Investigation of the smelting reduction mechanism and of iron extraction from high-iron red mud

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Abstract
High-iron red mud presents a problem due to its alkalinity which leads to significant risks to the environment. In order to realize the harmless and large-scale utilization of high-iron red mud, the smelting reduction experiments were carried out to investigate the reaction mechanism for extraction of iron from high-iron red mud. FactSage 6.4 software was used to conduct thermodynamic analysis of the carbon thermal reduction system. The results showed that the direct reduction with carbon involved a process of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$, in which the theoretical required molar ratio of $C/O$ (oxygen in $\text{Fe}_2\text{O}_3$) was 1:1. The maximum degree of iron extraction was 92.8% with anthracite as reductant and 88.8% without anthracite smelting at 1500 °C for 30 min in a graphite crucible. XRD was conducted to analyze the mineral phase of the samples and slags. The results showed that the minerals contained in high-iron red mud were hematite, quartz, rutile, and sodium aluminosilicate hydrate. The blank sample was consisted of hematite, nepheline quartz, and the reduced slag without quenching consisted of perovskite and gehlenite, indicating that the reaction processes occurred from sodium aluminosilicate hydrate to nepheline and then occurred from nepheline to gehlenite in slagging process. The overall smelting reduction process was described as three mass transfer steps and three chemical reaction steps. These results provide useful information for large-scale and harmless utilization of high-iron red mud.

1. Introduction
Red mud is a solid waste residue primarily generated in the Bayer process of alumina production [1–3]. Generally, about 1–2 tonnes of red mud are generated with the production of 1 ton of alumina [4, 5]. In global alumina production, approximately 4.6 billion tonnes of red mud were stockpiled in landfills and impoundments by 2018 with an annual growth of 200 million tonnes [6]. Nearly 100 million tonnes of red mud were produced in China in 2018, which accounts for about 50% of the red mud generated in the world. Due to its high alkalinity, the utilization of red mud is significantly impacted with an average utilization rate of only 15% worldwide and 4% in China [7]. The huge emission and long-term stockpiling lead to a vast amount of land are occupied, furthermore, soil, groundwater, and air, are contaminated, which presents a serious risk to the surroundings [8–10].

High-iron red mud contains alumina, silica, titanium oxide, calcium oxide, sodium aluminosilicates, and a substantial amount of iron oxide (usually higher than 30 wt%) [11]. Many previous studies focused on the integral utilization of high-iron red mud were carried out on various applications such as construction materials [12–15], environmental restorative materials [16–18], catalyst and adsorbents [19]. However, the integral utilization of high-iron red mud is of low value and would cause a waste of resources, especially iron resources. Given the global shortage of iron supply, the high-iron red mud can be considered as a secondary raw material for iron recovery [20]. In high-iron red mud, the predominant phase of iron is hematite ($\text{Fe}_2\text{O}_3$) which can be easily recovered by carbon thermal reduction [21, 22]. Considering the high content of $\text{Fe}_2\text{O}_3$ in high-iron red mud, the carbon thermal reduction, such as roasting reduction followed by magnetic separation and smelting...
reduction, has been demonstrated to be effective methods for iron recovery from high-iron red mud [23]. Although the roasting temperature and energy consumption of the roasting reduction followed by magnetic separation method are low, however, the grade of magnetic concentrate obtained by magnetic separation and recovery rate of iron are relatively low [24].

During the smelting reduction process, the entire material is smelted and transferred into a liquid state, which is beneficial to the mass transfer process and increase the reaction rate. Some studies have been reported that pig iron can be obtained from high-iron red mud by carbon thermal smelting reduction method with a blast/electric/low shaft blast furnace [25, 26]. Guo et al reported a nuggets production process by direct smelting reducing the carbon-bearing pellets of red mud and coal. The content of Si and Mn was low in the obtained nuggets, while that of S and P was high [27]. Valeev et al carried out reductive smelting experiments of red mud to obtain pig iron with the efficiency of iron recovery around 98%. The content of Ti, P, and V was high in the pig iron, while the content of S was low [28]. However, the reduction temperature was 1750 °C, resulting in considerably high energy consumption. Many previous studies focus more on recovering iron by smelting reduction from carbon-bearing pellets with red mud, however, few studies elaborate the reduction mechanism of high-iron red mud using mixed powder directly.

