Innovative Methodology for Separating of Rare Earth and Iron from Bayan Obo Complex Iron Ore

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A new process was proposed in this research, in order to address the problems of difficult treatment, low efficiency and heavy pollution of Bayan Obo complex iron ore. The isothermal reduction experiments, using carbon-bearing pellets which were mainly made of Bayan Obo complex iron ore and pulverized coal, were investigated in the temperature range of 1 623–1 723 K with different heating time. The results indicate that the pellets could not melt well at 1 623 K and 1 723 K, and the iron nugget and slag can separate in a clear manner at 1 673 K for 12 min. The contents of C and S in iron nugget are 2.09% and 1.62% respectively. The iron nugget can be used partly to substitute the steel scrap for EAF steelmaking. The RE2O3 content is 14.19% in the rare-earth-rich slag. Nearly all rare earth is concentrated into one phase during solidification, which is identified as cefluosil ([7(Ca, Ce, La, Nd)2·SiO4] (F, O)10). The slag was leached by hydrochloric acid and the leaching efficiency of rare earth is 98.70%. After being filtered, the solution can be used to extract rare earth and the leached residue will be treated to recover CaF2 and ThO2.

KEY WORDS: Bayan Obo complex iron ore; carbon-bearing pellets; iron nugget; rare-earth-rich slag.

1. Introduction

The Bayan Obo Mine in the Inner Mongolia region of North China is the largest iron-LREE-niobium ore deposit of hydrothermal origin known in the world. It accounts for 35% rare earth resource of world’s proven reserves and approximately 80% in China.1–4) Currently, it is mined mainly as an iron ore with a designed capacity of 12 million tons per year, thus the rest 230 million tons of ore in the Main and East Ore Body will be used up within 20 years. Therefore, the comprehensive utilization of Bayan Obo complex iron ore has become an urgent task.

The primary problems in the utilization of Bayan Obo complex ore are the efficient separation of rare earth and iron and the qualities of separated products for further process. Although many methods have been used for processing Bayan Obo complex ore, such as blast furnace process,5,6) mineral dressing7,8) and direct reduction-beneficiation process without melting reaction.9) Unfortunately, the running condition of blast furnace gets worse with the coke ratio increasing, the productivity dropping and furnace lining eroded seriously. Therefore, this process is no longer used. Through mineral dressing, iron concentrate is separated from raw ore at first with a recovery rate of 70%. The rare earth, coexisting with iron mineral, is recovered as a byproduct of iron ore mining and the recovery rate is only about 10%. And most of rare metal minerals remain in the tailings. Employing this method to treat this complex ore resulted in a waste of resources and environmental pollution. Because the reduced pellets obtained from solid direct reduction-beneficiation process contain a certain amount of metallic iron, they are difficult to be crushed. And even though after crushed, DRI powder is apt to suffer from oxidation owing to the small particle size and large specific area. In addition, rare-earth-rich slag is impossible to satisfy the needs of further process very well.

In order to efficiently utilize Bayan Obo complex iron ore and overcome the current problems, a new process has been proposed for the rare earth and iron separation based on carbon-bearing pellet reduction and melting technology, which is a kind of low CO2 emission, economical and environmental friendly innovative technology for the development of steel industry.10–15) In this work, a simulation test of rotary hearth furnace was conducted using Bayan Obo complex ore, pulverized coal and organic binder as raw materials. Firstly, the influences of temperature and time on the reduction and melting behavior of carbon-bearing pellets were investigated; and then the characteristics of the separation products were determined with the help of XRD, SEM-EDS (energy-dispersive spectrometry) and chemical analysis. Furthermore, acid leaching experiment was carried out for leaching rare earth from slag. This work is expected to provide information for separation and recovery of iron and rare earth when the new process is applied to treat Bayan Obo complex iron ore.

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2. Experimental

2.1. Raw Materials

Table 1 shows the chemical composition of Bayan Obo complex iron ore utilized as iron source in this investigation. The iron ore is run-of-mine ore with characteristics of low grade and multi component. After being ball milled, the granulometric distribution analysis of the iron ore powder determined by laser granulometer is shown in Fig. 1. The particle size of iron ore powder smaller than 56.156 μm occupies 90%, and the mean particle size is 16.475 μm.

