Catalyzing Carbothermic Reduction of Siderite Ore with High Content of Phosphorus by Adding Sodium Carbonate

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The characteristics of Huimin siderite ore with high content of phosphorus and the reduction of this ore bearing pulverized coal and sodium carbonate were investigated. The study focuses on the influence of Na_2CO_3 dosage on the carbothermic reduction process. Iron particle size in reduced ore is tiny and the fayalite is abundant without Na_2CO_3 additive. With ratio of Na_2CO_3 to ore at 1:20 or 1:10, iron particle size in reduced ore is coarse and the diffraction intensity of metallic iron increases obviously in the XRD pattern. The reduction of siderite can be catalyzed by adding an appropriate amount of Na_2CO_3 . The catalyzing activity may be caused by the increase of the reducing reaction activity of FeO and the acceleration of the carbon gasification reaction rate. The phosphorus compounds were not reduced in the low temperature reduction process and remained as fluorapatite in the gangue phases. Ultrafine grinding-magnetic separating of magnetic minerals is an efficient way to obtain qualified iron concentrate.

KEY WORDS: siderite ore; fluorapatite; sodium carbonate; reductive roasting; metal iron; catalysis.

1. Introduction

Siderite ore is one of the most important raw material used to prepare iron concentrate. There are about 16 billion tons of siderite deposit in the Huimin region of Yunnan Province, which accounts to 40% of the siderite resource in China.¹⁾ So, it is very important to utilize the siderite resource in the Huimin region for the production of iron concentrate in China. Due to the high content of impurities, especially phosphorus and the low iron grade of siderite ore, iron-rich and phosphorus-low materials can be obtained through refinement. Physical separation has been widely used for the removal of phosphorus,²⁾ but it is very difficult to remove the disseminated fine fluorapatite by physical separation.

Much effort has therefore been directed to the dephosphorization of siderite ore with high phosphorus content, but no solution has been worked out so far to achieve good dephosphorization by physical separation because of the similarity among such physical properties as density, size and shape of particle and the surface properties of carbonate and phosphate minerals.³⁾ Magnetic roasting is an effective way to process siderite ore, but the high contents of SiO_2 and Al_2O_3 , and the complex mineralogy in siderite ore in the Huimin region make the growth and reconstruction of magnetic minerals even more difficult. Therefore, it is the key to remove the phosphorus and reinforce the reduction of siderite to the utilization of siderite ore with high phosphorus content.

Sodium carbonate is a common alkaline additive used in the carbothermic reduction of iron ore, which dissociates

Na_2O and CO_2 at 874°C , meanwhile, the reduction reaction of iron oxide takes place.⁴⁻⁷⁾ Much work has been done on the carbothermic reduction of hematite with sodium carbonate used as an additive, and experimental results indicate the carbothermic reduction of hematite can be reinforced by adding Na_2O and the mass and heat transfer during the reducing reaction can be optimized by CO_2 .⁸⁻¹¹⁾ However, not much work has been done on the reinforcement of the reduction of siderite, mainly because of the low grade of raw ore and the complicated phase change of siderite.^{12,13)} Consequently, the exploration and utilization of the siderite ore with high phosphorus content becomes a challenging task.

Therefore, a dressing-metallurgy flowsheet, which consists of a sodium-salt-added catalyst reductive roasting-magnetic separation process is proposed in this paper for the treatment of siderite ore with high phosphorus content. The sodium-salt-added catalyst reductive roasting process is accomplished by adding Na_2CO_3 , which reacts with SiO_2 and prevents its counter catalysis on FeO, thereby reinforcing the reduction of siderite and improving the separation of iron from slag. It is therefore believed that more emphasis on the effect of Na_2CO_3 and its dosage on the reduction of siderite. The proposed in this paper will be of benefit to the exploitation of similar refractory iron ore.