In the present study, the mixed powder consisted of high-iron red mud, anthracite, calcium oxide, and calcium fluoride was used for recovering iron. FactSage 6.4 software (FactPS database) was used for the thermodynamic analysis of the smelting reduction mechanism. The smelting reduction mechanism of iron extraction and reaction processes in slagging process were investigated by carbon thermal smelting reduction with anthracite as a reducing agent. Calcium oxide and calcium fluoride were used to improve the viscosity of the slag. After smelting reduction, the metal of pig iron and slag were obtained. The further use of pig iron is steelmaking and the reduced slag can be used for the preparation of cement clinker directly. In view of this, this work will definitely be useful for feasible utilization of high-iron red mud in the environmentally and economically.

2. Materials and methods

2.1. Materials

Materials used in this work were high-iron red mud, anthracite, calcium oxide, and calcium fluoride. High-iron red mud was collected from an alumina refinery of the Weiqiao Pioneering Group, (Shandong province, China) randomly sampled and dried in a drying cabinet at 150 °C for 12 h. Then the dried high-iron red mud was crushed to 100 wt% and passing 150 μm sieve with a rod mill equipment. The chemical compositions of high-iron red mud were given in table 1. The content of Fe₂O₃ in high-iron red mud was 52.9 wt%. In addition, the content of Na₂O in high-iron red mud was 3.3 wt%. High alkalinity limits the application of high-iron red mud.

| Component | Fe₂O₃ | Al₂O₃ | SiO₂ | TiO₂ | Na₂O | CaO |
|-----------|-------|-------|------|------|------|------|
| Content   | 52.9  | 18.1  | 6.3  | 6.7  | 3.3  | 1.6  |

Anthracite, crushed and sieved to 100 wt% passing 150 μm sieve, was used as the reductant in the smelting reduction process. The properties of the anthracite, such as fixed carbon, volatile matter, and ash on an air dry basis were tested with the results of 83.8 wt%, 8.6 wt%, and 8.5 wt%, respectively. The main components of ash in anthracite were shown as the following compositions: 45.5 wt% Al₂O₃, 45.3 wt% SiO₂, 3.0 wt% CaO, and 4.5 wt% Fe₂O₃. The influence of low iron content in ash on iron recovery process assumed to be ignored. Calcium oxide and calcium fluoride, the analytical grade chemical reagent purchased from Aladdin (Shanghai, China), were used as additives for adjusting the viscosity of the slag.

2.2. Experimental methods

The carbon thermal smelting reduction experiments were performed in a reduction furnace (Northeastern University, Shenyang, China), whose diagram is shown in figure 1. High-iron red mud, anthracite, calcium oxide, and calcium fluoride were mixed in a rolling mixing machine with a mass proportion of high-iron red mud: anthracite: calcium oxide: calcium fluoride at 25: 4: 6: 1.

When the temperature of the reduction furnace was increased to 1500 °C, the mixed powders with 25 g of high-iron red mud, 4 g of anthracite, 6 g of calcium oxide, and 1 g of calcium fluoride were added in an open graphite crucible. The crucible dimensions (height/external diameter/inner diameter) was 120/48/40 mm. Then the temperature remained constant at a predetermined time. Sodium vapor, CO, and CO₂ produced by reduction were discharged out of the system with the flue gas and collected. When the reaction time was reached,
the graphite crucible was removed out of the reduction furnace. The molten iron and molten slag were casted in
the mould and cooled in the air. The pig iron and slag were separated well due to the higher density of iron.

In order to analyze the chemical compositions in samples of metals and slags, the samples were ground in a
planetary ball mill (FRITSCH, Germany) and sieved to 100 wt% passing 75 μm sieve. The element content of
iron in the metal was determined using the potassium dichromate titration method according to the National
standards of the People’s Republic of China GB/T 223.7-2002. X-ray fluorescence (ZSX Primus IV, Rigaku
Corporation, Japan), with standard curves, was used for quantitative analysis of the chemical compositions in
the raw materials and slags with the following sample preparation process: 0.7 g sample was weighted and added
in 7 g mixed solvent consisted of anhydrous lithium tetraborate and lithium metaborate. And 8 drops of
ammonium bromide solution with a mass fraction of 30% was added in mixed sample powder as the mold
release agent. Then the mixed sample powder was heated at 1050 °C for 800 s to prepare the sample for analysis.
In order to ensure the accuracy of the results, a series of standard samples with different chemical compositions
were used to calibrate the standard curves by calibration curve method.

