Effects of Particle Sizes of Iron Ore and Coal on the Strength and Reduction of High Phosphorus Oolitic Hematite-coal Composite Briquettes

Wen YU, Tichang SUN,* Zhenzhen LIU, Jue KOU and Chengyan XU

School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing, 100083 China.

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This study presents a process with coal-based direct reduction of high-phosphorus oolitic hematite before magnetic separation for producing direct reduction iron (DRI), where Ca(OH)₂ and Na₂CO₃ were used as additives in order to inhibit the reduction of fluorapatite and promote the reduction of hematite. The effects of particle sizes of iron ore and coal on the strength and reduction of cold-bonded composite briquettes were investigated. It showed that the decrease of the particle sizes of iron ore and coal increased the strength of composite briquettes. At the temperature of 1200°C, a sizable increase of recovery and iron content of DRI was observed when the particle size of iron ore decreased from –4 mm to –0.1 mm, however, the phosphorus content of DRI obtained from –0.1 mm iron ore was much higher than that from coarser iron ore. The results of SEM-EDS analyses showed that the reduction of fluorapatite in the iron ore was activated when using –0.1 mm iron ore and the reduced phosphorus melting into metallic iron. Moreover, the particle size of coal has less effect on the direct reduction-magnetic separation than iron ore within the scope of the study.

KEY WORDS: high-phosphorus oolitic hematite; coal; composite briquettes; particle size; strength; direct reduction; dephosphorization.

1. Introduction

The high-phosphorus oolitic hematite ore is one of the most refractory iron ores in China, because the relationship between iron oxides and fluorapatite are so intimately intermingled that it is not feasible to benefication of the iron ore by conventional mineral processing methods.¹ A new process has been developed to produce DRI with low content of phosphorus from high-phosphorus oolitic hematite ore, which is known as coal-based direct reduction-magnetic separation method.²⁶ In the process, hematite is reduced to metallic iron by coal and the metallic iron particle aggregated which promoted the separation of iron from slag. Meanwhile, the reduction of fluorapatite was inhibited by controlling roast temperature or adding additives, and then the roasted product was ground to liberation size and separated by magnetic separation.

In a previous publication,⁵ the function of Ca(OH)₂ and Na₂CO₃ on the reduction of high-phosphorus oolitic hematite-coal composite briquettes had been investigated, and the results showed that the addition of Ca(OH)₂ and Na₂CO₃ can promote the reduction of hematite and dephosphorization. The composite briquettes used in the study are cold-bonded briquettes which are produced by briquetting process. Since the composite briquettes go through a number of handling and transportation operations, it must have sufficient strength to withstand stresses.⁷⁸ The particle size of the raw material is an important factor affecting the strength of the briquettes. Meanwhile the particle sizes of iron ore and coal may affect the reduction of hematite and fluorapatite. Some work has been done on the effect of particle size on the reduction of the low content of iron ore.⁹¹⁰ However, few studies have been done on the effect of particle size of iron ore on the reduction of fluorapatite and the effect of particle size of coal in the composite briquette. So in order to determine the appropriate particle sizes of iron ore and coal for producing composite briquettes, integrated research must be done about the effect of iron ore and coal particle sizes on briquetting and reduction roasting-magnetic separation process.

In this paper, the effect of particle sizes of iron ore and coal on the strength of cold-bonded composite briquettes and the recovery, iron content and phosphorus content of DRI were studied.

2. Experimental

2.1. Materials

The iron ore samples used in this work was a typical Ningxiang high phosphorus oolitic hematite from Hubei Province, China. The iron content of iron ore was 43.58 mass%, the
content of phosphorus was 0.83 mass%, iron mainly occurred in the form of haematite and phosphorus occurred in the form of fluorapatite, with impurities including quartz, chlorite. The detail information of the iron ore has been described in the previous paper. The coal used as reductant contained 11.77 mass% moisture, 17.56 mass% ash, 24.86 mass% volatiles, 45.81 mass% fixed carbon. The chemical analysis of the coal ash found that it consisted mainly of SiO₂, Al₂O₃, 45.81 mass% fixed carbon. The chemical analysis of the coal ash found that it consisted mainly of SiO₂, Al₂O₃, CaO, and CaO, as shown in Table 1. Ca(OH)₂ and Na₂CO₃ were used in the experiments were analytical reagent (AR) content.