2. Experimental

2.1. Raw Materials

The raw ore used is the product of beneficiation of siderite ore with high contents of phosphorus and sulfur (TFe30.78%, P-content 1.02%, S-content 1.38%), which

was obtained through the flowsheet consisting of fine grinding-removal of sulfur and phosphorus by reverse flotation. The results of screen analysis of this product indicate the content of grain size below $45\ \mu\text{m}$ accounts to 82.45%. The chemical analysis of raw ore is as shown in **Table 1**. The pulverized coal used as the reductant with a particle size $<1\ \text{mm}$ was supplied by Kunming Iron And Steel Ltd, Yunnan, China. The results of industrial and ash fusibility analyses of pulverized coal are as shown in **Table 2**. The reactivity of pulverized coal is as shown in **Table 3**. The sodium carbonate used as the alkaline additive in the experiments was of analytical reagent (AR) grade.

2.2. Experimental Procedure

Reduction experiments were performed in a furnace with temperature controlled within $\pm 5^\circ\text{C}$. 50.0 g raw ore was mixed with appropriate amount of pulverized coal and sodium carbonate for each and every experiment. The mixture was placed in the graphite crucible of 600 mm in diameter and 800 mm in length. The reduction experiments were conducted in accordance with the temperature and duration schedule. Upon the completion of experiments the samples were taken out from the furnace and cooled down to ambient temperature under the protection of nitrogen. The reduced ores were ground to about 90% below $74\ \mu\text{m}$. This procedure was accomplished using XMQ 240 $\times$ 90 ball mill. The grinding fineness was determined using water-sieving and magnetic separation was conducted in XCGS-73 magnetic separator with a magnetic field intensity of 3.0 KOe. At the end of the experiment, the concentrate was filtered and TFe and P-content of concentrate were analyzed. The iron grade of magnetic concentrate, P-content in the iron concentrate and iron recovery were considered as the main basis for evaluation of test results.

2.3. Analysis and Characterization

After being cooled from high temperature, the reduced ores were divided into two parts: part of them was crushed and milled to below $75\ \mu\text{m}$ for chemical and XRD analysis, and the remaining was cut in halves for micro-topography analysis.

The chemical analyses were conducted by Kunming Metallurgy Research institute. The XRD patterns of raw material and reduced samples were detected with a Rigaku diffractometer using Cu K α radiation, with a scanning angle in the range from 10 to 90° (2θ) at a speed of $1.2^\circ/\text{min}$. The microstructure of reduction product was observed by scanning electron microscope (FEI Holland, Philip).

3. Results and Discussion

3.1. Mineralogy of Run-of-Mine Ore

It can be seen from the XRD pattern of raw ore shown in **Fig. 1** that the iron ore predominantly consists of siderite and a small quantity of iron minerals in the form of magnetite and daphnite. The gangue mineral is mainly quartz and the phosphorus is mainly fluorapatite. In addition, it is found through the chemical analysis of raw ore that the iron grade of run-of-mine is 31.64%, the content of silicon dioxide goes up to 27.62%, and the average content of phosphorus is 0.50%. Phosphorus is one of the most detrimental impu-

Table 1. Chemical analysis of raw ore.

Components	TFe	P	S	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O
wt(%)	31.64	0.50	0.36	27.62	3.68	2.63	1.88	0.18

Table 2. Industrial and ash fusibility analyses of pulverized coal.

Industrial analysis/wt.%				Ash fusibility/ $^\circ\text{C}$				S/wt.%
M _{ad}	A _d	V _d	FC _d	DT	ST	HT	MT	0.45
2.45	9.45	6.45	82.56	1 250	1 325	1 344	1 346	

M_{ad}: Moisture (dry basis), A_d: Ash (dry basis), V_d: Volatile Matter (dry basis), FC_d: Fixed Carbon (dry basis).

DT: Distortion Temperature, ST: Softening Temperature, HT: Hemispherical Temperature, MT: Melting Temperature.

Table 3. Reactivity of pulverized coal.