In this manuscript, the standard error was calculated according to the following equation:

\[ \sigma = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \]  

where \( \sigma \) is the standard error; \( x_i \) is one of the measured values; \( \bar{x} \) is the average of multiple measurements; \( n \) is the
number of measurements (set with 3 in this manuscript).

The results were shown with a three-digit value.

The mineral composition analysis of the slag was performed by an x-ray diffraction analyzer (D8 Advance,
Bruker, Germany) with a Cu target by scanning the spectrum from 10° to 90° at a rate of 12°·min⁻¹. The
operation voltage was 40 kV and the electrical current was 40 mA. The micrograph of the quenched sample was
observed by a scanning electron microscope (SEM, model: SU-8000, Japan).

The degree of iron extraction was defined by equation (2) to determine the effects of experimental
parameters on reduction processes.

\[ \eta_{Fe} = \frac{M_{M} \cdot \beta_{Fe}}{M_{RM} \cdot \alpha_{Fe}} \times 100\% \]  

where, \( \eta_{Fe} \) is the degree of iron extraction, %; \( \alpha_{Fe} \) and \( \beta_{Fe} \) are the iron contents in high-iron red mud and metal,
respectively, wt%; \( M_{RM} \) and \( M_{M} \) are the mass of the high-iron red mud and metal, respectively, g.

3. Results and discussion

3.1. Thermodynamic analysis

Figure 2 shows the standard Gibbs free energy for reactions involved in the carbon thermal reduction process for
different temperatures calculated by FactSage 6.4 software. The reactions could be summarized by
equations (3)–(15) only considering the carbothermal reduction process:

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

\[ \text{Fe}_3\text{O}_4 + \text{C} = 3\text{FeO} + \text{CO} \]  

\[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} \]
3Fe₂O₃ + CO = 2Fe₂O₄ + CO₂ \tag{6}
Fe₂O₄ + CO = 3FeO + CO₂ \tag{7}
FeO + CO = Fe + CO₂ \tag{8}
3Fe + C = Fe₃C \tag{9}
C + CO₂ = 2CO \tag{10}
Al₂O₃ + 3C = 2Al + 3CO \tag{11}
SiO₂ + 2C = Si + 2CO \tag{12}
TiO₂ + 2C = Ti + CO \tag{13}
Na₂O + C = 2Na + CO \tag{14}
2Na + 0.5O₂ = Na₂O \tag{15}

In figure 2(a), it could be seen that the direct reduction reactions of Fe₂O₃ (equation (3)), Fe₃O₄ (equation (4)) and FeO (equation (5)) with carbon were more feasible since their standard Gibbs free energies were more negative than those of indirect reduction with CO (equations (6)–(8)). As temperature increased from 1000 °C to 1800 °C, the carburization reaction of metallic iron with carbon (equation (9)) could occur as shown in figure 2(a). In figure 2(b), the curves showed that the reactions of Al₂O₃ (equation (11)) and TiO₂ (equation (13)) with carbon to produce aluminum and titanium could not occur with standard Gibbs free energies greater than 0 from 1000 °C to 1800 °C. As the temperature was higher than 1670 °C, silicon dioxide could be reduced to silicon with a much higher reduction temperature than that of iron oxides. However, sodium oxide contained in high-iron red mud could also be co-reduced to sodium at temperatures above 1012 °C (equation (14)). The reduced metallic sodium immediately evaporated because of its lower boiling point (883 °C), which means that the sodium vapor could be re-oxidized and recovered from the off-gas stream (equation (15)).

In order to study the thermodynamic sequence of ferric oxide reduction, the phase stability diagram of Fe–O–C system of hematite in high-iron red mud at different temperatures was obtained by FactSage 6.4 (FactPS database). The calculation did not care about the effect of impurities (Al₂O₃, SiO₂, CaO, and TiO₂) in high-iron red mud on the reduction process of the ferric oxide. With the increase of temperature, the phase stability area of Fe₃O₄ decreased and those of FeO and Fe increased.