The iron ore and coal were crushed to three particle sizes: –4 mm, –1 mm and –0.1 mm, respectively. The sizes distribution of iron ore and coal are shown in Table 2.

2.2. Experimental Procedure

2.2.1. Composite Briquette Preparation

In the previous paper the composite briquettes were made by a die and punch and the strength of the briquettes were not considered. In order to better simulate the actual production situation, in this paper the composite briquettes used were produced by a laboratory scale twin-roller briquette machine.

The ore, coal and additives were taken in the proportion of iron ore: coal: Ca(OH)₂: Na₂CO₃ = 1:0.25:0.15:0.03 (by mass) and mixed together with appropriate amount of water (8–12 mass%), the dosages of Ca(OH)₂ and Na₂CO₃ were determined in a previous study, then the mixtures were briquetted in the briquette machine. A piece of briquette weighed 8–10 g, having an almond shape of 14 × 25 × 25 mm.

The wet composite briquettes were cured naturally for 3–4 days in an ambient atmosphere. Curing was considered to complete when the strength of the briquettes was constant for 2–3 consecutive days.

2.2.2. Strength Test

Drop test: The drop strength is measured after curing by dropping five composite briquettes individually from a height of 50 cm onto a 10 mm-thick steel plate until its breakage. The final value was taken as the average of five such test values.

Compression test: The compressive strength is measured on a strength-testing instrument (YHKC-2A Yinhe Instruments Pvt. Ltd., Jiangqu, China). The final value was calculated as the arithmetic mean of five such test values.

2.2.3. Reduction and Separation

The reduction experiments were performed in a muffle furnace with a temperature control programmer. There were seven pieces of briquettes put in the graphite crucible of 70 mm in diameter and 75 mm in height in a run. The graphite crucible was put into the furnace and held for scheduled time under the air atmosphere after the temperature arrived at 1 200°C. Upon the completion of heating the graphite crucible was taken out of the furnace at 1 200°C and air cooled to room temperature.

After the reduced briquettes in the crucible had cooled, they were crushed to –2 mm and then treated by two-stage grinding and magnetic separation. The grinding experiments were conducted in a rod mill (RK/BM-1.0L, Wuhan Rock Crush & Grind Equipment Manufacture Co., Ltd, China) having ten Φ15 mm×120 mm rods at 60 mass% solid density and with a speed of 192 r/min. The first stage grinding time was 10 min. The XCGS-73 magnetic separator with a magnetic field intensity of 1120 Oe was used to separate metallic iron from the slurry. The iron concentrates obtained from the first separation were reground for 40 min and separation. The main evaluation specifications of test results were the iron content, P-content and the iron recovery of the DRI. The iron recovery refers to the percentage of the total iron metal contained in the ore that is recovered into the DRI.

2.2.4. Analysis and Characterization

The chemical analyses of the DRI and the coal ash were conducted by China University of Geosciences (Beijing) analysis laboratory. Scanning Electron Microscope with Energy Dispersive Spectrum (Carl Zeiss EVO18) analyses were carried out on roasted briquettes mounted in epoxy resin and polished followed by spraying carbon.

3. Results and Discussion

3.1. Effect of Particle Size on the Strength of Composite Briquettes

The effects of particle size of iron ore and coal on the strength of composite briquettes were investigated and the results are presented in Table 3.
As shown in Table 3, there is a marked influence of the particle size on the strength of composite briquettes including both drop strength and compressive strength. When the iron ore particle size decreases from –4 mm to –0.1 mm while the size of coal is maintained –1 mm, the strength of composite briquette increased to 10 times in drop strength and 229.7 N per briquette in compressive strength. Similarly, the strength of composite briquettes increased with decreasing size of coal particle. It can be explained that the decrease of particle size conduct to the increase of degree of compaction of the briquette resulting in higher strength.7)

The composite briquettes get more strength by the carbonate bonding. Originally, Ca(OH)₂ and Na₂CO₃ were added to enhance the effect of dephosphorization and increase the recovery of iron. However, in the process of briquetting, Ca(OH)₂ absorbs CO₂ gas from the air and forms CaCO₃ binding particles together.7,12) Moreover, the literature shows that the presence of Na₂CO₃ can promote the carbonate bonding between the particles.13)

3.2. Effect of Iron Ore Particle Size on the Reduction-Magnetic Separation

Studies on the effects of the iron ore particle size were conducted on composite briquettes with –1 mm coal particle at the temperature of 1 200°C, the results are shown in Fig. 1 as a function of roasted time.

