB fly ash (CFBFA), produced during combustion in CFB coal boilers, is discharged annually in China.⁶⁻⁸ The huge accumulation of CFBFA not only occupies land resources but also increases the economic and environmental burden.⁹,¹⁰ In recent years, more attention has been paid to environmental problems resulting from the disposal of CFBFA, and the treatment of CFBFA has been developing toward a high-value utilization. Among them,
extracting valuable metal elements such as aluminium (Al) from CFBFA is one of the directions of high-value utilization.11 The content of Al2O3 in CFBFA is typically as high as 20–50%, which can be utilized as a substitute for bauxite for Al extraction.7,12,13 CFBFA has a high chemical activity due to its formation at lower combustion temperatures (800–900 °C).14 Therefore, the valuable metal elements, such as Al, can be extracted from CFBFA by direct acid leaching with a low energy consumption and a simple technological process. However, the impurity of iron (Fe) will be leached into the acid-leaching solution together with Al, which not only will burden the subsequent separation process but also reduce the purity of the product. Thus, Fe removal is an important task in the process of extracting valuable metal elements from fly ash.

The operating temperature of CFB combustion is 800–900 °C, which is much lower than that of pulverized coal (PC) combustion (1300–1500 °C). The combustion temperature and atmosphere greatly affect the Fe-bearing mineral transformation during the formation of the coal fly ash,15 resulting in the different mineral phases between the CFBFA and PC fly ash (PCFA). It is reported that16,17 the occurrence of the most Fe in PCFA was as magnetite, which could be separated by the magnetic separation method, and about 70% of Fe could be removed after a direct magnetic separation. However, most of the Fe in CFBFA exists mainly as hematite (α-Fe2O3) with weak ferromagnetic properties,18–20 and it is difficult to remove Fe from CFBFA efficiently by direct magnetic separation.

So far, the main methods of removing Fe in coal fly ash are magnetic separation and acid selective leaching. Acid leaching could remove nonmagnetic or weakly magnetic Fe-bearing minerals, causing not only the loss of other valuable metals but also environmental pollution. As we all know, the most economic and environmentally friendly method to remove Fe is magnetic separation, and magnetite with strong ferromagnetic properties can be removed efficiently. At present, most studies focus on Fe removal from PCFA. Gong et al.21 could remove Fe from PCFA by magnetic separation, and the Fe removal rate can reach more than 60%, indicating magnetic separation could remove Fe from PCFA efficiently. Valeev et al.22 used the hydrochloric acid (HCl) leaching method to remove Fe from PCFA, and the Fe removal efficiency is 52%, with a low Al loss of 3.7%. Sun et al.23 removed Fe from PCFA by magnetic separation and acid leaching, which obtained a higher Fe removal than only by magnetic separation. To improve the Fe removal efficiency, Fe-bearing minerals could be deeply reduced and transformed into Fe at 1000 °C, as shown by Wang et al.,24 and the impurity Fe could be completely removed by both magnetic separation and the acid leaching method. In addition, it is demonstrated that24 some transition metal elements, such as Fe, Mn, Ni, Cu, and so on, could be enriched in magnetic fractions after magnetic separation from PCFA. Some research has been made to remove Fe from CFBFA by magnetic separation or the acid leaching method. Luo et al. studied the removal of Al, Fe, and Ca elements by acid leaching with HCl using roasted CFBFA and mainly investigated the reaction kinetics of each element.7 Wu et al.25 investigated the recovery of Fe from CFB fly ash by magnetization of roasting–magnetic separation and the extraction of Fe from fly ash by an additional reducing agent and studied the optimal reaction conditions.25 Liu et al. conducted a synergistic sulfur reduction and Fe beneficiation experiments on fly ash using CFB solid sulfur fly ash using the simultaneous reduction roasting–wet-weak-magnetic separation of the Fe concentrates.26 Whereas it has not been reported that the enrichment of some transition metal elements in magnetic fractions could be obtained after magnetic separation from CFBFA. Furthermore, no effort has been made to remove Fe by spinel ferrite transformation using residual carbon in the fly ash, and the effect of Fe removal on valuable metal extraction is not clear.