The thermodynamic sequence of ferric oxide reduction was described with the following three steps: at first Fe₂O₃ was reduced to Fe₂O₄. In the second stage, Fe₂O₄ was converted to FeO. Finally, metallic iron was obtained \[29, 30\]. Therefore, the direct reduction of Fe₂O₃ with carbon involved a processes as follows: Fe₂O₃ → Fe₂O₄ → FeO → Fe. The melting point of Fe₂O₄ is high (1594.5 °C) increasing the viscosity and melting point of the slag, which has negative effect on the reduction process. As a result, increasing the reduction temperature or reducing the partial pressure of CO₂ is beneficial to reducing the phase stability area of Fe₂O₄ shown in figure 3.

In order to determine the theoretical carbon consumption during the experiment, the equilibrium compositions of Fe₂O₃-C system with different carbon additions was calculated by FactSage 6.4 (FactPS database) at 1500 °C. Because the main iron-bearing phase in high-iron red mud was hematite and impurities such as Al₂O₃, SiO₂ and TiO₂ in red mud hardly reacted with carbon at 1500 °C, the pure substances system of Fe₂O₃-C was adopted for the calculation of equilibrium composition omitting the formation of iron-carbon liquid solution. And the slagging reactions involving Al₂O₃, SiO₂, CaO, and TiO₂ were also ignored. The result was shown in figure 4 with the assumption that 13.2 g Fe₂O₃ contained in 25 g high-iron red mud participated in
When the mass of carbon added in the system was less than 1.0 g, the mass of Fe₃O₄ increased first, then decreased, and finally disappeared. However, the mass of FeO increased rapidly at first reaching a maximum mass value. A small amount of iron began to appear as the mass of carbon increased from 0.5 g to 1.0 g. As the mass of carbon continued to increase from 1.0 g to 3.0 g, the amount of FeO decreased significantly and disappeared in the end. Correspondingly, the content of Fe increased step-by-step and stabilized as the mass of carbon increased from 2.5 g to 3.0 g, showing that iron oxides in high-iron red mud were completely reduced to metallic iron with the theoretical carbon consumption of 3.0 g. When the mass of carbon increased from 3.0 g...
to 3.5 g, the excess carbon reacted with the metallic iron to form a low melting point melt of Fe₃C, which was conducive to the separation of the metal from the slag. The overall reaction was summarized as follows:

$$\text{Fe}_2\text{O}_3(s) + 3\text{C}(s) = 2\text{Fe}(s) + 3\text{CO}(g)$$  \hspace{1cm} (16)

Accordingly, the suitable amount of carbon addition was 3.0 g per 25 g of high-iron red mud. As shown in table 1, 52.9 wt% of Fe₂O₃ was contained in high-iron red mud. According to the reduction reaction (16), the theoretical carbon addition required for complete reduction of Fe₂O₃ to metallic iron was 3.0 g. It indicated that the required molar ratio of C/O was 1:1, where O was only associated with iron.

In high-iron red mud, the total content of Fe₂O₃, Al₂O₃, and SiO₂ was 77.3 wt%. In the process of reduction, impurities such as Al₂O₃ and SiO₂ in high-iron red mud reacted with FeO to form low melting-point iron phases [31, 32], which reduced the recovery rate of iron. After reduction reaction, Fe₂O₃ was reduced to metallic iron and the precipitation separation resulted in molten iron and molten slag. The reduced slag consisted mainly of high-melting-point substances such as Al₂O₃ and SiO₂, leading to a raise of the liquidus temperature for slag, which hindered the separation of molten iron from molten slag. One way to lower the liquidus temperature and viscosity of slag and improve the degree of iron extraction is addition of calcium oxide [33, 34].