Figure 1(a) shows that the recovery of iron increased markedly with the particle size of iron ore decreasing. When the particle size of iron ore decreased from –4 mm to –1 mm then reduced to –0.1 mm, the corresponding recoveries are 51.40 mass%, 62.59 mass% and 70.4 mass% respectively at the roasted time of 10 min; When the roasted time increases to 40 min, the corresponding recoveries are 83.54 mass%, 92.20 mass% and 92.90 mass% respectively. In this case, the corresponding recoveries of –0.1 mm and –1 mm iron ore are substantially the same, but are significantly higher than that of –4 mm iron ore. When the roasted time increased to 50 min, a slight decrease of iron recovery was observed when used –1 mm and –0.1 mm iron ore, it may be caused by re-oxidation. Although the iron-coal composite briquette has antioxidant effect and it was protected by graphite crucible, the re-oxidation of the reduced briquette cannot be ignored, especially at the final stage of reduction, the residual carbon is in a very low level, re-oxidation may present an important effect on the metallization ratio.

Hematite was reduced to metallic iron following the route of Fe₂O₃→Fe₃O₄→FeO→Fe in reduction process,14) and then the metallic iron was recovered by grinding followed by magnetic separation, so the recovery of iron depends on the metallization ratio of hematite. Reduction of iron oxides in a direct reduction system has been known to occur by gaseous phases, rather than the solid carbon.15) For the reduction of hematite by CO is a gas-solid reaction, the reduction rate decreases with particle size increasing according to the unreacted-core mode,16) so coarse hematite takes longer time to reach the same metal rate achieved by the fine particles of hematite. Furthermore, since the iron ore and coal contain a large number of SiO₂ and Al₂O₃, part of the FeO may react with SiO₂ and Al₂O₃ to form fayalite and hercynite which are difficult to be reduced and can only be direct reduced by C in this system.9) The increase of iron ore size leads the reducing contact area of fayalite and hercynite and coal which is not conducive to their reduction. On the other hand, CaO decomposed from Ca(OH)₂ can replaced FeO from fayalite and hercynite, thereby enhance the reactivity of FeO.6) With iron ore particle size increases, fayalite and hercynite generated in the interior of the particle of iron ore are difficult to react with CaO. Therefore the recovery of iron decreased with increasing of particle size of iron ore.

Figure 1(b) shows the effect of ore particle size on the iron content of DRI. At the roasted time range from 20–50 min, the iron content of DRI obtained from fine-grained iron ore is higher than that from coarse particles. In addition, the iron content increases with the extension of roasted time, when roasted time is more than 20 min, the variation of iron content of DRI is small.

Figure 1(c) shows the effect of iron ore particle size on the phosphorus content of DRI. It can be seen that the phosphorus content of DRI produced from three levels of particle
sizes of iron ore decreases as roasted time increases from 10 min to 20 min. However, with a further increase of roasted time, the phosphorus content of DRI increases sharply when the iron ore particle size is –0.1 mm, while the phosphorus content of DRI maintains stable when the particle sizes are –4 mm and –1 mm respectively. It means that the effect of dephosphorization will be weakened when iron ore particles are too small. The phosphorus in DRI may exist in two forms, one is in the form of gangue mixed in the concentrate for grind-magnetic separation operations cannot remove all the gangue; the other is elemental phosphorus reduced from fluorapatite melting into metallic iron, which physical separation method is ineffective to remove. Since the iron content of DRI obtained from fine-grained iron ore is higher than that from coarse particles, it means that lower mount of slag was composite into the concentrate, so it can be inferred that the increasing phosphorus content of DRI may be caused by the reduction of the fluorapatite, it will be discussed in detail later.

In summary, the particle size of iron ore has a significant impact on direct reduction-magnetic separation, decreasing of ore particle size helps to improve the iron recovery and content of DRI, but too small particle size of ore employed will result in a sharp increase in phosphorus content of DRI.