In the present work, to efficiently remove the impurity of Fe existing in the form of α-Fe2O3 from CFBFA, spinel ferrite transformation using the carbothermal reduction process for enhanced Fe removal was proposed. The effects of the reduction temperature and reduction time on Fe removal and Al recovery were investigated. Meanwhile, the Fe-bearing mineral phase transformation during the carbothermal reduction process was investigated. In addition, the leaching behavior of metal elements and the enrichment degree of some transition metal elements in CFBFA were studied after magnetic separation. Using this method, an efficient Fe removal could be achieved, and at the same time, some transition metal elements might be enriched in the magnetic fractions, providing a pathway for Fe removal and recovery of value elements and transition metals from other resources.

2. EXPERIMENT

2.1. Raw Materials. The CFBFA used in the present experiments is supplied by a power plant in Pingshuo, Shaxi Province. The main chemical compositions were detected by X-ray fluorescence, and the loss on ignition (LOI) was determined according to GB/T 1596-2005, as shown in Table 1. According to Table 1, the main compositions in CFBFA are Al2O3, SiO2, CaO, Fe2O3, and SO3. The content of Al2O3 and SiO2 is 34.70 and 42.20%, respectively, indicating that the fly ash might be used as a raw material for the extraction of Al. However, the content of Fe2O3 is as high as 4.40%, which affects the purity of Al2O3 produced from CFBFA.

The mineralogical compositions in CFBFA were characterized by X-ray diffraction (XRD), as shown in Figure 1. The main crystalline phases are quartz (SiO2), anhydrite (CaSO4), and hematite (α-Fe2O3) coupling with some amorphous phase, and the Al-containing crystalline phase cannot be detected, implying Al2O3 exists in the form of amorphous components, which can be confirmed by the literature.13 Most of the Fe in CFBFA is in the form of weakly magnetic α-Fe2O3, which was further confirmed by the X-ray photoelectron spectroscopy (XPS) results in Figure 7.

The specific experimental process of the LOI is as follows:
Take the sample according to the quadratic method and accurately weigh 1 g of the sample. Put it in a constant weight porcelain crucible and place the cover on the crucible diagonally. Put it in a high-temperature furnace, gradually

| compounds | Al2O3 | SiO2 | CaO | Fe2O3 | SO3 | TiO2 | LOI |
|-----------|-------|------|-----|-------|-----|------|-----|
| content   | 34.70 | 42.20| 4.76| 4.40  | 4.14| 1.40 | 4.79|

*LOI: loss on ignition.*
increase the temperature from low temperature, and burn it at 950−1000 °C for 15−20 min. Then, take out the crucible, put it in a desiccator, and cool it to room temperature. Weigh and repeatedly cauterize until the sample achieves a constant weight.

The morphology and microcomposition analysis of CFBFA were analyzed by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), as shown in Figure 2. The particles are mostly distributed in irregular shapes due to the low combustion temperature (800−900 °C). Different areas were selected for microcomponent analysis using EDS to determine the content of individual elements. According to the microcomponent analysis, the mass ratio of Al to O in Al2O3 is 1.125, the mass fraction of Al is 3.28%, so the mass fraction of O combined with Al is 2.92%. Similarly, the mass ratio of Si to O in SiO2 is 0.88%, and it is known that the mass fraction of Si is 3.94%, so the mass fraction of O combined with Si is 4.5%. The mass fraction of the total O is 32.32%, and minus the O combined with Al and Si, it is about 2.41, which is almost close to the stoichiometric ratio of Fe to O in α-Fe2O3 (2.33), demonstrating that the Fe in CFBFA mainly exists in the form of α-Fe2O3, which is consistent with the XRD analysis.

The particle size distribution of CFBFA was determined by a laser particle size analyzer, and the results are presented in Figure 3. It is clearly observed that the CFBFA has a wide particle size distribution in the range of 0.7−150 μm, with a D(50) of 24.8 μm, D(90) of 78.8 μm, and volume mean diameter D[4,3] of 34.0 μm. The finer the particle size, the higher the fly ash activity, which facilitates the removal of Fe from CFBFA and the extraction of valuable elements.