Figure 5(a) is the liquidus isotherm contour plot of Al₂O₃–SiO₂–CaO system for different temperatures calculated by FactSage 6.4 Software (FToxid and FToxCN database). The molar ratio of SiO₂/(Al₂O₃ + SiO₂) in high-iron red mud was 0.4 shown in point (a) indicated on Gibbs triangle. It could be seen that the liquidus temperature of the slag was high with low content of calcium oxide. With the increase of calcium oxide addition from point (a) to point (b), the liquidus temperature gradually decreased and then raised again. Therefore, according to the content of Al₂O₃ and SiO₂ in high-iron red mud, the addition amount of calcium oxide was suitable when the mineral composition of slag was in the domain of melilite (Ca₂Al₆Si₈O₂₄). Figure 5(b) is the isothermal section plot of Al₂O₃–SiO₂–CaO for 1500 °C. As shown in figure 5(b), there were two separate liquid phase domains (2 and 6) in the Al₂O₃–SiO₂–CaO system. The main equilibrium phase assemblage at 1500 °C was melilite shown in domain 3, which was consistent with the XRD patterns of the reduced slags without quenching.

3.2. Reaction process of reduced slag in slagging process

The carbon thermal reduction experiments were conducted in graphite crucible at 1500 °C for 30 min. And then the reduced slags were casted and cooled in the air to investigate the reaction process of reduced slag in slagging process. A blank experiment was performed without anthracite, calcium oxide and calcium fluoride addition to study the reaction process of components in high-iron red mud at 1500 °C for 30 min. An alumina crucible was used in the blank experiment to eliminate the reduction of graphite crucible.

Figure 6(a) shows the XRD pattern of the high-iron red mud. The result indicated that the high-iron red mud consisted of hematite (Fe₂O₃), goethite (FeO(OH)), boehmite (AlO(OH)), quartz (SiO₂), rutile (TiO₂), and sodium aluminosilicate hydrate (Na₃Al₅Si₈O₂₄(H₂O)). And the predominant phase of iron was hematite. Figure 6(b) was the XRD pattern of the blank sample. The result showed that the blank sample mainly consisted of hematite, nepheline (NaAlSiO₄) and quartz. Compared with the result of figure 6(a), goethite disappeared after heated at high temperature to form hematite, the diffraction peaks of which were much higher. The sodium aluminosilicate hydrate was decomposed to form a new phase of nepheline. Figure 6(c) expressed the XRD pattern of the reduced slag and the result showed that the main phases in the reduced slag were perovskite.
(CaTiO₃) and gehlenite (Ca₂Al₂SiO₇). The diffraction peaks of hematite disappeared indicating that hematite was completely reduced to metallic iron. Perovskite was formed from titanium dioxide in the presence of calcium oxide. The results of comparison between figures 6(a)–(c) showed that the reaction processes occurred from sodium aluminosilicate hydrate to nepheline, and then occurred from nepheline to gehlenite. The Gibbs free energies of reactions (19) and (21) were calculated by FactSage 6.4 Software (FactPS database). One of the reaction product of reaction (21) was sodium silicate [34], which was amorphous, with no diffraction peaks in the XRD pattern result. The reaction process could be described by the following reaction pathway:

\[ \text{Na}_3.6\text{Al}_{1.6}\text{Si}_{8.4}\text{O}_{24}(\text{H}_2\text{O}) = 3.6\text{NaAlSiO}_4 + 4.8\text{SiO}_2 + \text{H}_2\text{O} \]  
\[ \Delta G^\circ_{1500 \degree C} = -63.52 \text{ kJ mol}^{-1} \]  

\[ \text{TiO}_2 + \text{CaO} = \text{CaTiO}_3 \]  
\[ \Delta G^\circ_{1500 \degree C} = -9.48 \text{ kJ mol}^{-1} \]  

\[ 2\text{NaAlSiO}_4 + 2\text{CaO} = \text{Ca}_2\text{Al}_2\text{SiO}_7 + \text{Na}_2\text{SiO}_3 \]  
\[ \Delta G^\circ_{1500 \degree C} = -2.64 \text{ kJ mol}^{-1} \]  

The set of reactions (17)–(19) belongs to sample of figure 6(b). And all the reactions (17)–(21) belongs to sample of figure 6(c) with addition of CaO.