3.3. Effect of Particle Size of Coal on the Reduction-magnetic Separation

Figure 2 shows the effect of coal particle size on the direct reduction-magnetic separation of the composite briquette, where ore particle size was fixed at –1 mm, the roasting temperature at 1 200°C.

Figure 2(a) shows that the iron recovery exhibited a lesser sensitivity to the coal particle size than that of the iron ore. At the roasting time range from 20 to 50 min, when the coal particle size decreases from –4 mm to –0.1 mm, no significant difference of the recovery is observed. The recoveries increased with increasing of roasted time from 10 to 40 min. With a further increase of roasted time the recoveries of iron start to drop, it may be caused by re-oxidation.

The effects of particle size of coal on the iron content and phosphorus content of DRI are shown in Figs. 2(b) and 2(c), respectively. The iron content of DRI which obtained from –1 mm iron ore presents a slightly higher than that from –4 mm and –0.1 mm iron ore, the difference is visible but very small. The phosphorus content of DRI decrease with increasing roasted time from 10 min to 20 min and when roasted time further increased, no sharp increasing of the phosphorus content of DRI is observed.

The particle size of the coal affects coal gasification rate, the coarser granularity, the slower rate of gasification reaction. RAO reported that the rate of carbothermal reduction of hematite increases as coal particle size decreases and the coal size effect weakens with increasing temperature from 947 to 1 087°C. It is generally agreed that the overall rate of carbothermal reduction of iron oxide under 1 100°C is controlled by gasification of coal and above this temperature the reaction rate is jointly controlled by coal gasification and chemical reaction. Moon’s study showed that the degree of coal gasification reaction control on the carbothermic reduction decreases as increasing the temperature, using carbonaceous materials with higher reactivity as well as adding gasification reaction catalyst. Considering the fact that this experiments were conducted at 1 200°C, the coal used is a bitumite which has a good reactivity and Ca(OH)₂ and Na₂CO₃ were added in reduction process which are catalysts for the gasification reaction, the result obtained from the present study that the effect of coal particle size has a very slight influence on the reduction of iron ore was reasonable.

In general, the particle size of coal has a much smaller effect on the reduction of composite briquette than that of iron ore.

4. Characteristics of Roasted Briquettes

Figure 3 shows the SEM images of roasted briquettes and Table 4 lists the EDS analysis for the points numbered in the Figures in Fig. 3.

Figures 3(a) and 3(b) show the SEM images of composite
Fig. 3.  SEM images of roasted briquettes.
particulate which made of −4 mm iron ore and −1 mm coal and roasted for 10 min. The degree of reduction and sintering are significantly different between the periphery and core of briquette. The metallic iron particles (bright white) appeared in the periphery of the briquette and the gangues were partially sintered while in the core of briquette there are less metallic iron particles but ferrous oxide and no significant sintering phenomena was observed. This implies reduction has not yet completed for 10 min.

EDS analyses shows no phosphorus was found in metallic iron particle (point 1) when roasted for 10 min, which suggests that the phosphorus in the DRI is mainly in the form of gangue mixed into the concentrate.

Figures 3(c) and 3(d) show the SEM images of briquette roasted for 40 min which made of −4 mm iron ore and −1 mm coal, there is large amounts of metallic iron in the observed area and the size of iron particle is coarser than that in the briquette roasted for 10 min. Moreover, the degree of sintering of the periphery and core of briquette is alike and the metallic iron particles are basically the same size, which reveal the reduction reaction is substantially complete. Since the coarsening of metallic iron particles, the liberation of metallic iron and gangue has improved and thereby increases the iron content of DRI. In addition, the result of point analysis of the metallic iron (point 3) shows that no phosphorus was found in the metallic iron. So a good dephosphorization effect can be achieved by grinding-magnetic separation.