2.2. Experimental Mechanism. From the characterization and analysis of CFBFA, the α-Fe2O3 in CFBFA cannot be directly separated using the magnetic separation method. Therefore, the transformation of α-Fe2O3 to magnetite (Fe3O4) using carbothermal reduction at a low temperature could be beneficial to efficiently remove the impurity of Fe before magnetic separation. According to the property of weakly ferromagnetic α-Fe2O3, which can be reduced to Fe3O4,27−29 the reducing agents are usually C, CO, and H2. The reaction theory can be expressed with the following equations

\[
3\text{Fe}_2\text{O}_3 + \text{C} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}↑
\]

\[
3\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2↑
\]

\[
3\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O}↑
\]

The residual carbon in CFBFA was analyzed and verified by the thermogravimetric method. As shown in Figure 4, two weight loss peaks appeared at room temperature ~416 and 416−750 °C, respectively, for the water volatilization and carbon oxidation stages, and the weight loss rate of the carbon oxidation stage was calculated to be 4.56%, indicating that the residual carbon of CFBFA was 4.56%. According to the content of Fe2O3 in CFBFA and eq 1, it can be calculated that 0.1% carbon was theoretically needed, which was far less than the residual carbon content in CFBFA. Thus, the residual carbon in the CFBFA is enough for the spinel ferrite transformation during the carbothermal reduction process.

2.3. Experimental Method. To investigate the effects of important parameters such as the reduction temperature and reduction time on Fe removal and Al recovery from CFBFA during the carbothermal reduction process, a series of experiments were carried out. 35 g of CFBFA was taken into...
an alumina crucible, compacted, and then reduced at a certain temperature in a furnace stove before the Ar gas flowed into the seal stove. The temperature of the stove was regulated at 550, 600, 650, 700, 750, and 800 °C by a temperature control procedure during the reduction reaction process, and the reduction time was set as 10, 30, 60, 90, and 120 min. To avoid the magnetite being re-oxidized to the feebly magnetic α-Fe₂O₃, the Ar gas was shut off when the temperature dropped below 200 °C, and the reduced samples were cooled to room temperature, and the reduced CFBFA (RCFBFA) samples were obtained.

The RCFBFA were separated by a magnetic separator using a magnetic field intensity of 0.4 tesla with the solid-to-liquid ratio of 1:20 g·L⁻¹. The separated products were divided into magnetic concentrates and nonmagnetic fractions. Then, both the samples were separately filtered and weighted. 0.10 g of CFBFA, RCFBFA, magnetic concentrates, and nonmagnetic fractions were placed in different vessels, respectively, and then 4 mL of hydrofluoric acid and 4 mL of aqua regia were added for microwave digestion (Multiwave ECO, Anton Paar, Austria) at 180 °C for 60 min. Finally, the liquor samples obtained from microwave digestion were analyzed by an inductively coupled plasma emission spectrometer (ICP-OES). According to the mass balance during the magnetic separation process, the removal ratio of Fe [η(Fe)] and the recovery efficiency of aluminum [η(Al)] were calculated using the following formulas, respectively.

\[
\eta(\text{Fe}) = \left(1 - \frac{M_n \cdot C_n}{M_t \cdot C_t}\right) \times 100\% \quad (4)
\]

\[
\eta(\text{Al}) = \left(\frac{M_n \cdot C_n}{M_t \cdot C_t}\right) \times 100\% \quad (5)
\]

where \(C_n\) and \(C_t\) represent the Fe content in mass % for the nonmagnetic fraction and raw CFBFA, while \(M_n\) and \(M_t\) indicate the mass of the nonmagnetic fraction and raw CFBFA, respectively; \(W_n\) and \(W_t\) represent the Al content in mass % for the nonmagnetic fraction and raw CFBFA, respectively.

2.4. Characterizations. The chemical compositions of CFBFA were analyzed by an X-ray fluorescence spectrometer (S8 Tiger, Bruker). The mineralogical composition in CFBFA was determined by XRD (D2, Bruker), using Cu Kα radiation (40 kV, 30 mA) at the scanning rate of 5°/min from 10 to 80°.

The morphological structure and microcomponent of samples were detected by SEM with EDS (SEM−EDS, JEOL, JSM-IT500HR), and the samples were observed under a 1000× magnification and an acceleration voltage of 10 kV with a high vacuum mode and a ZAF quantification method.

The particle size distribution of CFBFA was determined by a laser particle size analyzer (Matersizer 3000). An X-ray photoelectron spectrometer (AXIS UltraDLD, Japan) was used to test and analyze the valence state.