The mineral composition of the ore was investigated by means of XRD. The pattern was analyzed using the Search-match software as shown in Fig. 2. And the SEM micrograph of iron ore together with EDS profiles of selected positions is presented in Fig. 3. It indicates that the mineral phases are hematite, magnetite, bastnaesite-(Ce), fluorite, quartz, calcite and barites.

The pulverized coal is used as reductant and carburizer and its chemical composition is listed in Table 2, which indicates that the coal is high in fixed carbon, low in ash and sulfur. The chemical composition enables the coal to be a

<table>
<thead>
<tr>
<th>TFe</th>
<th>FeO</th>
<th>RE₂O₃</th>
<th>Nb₂O₅</th>
<th>F</th>
<th>P</th>
<th>S</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.20</td>
<td>7.92</td>
<td>7.04</td>
<td>0.09</td>
<td>10.51</td>
<td>0.82</td>
<td>1.00</td>
<td>0.79</td>
</tr>
<tr>
<td>CaO</td>
<td>MgO</td>
<td>Al₂O₃</td>
<td>SiO₂</td>
<td>K₂O</td>
<td>Na₂O</td>
<td>BaO</td>
<td>ThO₂</td>
</tr>
<tr>
<td>22.70</td>
<td>0.92</td>
<td>0.60</td>
<td>7.43</td>
<td>0.14</td>
<td>0.78</td>
<td>1.05</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Fig. 1. Granulometric distribution of Bayan Obo complex iron ore.

Fig. 2. XRD pattern of Bayan Obo complex iron ore.

Fig. 3. SEM micrograph of Bayan Obo complex iron ore together with EDS profiles of selected positions.
good reductant and carburizer in present experiments. It can be seen from Fig. 4, the mean particle size of pulverized coal is 37.591 μm and 90 percent is smaller than 188.29 μm.

2.2. Experimental Procedure

The carbon-bearing pellets used in this work were prepared with iron ore and pulverized coal in such amounts that maintained the mixing ratio of [reducible oxygen mol (O)]/[fixed carbon mol(C)] = 1.0 (carbon necessary for the reduction reactions), and plus the amount of carbon corresponding to 4% of the total iron of pellet for carburizing the reduced iron. The iron ore and pulverized coal were mixed thoroughly with 7% moisture and 2% organic binder. The carbon-bearing pellets were made by a laboratory scale horizontal twin-roller machine, with a pillow shape of 40 mm × 30 mm × 20 mm in size and 30 g in weight after being dried adequately at 378 K in a drying oven for 8 hours. And the chemical composition of carbon-bearing pellet is listed in Table 3.

The isothermal reduction and melting process of carbon-bearing pellets were investigated in the temperature range 1 623–1 723 K and designated reaction time. The experiments were conducted in a laboratory scale resistance box furnace. The temperature of hot zone was maintained within ±5 K. In the experiments, the dried pellets were placed in a graphite plate and then heated in the furnace. The graphite plate had already been heated to the target temperature before the reduction beginning. During the sample charging, the temperature of the furnace dropped 5–10 K and soon reached the desired level within 2–3 min after the door of furnace was closed. In addition, experiments were run at atmospheric conditions and purge gases were not utilized. Once the reduction experiments finished, the samples were taken out of the furnace rapidly and cooled to ambient temperature and then prepared for chemical analysis.

The pellets, which didn’t melt and became into metallized pellets, were tested by the index of metallization rate (ηFe).

The metallization rate of iron components (ηFe) can be expressed as Eq. (1):

\[ \eta_{Fe} = \frac{M_{Fe}}{T_{Fe}} \times 100\% \] ........................... (1)

\( M_{Fe} \): metallic iron content in the reduced pellets;
\( T_{Fe} \): total iron content in reduced pellets.