The SEM images of roasted briquettes which made of different sizes of iron ore particles are shown in Figs. 3(c)–3(h). It shows that when the particle size of iron ore decreases from −4 mm to −1 mm, the microstructures of the briquettes are similarly and the microstructures of periphery and core of the briquette are almost the same in one briquette. Moreover, the results of point analysis show that phosphorus element is not found in the metallic iron particles of briquettes which made of −4 mm and −1 mm iron ore particles, concluding that the reduction of fluorapatite in the iron ore was not obviously under this condition and the phosphorus in the DRI obtained from these reduced briquettes is mainly in the form of gangue. However, when the particle size of iron ore decreases to −0.1 mm, significant changes of the morphology of the briquette were observed as show in Figs. 3(g) and 3(h), the particle sizes of metallic iron in the periphery are coarser than that in the core and in Figs. 3(c)–3(f). What’s more, the results of point analyses show that the metallic iron (point 7) contains 1.34 mass% P in the periphery of briquette while no phosphorus was observed in metallic iron (point 8) produced in the core of briquette. So, it can be inferred that the reduction of fluoapatite was activated under this condition and the generated element phosphorus melting into metallic iron. The carbothemeral reduction equation of fluorapatite is as follows:

$$\text{Ca}_{10} \left( \text{PO}_4 \right)_6 \text{F}_2 + 15 \text{C} + 9\text{SiO}_2 \rightarrow 3\text{P} + 15\text{CO} + 9\text{CaO} \left( \text{SiO}_2 \right) + \text{CaF}_2$$

Jacob’s studies showed that in the temperature range from 1 100°C to 1 250°C, the limiting step of reduction appears to be diffusion of phosphorus-bearing species to carbon particles. Figure 4 shows that the melting degree of the reduced composite briquettes made by −0.1 mm iron ore is much higher than that of composite briquettes made by −4 and −1 mm iron ore as glass phase appears in the lower half of the briquettes made by −0.1 mm iron ore. This indicated that more liquid phase is formed in the roasting process. Since the presence of liquid phase in the reduction process is conducive to the diffusion of phosphorus-bearing species to carbon particles, the reduction of fluorapatite therefore can be promoted and thereby more of phosphorus melting into the metallic iron. The reasons for more liquid phase formed in this case are not clear now.

Literature displayed Guo et al. treated the high phosphorus olitic hematite by means of coal-based reduction-magnetic separation, high phosphorus iron ore used in their research work was ground to an average particle size of 19.33 μm. The results show that the dephosphorization rate was 55 mass% under optimal conditions, and the content of phosphorus in the concentrate was 0.7 mass%. Fine ground high phosphorus iron ore was also used by Zhou et al., and the results shown that the phosphorus content of DRI was between 0.2 mass% to 0.5 mass%. Too fine iron ore employed may be responsible for the low dephosphorization rate.

The SEM images of roasted briquettes with different sizes of coal particle are shown in Figs. 3(i) and 3(j), 3(c) and 3(f), 3(k) and 3(l), respectively. As can be seen from the images, coal particle size has little effect on the microstructure of roasted briquettes, the degree of sintering and particle size of metallic iron in their images are quite similar. In addition, the point analysis results show that phosphorus was not found in metallic iron under the condition of different coal particle sizes. Combined with the results shown in Fig. 3, it can be concluded that within the scope of the study coal particle size has little impact on reduction of hematite and fluorapatite, and the melting behavior of briquettes.

Tables and figures:

Table 4. Chemical composition of points indicated in Fig. 3.

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<tr>
<th>Points</th>
<th>C (mass%)</th>
<th>Fe (mass%)</th>
<th>P (mass%)</th>
<th>O (mass%)</th>
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</table>

*The C-content of the points is mainly caused by the treatment of spraying carbon.
surface of the metallic iron of the outermost layer of the reduced briquette. It is the evidence of re-oxidation of the briquette during the last stage of reduction and air cooling.

5. Conclusions

The following conclusions can be drawn from the current study:

(1) The particle sizes of ore and coal affect both the strength of the composite briquettes and roasting-magnetic separation, decreasing the particle sizes of ore and coal can increase the compressive strength and drop strength of the composite briquettes.

(2) Decreasing the particle size of iron ore can increase the recovery and iron content of DRI, but too small iron ore particle may increase phosphorus content of DRI. More liquid phase, which promotes the reduction of fluorapatite and therefore resulting in more elemental phosphorus melting into the metallic iron, was formed in the reduction process when using –0.1 mm iron ore.

(3) The effect of coal particle size on the direct reduction-magnetic separation is less than that of the iron ore size within the scope of the study.

(4) Considering ore and coal particle size on the strength of cold-bonded composite briquettes and reduction-magnetic separation, the coal particle size can be decreased to increase the strength of briquettes, while the decrease of size of iron ore particle need to be cautious to prevent activation of the reduction of fluorapatite.

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