The concentration of elements, such as Al, Fe, and transition metal elements in samples, was determined by an inductively coupled plasma emission spectrometer (ICP-OES). A magnetic cube (XCGS-500/50) was used for the magnetic separation with an applied magnetic field of 0.4 T.

3. RESULTS AND DISCUSSION

3.1. Fe Removal by Magnetic Separation after Carbothermal Reduction. In the process of carbothermal reduction, the residual carbon in CFBFA was used as a reductant, and the effect of the main influencing factors during the carbothermal reduction process, namely, the reduction temperature and reduction time on Fe removal and Al recovery

Figure 4. Analysis of the residual carbon in CFBFA.

![Figure 4](ACS Omega http://pubs.acs.org/journal/acsona)
were investigated. The reduction temperature is one of the most important factors, which could have a great influence on the carbothermal reduction reaction. Elevating the reduction temperature to some extent could accelerate the reduction rate and degree; however, a high reduction temperature (>900 °C) might result in over-reduction, besides a high energy consumption and a harsh requirement for equipment. It is reported that the starting reduction temperature for α-Fe₂O₃ is about 500 °C; nevertheless, the over-reduced phase [non-magnetic wustite (FeO)] could be formed if the reduction temperature is increased to 900 °C, and the Fe removal becomes decreased. As a result, the reduction temperatures 550, 600, 650, 700, 750, and 800 °C were chosen to study their effect on the Fe removal and Al recovery and the Fe contents in each sample after magnetic separation, and the results are plotted in Figure 5.

From Figure 5, with an increasing reduction temperature from 550 to 800 °C, the Fe removal efficiency is first increased and then decreased, which is opposite to the trend of the Al recovery efficiency. The Fe content in the samples after magnetic separation could be reduced from 3.05 to 1.26%. At 700 °C, the Fe removal could reach the maximum (62.8%), lower than that found in the literature, but the Fe content in the nonmagnetic fraction is similar. This might be due to the fact that some Al in CFBFA is wrapped in the Fe-bearing phase or coexists with the Fe-bearing phase, as shown in Figure 2. As a result, a higher Fe removal efficiency could lead to a lower Al recovery efficiency. In addition, the reason why the Fe removal efficiency is lower than that found in the literature is because of the lower initial Fe content in raw materials. Therefore, the optimum temperature for the reduction is chosen at 700 °C.

The Cₙ, Cₜ, Mₙ, and Mₜ value in each operation condition with different temperatures are shown in Table 2.

Table 2. Results of Magnetic Separation for Each Operation Condition with Different Temperatures

| operation condition | temp (°C) | time (min) | Mₜ (g) | Mₚ (g) | Mₙ (g) | Cₜ (%) | Cₚ (%) | Cₙ (%) | Wₙ (%) | Wₚ (%) | η(Al) (%) | η(Fe) (%) |
|---------------------|---------|----------|-------|-------|-------|-------|-------|-------|-------|-------|---------|---------|
| 550                 | 60      | 35.0     | 33.0  | 30.9  | 9.1   | 3.05  | 2.32  | 3.85  | 18.37 | 20.14 | 2.26    | 96.8    | 32.8    |
| 600                 | 60      | 35.0     | 33.3  | 31.4  | 8.5   | 3.05  | 1.62  | 6.57  | 18.37 | 18.72 | 6.48    | 91.4    | 52.3    |
| 650                 | 60      | 35.0     | 33.1  | 30.3  | 10.1  | 3.05  | 1.36  | 6.49  | 18.37 | 17.35 | 11.6    | 81.8    | 61.3    |
| 700                 | 60      | 35.0     | 33.4  | 30.5  | 9.5   | 3.05  | 1.26  | 7.19  | 18.37 | 17.12 | 9.06    | 81.2    | 62.8    |
| 750                 | 60      | 35.0     | 32.8  | 30.3  | 9.1   | 3.05  | 2.18  | 4.47  | 18.37 | 16.89 | 8.42    | 88.1    | 38.2    |
| 800                 | 60      | 35.0     | 32.9  | 30.3  | 9.4   | 3.05  | 2.20  | 4.26  | 18.37 | 19.69 | 4.90    | 91.2    | 37.5    |

*Mₜ represents the mass of RCFBFA. Mₙ and Mₚ are the mass of wet magnetic concentrates and wet nonmagnetic fractions, respectively.