In order to evaluate the leaching efficiency of rare earth from rare-earth-rich slag, the normal pressure acid leaching method was applied. The parameters of the method were described as follows: Amount of rare-earth-rich slag: 5.00 g; Particle size of slag: 100% smaller than 74 μm; Concentration of acid: 18% HCl; Volume of acid solution: 40 ml and Leaching time: 4 h. The rare earth contents of rare-earth-rich slag and leached residue were measured with gravimetric method (GB/T 6730.25-2006). The leaching efficiency of rare earth was defined by Eq. (2).

\[ \eta_{RE} = \left( 1 - \frac{R_{RE}}{T_{RE}} \right) \times 100\% \] ........................... (2)

\( T_{RE} \): rare earth amount of rare-earth-rich slag;
\( R_{RE} \): rare earth amount of leached residual slag.

2.3. Thermodynamic Consideration

The behaviors of iron, rare earth elements and niobium in the reduction and melting process are analyzed from thermodynamics. The diagram of relationship between standard Gibbs free energy of formation for oxides and temperature can be drawn based on the thermodynamic data.\(^{16,17}\) As shown in Fig. 5, the reduction of iron oxides can be divided into three steps, Fe₂O₃→Fe₃O₄, Fe₃O₄→FeO and FeO→Fe in order at the temperature above 843 K.

Bastnaesite is the main rare earth mineral in Bayan Obo complex iron ore and is decomposed into Ce₂O₃ during the heating process. The direct reduction temperature of Ce₂O₃ by carbon is above 2 600 K in standard state, and it is much higher than the experimental temperature. Therefore, Ce₂O₃ is difficult to be reduced by carbon in the experiment, although the reduction temperature will reduce with the decreasing of the partial pressure of CO. Finally, the rare earth oxides, together with the gangue minerals contained in

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ash analysis</th>
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<tbody>
<tr>
<td>FC</td>
<td>VM</td>
</tr>
<tr>
<td>81.40</td>
<td>5.40</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Ash analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>TFe</td>
<td>FeO</td>
</tr>
<tr>
<td>24.54</td>
<td>7.12</td>
</tr>
<tr>
<td>CaO</td>
<td>MgO</td>
</tr>
<tr>
<td>20.33</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Fig. 4. Granulometric distribution of pulverized coal.

Fig. 5. Diagram for ΔG° of the formation of oxides.
the feed, will fuse into slag phase.

In Bayan Obo complex iron ore, niobium is mainly hosted in niobite and ilmenorutile. The carbothermic reduction of niobium pentoxide is carried out in the following overall reaction:18)

\[ \text{Nb}_2\text{O}_5 + 3\text{C} = 2\text{Nb} + 3\text{CO} \]

The niobium oxides not only can be reduced by carbon, but also react with carbon to form niobium carbide. The tendency of formation of niobium carbide increases with temperature rising.

\[ \text{Nb}_2\text{O}_5 + 7\text{C} = 2\text{NbC} + 5\text{CO} \]

Based on the previous studies,19,20) the productions of the niobium pentoxide reduced by carbon are lower oxide and carbide, and it is generally difficult to gain metal Nb.

3. Results and Discussion

3.1. Effect of Temperature and Time on the Reduction and Melting Behavior

As illustrated in Fig. 6, the temperature and heating time have significant effect on the metallization rate of composite pellets. The metallization rate increases from 69.23% to 96.53% with temperature increasing from 1623 K to 1723 K for 5 min. The metallization rate increases from 16.47% to 97.57% when the heating time prolonged from 2 to 9 min at 1673 K.

In the coal-based direct reduction processes, the iron oxides are reduced by solid carbon, volatile matter and reducing gas generated from gasification of carbon in coal. Volatile matter in the coal evolves and hydrocarbons in the volatiles are cracked into lower hydrocarbon, \( \text{H}_2 \) and \( \text{CO} \).21) The direct reduction takes place by the solid-solid reaction between carbon and iron ore as shown in Eq. (6). And the indirect reduction occurs through gaseous intermediates as shown in Eq. (7). The carbon is gasified by the \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) produced in Eq. (7). And the product \( \text{CO}_2 \) and \( \text{H}_2\text{O} \), which in turn gasifies carbon to generate \( \text{CO} \) and \( \text{H}_2 \) in Eq. (8). The CO produces \( \text{CO}_2 \) through iron oxides reduction as shown in Eq. (7).22,23)

\[ \text{Fe}_x\text{O}_y + \text{C} = \text{Fe}_{x-1}\text{O}_y + \text{CO} \]
\[ \text{Fe}_x\text{O}_y + \text{CO}/\text{H}_2 = \text{Fe}_{x-1}\text{O}_y + \text{CO}_2/\text{H}_2\text{O} \]
\[ \text{C} + \text{CO}_2/\text{H}_2\text{O} = 2\text{CO}/(\text{CO} + \text{H}_2) \]