Figure 6(d) shows the XRD pattern of the metal product. It could be seen in figure 6(d) that, the main phases in the metal were Fe and Fe₃C, which was consistent with the equilibrium composition result shown in figure 4. The formation of Fe₃C was conducive to the separation of the metal from the slag due to the low melting point. After smelting reduction at 1500 °C for 5 min and 30 min in the graphite crucible, the reduced slags were quantitatively determined by x-ray fluorescence with standard curves to detect the main chemical compositions. The results were shown in table 2. As the smelting time increased from 5 min to 30 min, the total content of iron (TFe) was decreased from 8.0% to 0.8% illuminating that the hematite in red mud was easily reduced and the smelting reduction achieved good result. Almost all titanium (Ti) was concentrated in slag. The mineral phase of titanium in slag was CaTiO₃ shown in figures 6 and 8. It was possible to extract titanium from slag by acid leaching method or flotation method using flotation reagents.
According to the content of chemical components in the reduced slag smelting for 30 min shown in table 2, the molar ratio of SiO2/(Al2O3 + SiO2) and Al2O3/(Al2O3 + CaO) were calculated for 0.4 and 0.3, respectively. In the phase diagram of Al2O3-SiO2-CaO (figure 5), point (a) with a molar ratio of SiO2/(Al2O3 + SiO2) for 0.4 was first determined on the line of Al2O3-SiO2 in Gibbs triangle. Then line (ab) was drawn from point (a) to point (b) (vertex of CaO in Gibbs triangle). In a similar way, a line from the point with a molar ratio of Al2O3/(Al2O3 + CaO) for 0.3 to the vertex of SiO2 in Gibbs triangle was drawn. The point (c) where the two lines intersected was determined as the corresponding position of the reduced slag smelting for 30 min shown in figure 5. In figure 5, point (c) was located in the phase region of melilite, which was consistent with the result in figure 6(c). Further research on slags would be carried out, such as using the reduced slag as raw materials for preparation of cement clinker.

Table 2. Main chemical components of reduced slags without quenching (wt%).

| Smelting time | Al2O3 | SiO2 | CaO | TiO2 | Na2O | TFe |
|---------------|-------|------|-----|------|------|-----|
| 5 min         | 27.6  | 10.7 | 33.3| 7.4  | 4.2  | 8.0 |
| 30 min        | 31.4  | 12.0 | 39.6| 7.7  | 1.9  | 0.8 |

According to the content of chemical components in the reduced slag smelting for 30 min shown in table 2, the molar ratio of SiO2/(Al2O3 + SiO2) and Al2O3/(Al2O3 + CaO) were calculated for 0.4 and 0.3, respectively. In the phase diagram of Al2O3-SiO2-CaO (figure 5), point (a) with a molar ratio of SiO2/(Al2O3 + SiO2) for 0.4 was first determined on the line of Al2O3-SiO2 in Gibbs triangle. Then line (ab) was drawn from point (a) to point (b) (vertex of CaO in Gibbs triangle). In a similar way, a line from the point with a molar ratio of Al2O3/(Al2O3 + CaO) for 0.3 to the vertex of SiO2 in Gibbs triangle was drawn. The point (c) where the two lines intersected was determined as the corresponding position of the reduced slag smelting for 30 min shown in figure 5. In figure 5, point (c) was located in the phase region of melilite, which was consistent with the result in figure 6(c). Further research on slags would be carried out, such as using the reduced slag as raw materials for preparation of cement clinker.

3.3. Influence of reduction time in carbon thermal reduction process

Figure 7 shows the degree of iron extraction with and without anthracite for different smelting time at 1500 °C. As shown in figure 7, the degree of iron extraction with anthracite was a little higher than that without anthracite, illuminating that the carbon in graphite crucible could reduce the iron oxide in high-iron red mud to metallic iron at high temperature. In the reduction process with anthracite, the reduction reactions occurred on both the surface of carbon particles and the surface of graphite crucible with the carbon particles suspended in the melt. Therefore, the increase of the contact area between melt and carbon resulted in a faster rate of the carbothermal reduction. The reduction reaction with anthracite occurred not only on the surface of anthracite particles but also at the interface between the graphite crucible and the melt. While, it only occurred at the interface between the graphite crucible and the melt without anthracite. As smelting time of 5 min, the degree of iron extraction was 66.5% with the addition of anthracite, showing that hematite in high-iron red mud was easy to be reduced at high temperature. The degree of iron extraction increased sharply with time from 0 min to 5 min and then increased slightly, reaching a maximum degree of iron extraction of 92.8% with anthracite and 88.8% without anthracite at 30 min in a graphite crucible.