Figure 6. Effects of the reduction time on Fe removal, Al recovery (a), and the Fe content (b) in fly ash after magnetic separation (reaction temperature: 700 °C).

Table 3. Results of Magnetic Separation for Each Operation Condition with Different Times

| operation condition | temp (°C) | time (min) | Mₙ (g) | Mₜ (g) | Cₙ (%) | Cₜ (%) | Wₙ (%) | Wₜ (%) | η(Al) (%) | η(Fe) (%) |
|---------------------|---------|----------|-------|-------|-------|-------|-------|-------|---------|---------|
| 700                 | 10      | 31.5     | 35    | 1.44  | 3.05  | 17.84 | 18.37 | 87.4  | 57.6    |
| 700                 | 30      | 30.6     | 35    | 1.34  | 3.05  | 17.51 | 18.37 | 81.9  | 61.7    |
| 700                 | 60      | 31.5     | 35    | 1.26  | 3.05  | 17.12 | 18.37 | 81.2  | 62.8    |
| 700                 | 90      | 31.7     | 35    | 1.47  | 3.05  | 16.75 | 18.37 | 82.6  | 56.3    |
| 700                 | 120     | 31.6     | 35    | 1.51  | 3.05  | 17.57 | 18.37 | 86.4  | 55.5    |

Table 4. Comparison of the Fe Removal Efficiency, Fe Content, and Al Recovery Efficiency after Direct Magnetic Separation and Reduction–Magnetic Separation of CFBFA

| sample      | η(Fe) (%) | Cₙ (wt %) | η(Al) (%) |
|-------------|-----------|-----------|-----------|
| CFBFA       | 17.1      | 2.9       | 97.4      |
| RCFBFA      | 62.8      | 1.3       | 81.2      |

From Figure 5, with an increasing reduction temperature from 550 to 800 °C, the Fe removal efficiency is first increased and then decreased, which is opposite to the trend of the Al recovery efficiency. The Fe content in the samples after magnetic separation could be reduced from 3.05 to 1.26%. At 700 °C, the Fe removal could reach the maximum (62.8%), lower than that found in the literature but the Fe content in the nonmagnetic fraction is similar. This might be due to the fact that some Al in CFBFA is wrapped in the Fe-bearing phase or coexists with the Fe-bearing phase, as shown in Figure 2. As a result, a higher Fe removal efficiency could lead to a lower Al recovery efficiency. In addition, the reason why the Fe removal efficiency is lower than that found in the literature is because of the lower initial Fe content in raw materials. Therefore, the optimum temperature for the reduction is chosen at 700 °C.

To save energy and maximize the production efficiency, the effect of reduction time on the reduction reaction was investigated at the 700 °C reduction temperature. The...
The reduction time is between 10 and 120 min. The effect of reduction time on Fe removal and Al recovery by magnetic separation of CFBFA and the change of Fe content in fly ash after Fe removal are shown in Figure 6. From Figure 6a, in the initial stage of carbothermal reduction, the removal efficiency of Fe increases gradually, reaching the maximum (62.8%) at 60 min, and then declines. This is due to in the initial stage of the reaction, where the reducing agent content is higher and there is a sufficient contact between the fly ash and the reducing agent, so the reaction rate is fast, and the reduction reaction is fierce. With the prolongation of the reduction time, the reducing agent is consumed, and the reducing material is gradually reduced, resulting in the reduction reaction rate being gradually reduced. At the same time, too long a reduction time will also promote the transformation of magnetite to FeO with weak magnetic properties, occurring due to excessive reduction, resulting in a decline in Fe removal efficiency. It can be inferred that when the reduction temperature was 700 °C, the optimum reduction time was about 60 min, during which the reduction reaction of α-Fe₂O₃ was mostly completed. Therefore, the prolongation of the reduction time to increase the removal efficiency of Fe did not do much help and will cause energy wastage and affect the Al recovery efficiency. From Figure 6, it also can be seen that the

![Figure 7. XRD patterns of samples at different reduction temperatures (a), and enlarged figure of the selected area (b).](image)