The carbothermic reduction is dominated by the direct reduction at the initial stage of reduction, and it is determined by the indirect reduction when the CO partial pressure exceeds a certain value.24) And then the carburization reaction accompanied as shown in Eq. (9).

\[ \text{C} = [\text{C}] \]

The direct carburization through direct contact points is the major reaction and the gaseous (such as CO) carburization is the minor one. The reaction (9) is the most important step from the viewpoint of saving energy.25,26)

The apparent morphology of the pellets during the reduction process at 1673 K is listed in Fig. 7. The result shows that the pellet will swells at the beginning, and then shrinks during the reduction process. Nine minutes later, the slag melted partially. Finally, slag and iron can be separated sufficiently at 1673 K for 12 min.

At 1623 K with 15 min, a metallic shell formation containing molten slag only in the center and the metallization rate of pellets is about 98%. It can be concluded that the reduction reaction essentially finished, but the pellets can’t be melted. The reason is that the carburization of the reduced iron is not enough to make it melt. By contrast, slag and iron can also separate only in 6 min at 1723 K. There are about 5% FeO in the slag and the recovery ratio of iron is low.

The morphology of iron nugget and slag is lamellar shape as shown in Fig. 7. And the specific reasons need iron and slag separation process analysis. The separation of liquid metal and molten slag from each other is mainly controlled by the difference of specific gravities and surface tensions between metal and slag. The density of molten iron is about 7.0 g/cm\(^3\) and slag is 3.0 g/cm\(^3\), so slag and iron can be separated from each other.27) The S is a surface-active component. Therefore, molten metal with high S content has a lower surface tension and tends to occupy the surface layer in much higher concentrations than that exist in the bulk. On the other hand, the slag with high content of CaF\(_2\), the surface tension of molten slag is low. Therefore, the slag and iron could not form spherical shape effectively and only get lamellar shape slag and iron nugget.

3.2. Property of Iron Nugget

The iron nugget, produced for 12 min at 1673 K, was cut into two parts. One part was used for chemical analysis of C, S and other elements. The other was mounted in epoxy resin, then sectioned, polished and etched (4% nital) for cross section observation by SEM-EDS.

The chemical composition of the iron nugget is presented in Table 4. The results show that the property of the nugget is compatible with pig iron and the recovery ratio of Fe is about 97.5% through theoretical analysis. The iron nugget...
can be used partly to substitute the steel scrap EAF steel-making. However, the content of sulfur is 1.62%, which is higher than the common blast furnace pig iron. The most important reason is that the sulfur content is very high in the raw material (i.e., Bayan Obo complex iron ore). In addition, it is difficult for iron nugget to desulfurize during the reduction and melting process of the composite pellets due to the short contacting time and the bad fluidity of iron and slag. It needs further research on the desulfurization method. Because of the short contacting time between iron and slag and thermodynamic difficulty of Nb2O5 reduction by carbon, the amount of niobium is too low to be detected.

The microstructure observed by SEM is shown in Fig. 8. The main phase components are eutectic cementite (dark area) and pearlite (white area). The iron nugget is really clean without any oxide inclusion.

<table>
<thead>
<tr>
<th>Table 4. Property of iron nugget.</th>
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<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Content/wt %</td>
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</tbody>
</table>

3.3. Property of Rare-earth-rich Slag

The chemical composition of slag is shown in Table 5. The rare earth oxides cannot be reduced in this experimental condition and nearly all are enriched in the slag. The slag, with a RE₂O₃ content of 14.19%, meets the requirements of grade I rare-earth-rich slag. So the slag can be used as raw material for extracting rare earth. The content of CaF₂ in slag is as high as 36.82%, and the melting temperature of slag is only 1386 K measured by the automatic slag melting point tester.