The XRD patterns for the slags smelting at 1500 °C for different smelting times are shown in figure 8. The figure showed that at smelting time of 5 min, the slag was consisted of perovskite, gehlenite, and unseparated metallic iron due to high viscosity of the slag. However, the diffraction peaks of gehlenite were very weak. With
the increase of smelting time, the metallic iron disappeared indicating that molten iron and slag were separated well. From 10 min to 15 min, the diffraction peaks of gehlenite had changed obviously which indicated that the mineral phase transformation of the slag occurred. After reduction for 15 min, a fusible precipitate formed and the metal was able to fall to the bottom. However, prolonging the melting time from 15 min to 30 min, the diffraction peaks for the slags were similar showing that mineral phase transition had been completed with smelting time of 15 min.

3.4. Mechanism of smelting reduction for iron recovery

In the smelting reduction experiments with anthracite, the mixed powder was melted and reduced rapidly with carbon immediately after the mixed powder was added into the graphite crucible. When the reaction was over, the low melting point resulting molten iron with carbon dissolved in it settled at the bottom of the crucible. There was a molten slag layer on the molten iron, protecting the molten iron from oxidation.

Ultimately, according to the phenomena of the smelting reduction process and results in 3.1 and 3.3, the melt in the graphite crucible could be divided into three layers from top to bottom: slag layer, reaction layer and molten iron layer. In the slag layer, the main reactions were shown in reactions of (17)–(21). In the reaction layer, as shown in (4)–(6), the hematite (\(\text{Fe}_2\text{O}_3\)) was reduced to magnetite (\(\text{Fe}_3\text{O}_4\)), wustite (\(\text{FeO}\)), and solid metallic iron in sequence by the carbon in anthracite and graphite crucible. A lot of CO bubbles were produced in the melt, constantly overflow to the surface of the melt, and burnt in the air, resulting in bright flames. The solid metallic iron from reduction settled at the bottom of the graphite crucible and dissolved with carbon from anthracite and graphite crucible to form the low melting point Fe–C melt. On the top interface of the Fe–C melt, FeO was reduced to metallic iron by 'C'. The symbol 'C' was the carbon dissolved in Fe–C melt. The reactions in the molten iron layer could be described by the following reaction pathway:

\[
\text{C} = C
\]

\[
\text{FeO(l)} + C = \text{Fe(s)} + \text{CO(g)}
\]

The overall smelting reduction process, shown in figure 9, could be described as three mass transfer steps in (b), (d), and (f) and three chemical reaction steps in (a), (c), and (e):

(a) Reactions of (4)–(6) occurred at reaction layer;
(b) CO bubbles transferred to the surface of the slag;
(c) Metallic iron was carburized by carbon to form a Fe-C melt;
(d) The dissolved carbon 'C' transferred to the top interface of the Fe-C melt;
(e) Reaction of (23) occurred on the top interface of the Fe-C melt;
(f) Carbon transferred to Fe-C melt;
4. Conclusion

In this study, the reaction mechanism for iron extraction was investigated in terms of utilization of high-iron red mud. The thermodynamic analysis showed that the direct smelting reduction involved a three-stage process of Fe$_2$O$_3 \rightarrow$ Fe$_3$O$_4 \rightarrow$ FeO $\rightarrow$ Fe with the theoretical required molar ratio of C/O of 1:1.

The smelting reduction experimental results showed that the maximum degree of iron extraction was 92.8% with anthracite and 88.8% without anthracite smelting at 1500 °C for 30 min in a graphite crucible. XRD analysis showed that the reaction processes occurred from sodium aluminosilicate hydrate to nepheline, and then occurred from nepheline to gehlenite in cooling process in the air. The mechanism of smelting reduction for iron extraction was described as three mass transfer steps and three chemical reaction steps.

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Conflicts of interest

The authors declare no conflict of interest.

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Figure 9. Overall smelting reduction process of iron oxide by carbon in the graphite crucible.
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