![Figure 8. XPS spectrum of Fe 2p from the CFBFA (a) and the RCFBFA (c) at 700 °C for 1 h; The XPS spectrum of Fe 3p from the CFBFA (b) and the RCFBFA (d) at 700 °C for 1 h.](image)
Al recovery efficiency decreased at first, then increased, and reached the minimum at 60 min. This is because $\alpha$-Fe$_2$O$_3$ in CFBFA does not exist independently, and the majority is embedded with aluminosilicates, resulting in a higher Fe removal ratio with a lower Al recovery efficiency. The $C_{\text{Fe}}$, $C_{\text{Al}}$, Mn, and Mt value in each operation condition with different times were shown in Table 3.

The results of a comparison between direct magnetic separation and reduction−magnetic separation of CFBFA were shown in Table 4. From Table 4, the Fe removal efficiency of CFBFA was only 17.1%, and the Fe content of CFBFA after magnetic separation was 2.9%, but the Fe removal efficiency can be increased to 62.8% in magnetic separation after reduction, which indicates that the carbothermic reduction can significantly improve the Fe removal efficiency of CFBFA by magnetic separation.

### 3.2. Transformation Mechanism for the Carbothermic Reduction Process

As the results mentioned above, the carbothermal reduction has a great effect on Fe removal, and 17.1% is the Fe removal efficiency of sample CFBFA without carbothermal reduction. To reveal the transformation mechanism for the reduction process, the mineral phase, morphology, chemical compositions, and the existent form of Fe for the samples at different reduction temperatures were analyzed. Figure 7 shows the XRD patterns of the samples at different reduction temperatures. From the XRD patterns, as shown in Figure 7a, the diffraction peaks of CaSO$_4$ gradually decrease with increasing the reduction temperature and then almost disappear when the temperature was increased to 800 °C. It was reported that the decomposition of CaSO$_4$ under an air atmosphere occurs in the temperature range of 1097−1497 °C. However, the decomposition temperature can be significantly reduced to 600−800 °C in the presence of carbon, which was mainly attributed to the solid−solid reaction ($2C + CaSO_4 \rightarrow CaS + 2CO_2$). Therefore, the diffraction peaks of CaSO$_4$ disappeared when the reduction temperature was at 800 °C.

Furthermore, it can be observed that when the reduction temperature was controlled at 700 °C, the diffraction peaks of Fe$_3$O$_4$ could be found. Considering that the diffraction peaks intensity of SiO$_2$ is much too high, the partial XRD patterns with 2θ from 30 to 50° are also given, as presented in Figure 7b. The diffraction peaks of $\alpha$-Fe$_2$O$_3$ decrease with increasing the reduction temperature from 25 to 700 °C and then disappear when the temperature was increased to 750 °C or higher. Meanwhile, the intensity of diffraction peaks for Fe$_3$O$_4$ gradually increased with increasing the reduction temperature to 700 °C. However, when the reduction temperature was further increased to 750 °C, the diffraction peaks of Fe$_3$O$_4$ become decreased, and nearly disappeared when the temperature was increased to 800 °C, implying that a higher reduction temperature works against the formation of Fe$_3$O$_4$. In other words, when the reduction temperature is increased to 550 °C, $\alpha$-Fe$_2$O$_3$ starts to transform into Fe$_3$O$_4$, and the transformation from $\alpha$-Fe$_2$O$_3$ to Fe$_3$O$_4$ could be completed while the temperature is controlled at 700 °C, and further increasing the reduction temperature could not be facilitated to form Fe$_3$O$_4$. This phenomenon may attribute to the fact that Fe$_3$O$_4$...
transformed to FeO, resulting in over-reduction. And the composition of fly ash is complex, in which FeO reacts with SiO2 to form ferrous silicate, namely due to over-reduction.34