Figure 9 shows the XRD pattern of rare-earth-rich slag. The main crystalline phases present in the slag are cuspide (Ca₄Si₂O₇F₂), britholite (Ca₃Ce₂ [(Si, P) O₄]₃F) and fluorite (CaF₂).

The slag cooled in air is mainly composed of three phases: dark grey, light grey and white (Fig. 10). The rare earth elements were observed to co-exist with Ca, Si, O, and F in the white phase. Compatible with previous studies, rare

<table>
<thead>
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<th>Table 5. Chemical composition of rare-earth-rich slag (wt%).</th>
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<tbody>
<tr>
<td>CaF₂</td>
</tr>
<tr>
<td>36.82</td>
</tr>
</tbody>
</table>

Fig. 8. SEM image of the iron nugget produced at 1673 K for 12 min.

Fig. 9. XRD pattern of rare-earth-rich slag.

Fig. 10. SEM micrograph of rare-earth-rich slag together with EDS profiles of selected positions.
carbon-bearing pellet closely depend on temperature and time. The iron nugget and slag can separate well at 1,673 K for 12 min. In lower temperature or shorter heating time, pellets can’t melt effectively.

(2) The contents of C and S in iron nugget produced at 1,673 K for 12 min are 2.09% and 1.62% respectively. And the iron nugget has comparable physical and chemical properties with blast furnace pig iron. Except for the the shortcoming of higher sulfur, the iron nugget can be used as a high-quality charge for EAF steelmaking.

(3) The content of RE$_2$O$_3$ in the slag is 14.19%. The air cooling rare-earth-rich slag with a good crystallization and the main phases are cefluosil ([7(Ca, Ce, La, Nd)$_2$SiO$_4$] (F, O)$_{10}$), fluorite (CaF$_2$) and cuspidine (Ca$_4$Si$_2$O$_7$F$_2$).

(4) The rare-earth-rich slag with a rare earth leaching efficiency of 98.70% meets the needs of further process to extract rare earth. Fluorite (CaF$_2$) is the main phase in leached residue and the content of ThO$_2$ is 0.05%. The leached residue is a kind of good raw material to recover CaF$_2$ and ThO$_2$.

Acknowledgement
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REFERENCES
9) P. Gao, Y. X. Han, Y. J Li and Y. S. Sun: J. Northeastern Univ. (Natural Science), 31 (2010), 886.
29) N. Xu, M.Y.Li and M. C. Hao: Chinese Rare Earths, 18 (1980), 1.

Table 6. Chemical composition of leached residue (wt%).

<table>
<thead>
<tr>
<th>Component</th>
<th>CaF$_2$</th>
<th>RE$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>FeO</th>
<th>BaSO$_4$</th>
<th>BaF$_2$</th>
<th>Al$_2$O$_3$</th>
<th>PbO</th>
<th>Nb$_2$O$_5$</th>
<th>ThO$_2$</th>
</tr>
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<tbody>
<tr>
<td>wt%</td>
<td>64.45</td>
<td>0.06</td>
<td>30.15</td>
<td>0.41</td>
<td>3.13</td>
<td>1.42</td>
<td>0.08</td>
<td>0.14</td>
<td>0.01</td>
<td>0.05</td>
</tr>
</tbody>
</table>

3.4. Acid Leaching of Rare-earth-rich Slag

The rare-earth-rich slag was crushed to a particle size smaller than 0.074 mm. The slag and acid solution were poured into a conical flask, shaken up and set aside. Four hours later, the mixture was discharged from the device and separated through vacuum filtration. The leached residue was dried and weighted, and the contents of rare earth and fluoride were assayed.

As is shown in Fig. 11 and Table 6 that fluoride (CaF$_2$) is the main phase in leached residue while the content of RE$_2$O$_3$ is only 0.06%. The leaching efficiency of rare earth from the rare-earth-rich slag is as high as 98.70% in this study. The filtered solution can be used to extract rare earth. It means that the rare-earth-rich slag cooled in air meets the needs of further process to extract rare earth very well. Meanwhile, leached residue contains 0.05% of ThO$_2$, which might be used for further extracting nuclear fuels material.

4. Conclusions

This paper provides some insights into the comprehensive utilization of Bayan Obo complex iron ore. The following conclusions have been obtained from the present study:

(1) The metallization rate and melting morphology of...