The XPS spectrum Fe 2p and Fe 3p for CFBFA and RCFBFA at 700 °C for 1 h are shown in Figure 8. From Figure 8a, it can be seen that the peak position of Fe 2p3/2, Fe2p3/2, and the satellite are 711.23, 724.71, and 718.05 eV, respectively, which is close to the binding energy of Fe 2p3/2, Fe 2p3/2, and the satellite of Fe2O3 obtained from a previous study.30,35−37 Treating the Fe 3p peak as a single peak, the Fe 3p for Fe3+ were determined from the spectrum. The Fe 3p peak position for Fe3+ was found to be 56.15 eV. Thus, the presence of Fe in CFBFA is Fe2O3. From Figure 8c, the satellite peak disappeared, and the peak position of Fe 2p3/2 and Fe 2p3/2 were 710.81 and 724.11, respectively. The absence of the satellite and the binding energy of Fe 2p3/2 and Fe 2p3/2 are consistent with the Fe 2p3/2 and Fe 2p3/2 for Fe3O4.35,38 The Fe 3p peak (Figure 8d) was deconvoluted into the Fe2+ and Fe3+ peaks by curve fitting using XPS PEAK4.1. The mean relative areas of each constituent peak assigned to Fe2+ and Fe3+ were calculated, and the ratio of Fe2+ and Fe3+ is 0.35:0.65. Since stoichiometric Fe3O4 also can be expressed to FeO·Fe2O3, the Fe2+/Fe3+ ratio should be 0.33:0.67. Therefore, the Fe2O3 from CFBFA can transform into Fe3O4 thoroughly.

To further confirm the transformation laws of the Fe-bearing phase during the reduction process, the morphology and microarea chemical compositions of the samples reduced at 550, 700, and 750 °C were analyzed by SEM−EDS, and the results are shown in Figure 9. It can be observed that Fe in the samples is embedded with aluminosilicates rather than existing independently, leading to a lower Al recovery efficiency, resulting from a high Fe removal efficiency. From the analysis of microarea chemical compositions, it can be found that when the reduction temperature is controlled at 550 °C, the mass ratio of Fe to O is 2.53 for region a and 2.24 for region b, respectively, which are between the theoretical value (2.62) of the mass ratio of Fe to O for Fe3O4 and the theoretical value (2.33) of the mass ratio of Fe to O for α-Fe2O3, implying that α-Fe2O3 has begun to be partially reduced and transformed to Fe3O4 at 550 °C. At 700 °C, the mass ratios of Fe to O for regions d, e, and f are 2.60, 2.79, and 2.75 (except for the oxygen bonding with Al and Si), respectively, which are close to the theoretical value (2.62) of that for Fe3O4, indicating that α-Fe2O3 has been completely reduced to Fe3O4. When the

Table 5. Contents of Metal Elements in RCFBFA, Magnetic Concentrates, and Nonmagnetic Fractions

| elements | RCFBFA contents (μg/g) | magnetic fractions | nonmagnetic fractions | relative enrichment indexa |
|----------|------------------------|-------------------|----------------------|--------------------------|
| Fe       | 35 731                 | 125 989           | 14 345               | 3.5                      |
| Mn       | 133                    | 389               | 81                   | 2.9                      |
| Cr       | 153                    | 277               | 119                  | 1.8                      |
| Co       | 25                     | 37                | 22                   | 1.5                      |
| Zn       | 159                    | 223               | 156                  | 1.4                      |
| Cu       | 39                     | 51                | 37                   | 1.3                      |

Relative enrichment index: a ratio of element content in magnetic fractions to the respective element content in RCFBFA.

Figure 11. Comparison of the leaching behavior of elements in CFBFA and CFBFA after Fe removal by the carbothermal reduction−magnetic separation process.
reduction temperature was increased to 750 °C, the mass ratios of Fe to O for regions g and h are 2.61 and 2.94, respectively, demonstrating that some Fe$_3$O$_4$ begins to transform to FeO and over-reduction has occurred. Therefore, the Fe removal efficiency significantly decreased when the reduction temperature reached 750 °C. The results are in accordance with the XRD patterns analysis.

3.3. Magnetic Separation, Extraction of Target Metals, and Transition Metal Enrichment. After the carbothermal reduction process at the optimal conditions, magnetic separation was adopted to remove the Fe-bearing phase. Figure 10 shows the XRD patterns of magnetic and nonmagnetic fractions after magnetic separation for the carbothermal reduction of CFBFA. The mineral composition in the magnetic concentrates is mainly composed of SiO$_2$, CaSO$_4$, and Fe$_3$O$_4$, indicating that \( \alpha \)-Fe$_2$O$_3$ has been reduced to Fe$_3$O$_4$. The phase transformation made the reduced sample easy to be separated by magnetic separation. Meanwhile, in the nonmagnetic fractions, the Fe-bearing phases could not be detected, further confirming that the Fe-bearing phase after the carbothermal reduction process could be removed by magnetic separation.

To investigate whether the carbothermal reduction–magnetic separation process affects the element extraction process in CFBFA, the leaching behavior of metallic elements in CFBFA after the carbothermal reduction–magnetic separation process to remove Fe was investigated. The concentration of the experimental HCl for extraction is 6 mol/L, and the reaction temperature is 100 °C. The results are shown in Figure 11. The leaching behavior of Al, Li, and Ga in CFBFA is not affected by the carbothermal reduction–magnetic separation process, which means that the carbothermal reduction process will not change the existing form of Al, Li, and Ga in the original CFBFA. The leaching efficiency of Fe in CFBFA after the carbothermal reduction–magnetic separation to remove Fe is reduced relative to the leaching efficiency of Fe in the original CFBFA, indicating that the carbothermal reduction–magnetic separation process inhibits the dissolution of Fe in HCl, which may be due to the following reasons: (1) the reactivity of Fe$_3$O$_4$ with HCl is lower than that of \( \alpha \)-Fe$_2$O$_3$; (2) the remaining Fe in ash after the carbothermal reduction–magnetic separation is distributed with an amorphous aluminosilicate phase adhesion nested wrapping, which is not easy to contact with HCl for reaction and leaching.

To further confirm the enrichment of transition elements such as Mn, Cr, Co, Zn, and Cu in the magnetic concentrates, the distribution of transition elements in the magnetic concentrates was analyzed by SEM and EDS, as presented in Figure 12. From Figure 12, it can be observed that transition
elements such as Mn, Cr, Co, Zn, and Cu have a similar distribution with Fe rather than Al, Si, which are in accordance with the metal element content results. Therefore, the carbothermal reduction–magnetic separation process can remove transition elements together.

4. CONCLUSIONS

In this paper, the carbothermal reduction–magnetic separation method was performed to remove Fe from CFBFA. The transformation process and mechanism of the Fe-bearing phase in CFBFA at different reduction temperatures were investigated. In addition, the enrichment of transition metal elements in magnetic concentrates obtained by magnetic separation was observed. By the carbothermal reduction with residual carbon in CFBFA, the Fe removal by magnetic separation from CFBFA can be improved efficiently. Non-magnetic fractions can be used to extract Al, Li, and Ga, which is beneficial to the high-value utilization of CFBFA. The main conclusions of this study are as follows:

1. The residual carbon in CFBFA, whose contents exceed more than the theoretical carbon content required for carbothermal reduction, is the reductant in the carbothermal reduction process. The reduction temperature and reduction time were two main factors which had effects on the removal of Fe from CFBFA. Through corresponding two groups of experiments, the optimum reduction reaction conditions were obtained as the following: the reduction temperature is 700 °C, and the reduction time is 60 min. Under the optimum reaction conditions, the two main parameters of the removal process of magnetic separation were obtained as the following: the removal ratio of Fe could reach 62.8%, and the recovery ratio of alumina can be maintained at 80.7%.

2. With the increase in the reduction temperature, the α-Fe$_2$O$_3$ in CFBFA first converts into a strongly magnetic magnetite, so the Fe removal ratio is greatly improved. When the reduction temperature is higher than 700 °C, an excessive reduction will occur, so the Fe removal rate will decrease dramatically. Since Fe in CFBFA does not exist independently and most aluminosilicates and Fe are embedded, a high Fe removal ratio always follows a lower Al recovery efficiency.

3. The carbothermal reduction–magnetic separation process slightly affects the existing form and leaching behavior of Al, Li, and other elements. After magnetic separation, transition metal elements such as Fe, Mn, Co, Cu, and Cr will be enriched in the magnetic phase and could be separated together with Fe.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was financially supported by the National Key R&D Program of China (no. 2020YFB0606205), the National Natural Science Foundation of China (no. 51804192), the Shanxi Province Applied Basic Research Project (no. 201801D221325), and the Xiangyuan Country Comprehensive Utilization Science and Technology of Solid Waste Research Projects (no. 2018XYSDJ-S04).

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