Temperature/ $^\circ\text{C}$	1 000	1 050	1 100	1 105	1 200
α	13.46	22.68	38.65	68.95	88.65

The reactivity of pulverized coal is chemical reaction ability between the pulverized coal and carbon dioxide at certain temperatures. α is the reduction degree of carbon dioxide.

Fig. 1. XRD pattern of raw ore.

rities in steels and it reduces the low-temperature toughness of iron and steel products.¹⁴⁾ Optical microscopic examination and EDAX measurements were employed to determine the occurrence and distribution of iron and phosphorus minerals and the results are shown in **Figs. 2–5** respectively.

It can be seen through the visual inspection of images that many off-white particles clump together and some dark particles are either liberated particles or attached to the edges of off-white particles. The granularity of off-white particles is below $10\ \mu\text{m}$ (Fig. 2(a), 2(b)). In addition, it is found through X-ray energy spectrum analysis that the off-white particles are composed of carbonate minerals which contain a small amount of Ca, Al, Si, P, As (Figs. 3, 4), and the iron minerals are mainly siderite. The dark particles are quartz of $10\text{--}20\ \mu\text{m}$ in size (Fig. 5). It can be seen through the X-ray energy spectrum analysis that the content of quartz is high, and there is almost no other mineral (Fig. 2(c)). It can therefore be concluded that siderite ores are the most abundant phase and quartz is a gangue phase which can be easily distinguished from all the other iron oxides.

Fig. 2. Microstructure of raw ore.

Fig. 3. X-ray energy spectrum of siderite.

Fig. 4. X-ray energy spectrum of siderite.

It is found through the mineralogical analysis of test samples that this iron ore is a refractory ore, due to its low grade and its complex mineral dissemination particle sizes and its high content of phosphorus. It is therefore very difficult to upgrade or dephosphorize by traditional dressing, such as magnetic separation, gravity concentration, flotation or combination of magnetic separation and flotation. It is of

Fig. 5. X-ray energy spectrum of quartz.

necessity to develop a reduction roasting to beneficiate this siderite ore with high content of phosphorus.

3.2. Reduction of Siderite Ore with High Content of Phosphorus

Experiments were conducted at different temperature, reducing time and mass ratio of pulverized coal to ore to investigate the reduction characteristics of the siderite ore with high content of phosphorus. Experimental results indicate that the optimum reduction temperature is 1 050°C, the reducing time is 150 min and mass ratio of pulverized coal to ore is 1:5. An iron concentrate with 61.5% Fe, and 0.34% P can be obtained, at an iron recovery of 68.36%. It can therefore be concluded that it is difficult to restore and beneficiate the siderite ore with TFe 31.64% and P-content 0.5% because its reduction needs high temperature, long reducing time, and strong reducing atmosphere.

As shown in **Fig. 6**, the main iron phase is metallic iron and part of iron phase exists as fayalite ($2\text{FeO}\cdot\text{SiO}_2$) and hedenbergite ($\text{Fe}_{1.3}\text{Ca}_{0.7}(\text{Si}_2\text{O}_6)$) in the reduced ore, while the gangue phase is mainly quartz. It can be seen through the visual inspection of microstructure images that the distribution of iron grain is widespread, but the iron grain is tiny, which means that it is difficult for iron grain to grow and aggregate due to the high content of SiO_2 . On the one hand, iron grains form only after the nucleation barrier is overcome, when the iron grains proliferate to the mineral surface bearing with SiO_2 , iron grains disappear and a new phase of fayalite ($2\text{FeO}\cdot\text{SiO}_2$) forms. Although fayalite can be reduced to metallic iron by solid carbon, but it is more difficult than the reduction of FeO because the reduction of FeO in fayalite must go through a dissociation reaction of complex compound. On the other hand, once fayalite forms, it will act as a nucleating agent and lead to the growth and reconstruction of metallic iron in the fayalite's interface as the reduction continues and as a result, fayalite will be separated from the reducing agent, which makes the reduction of fayalite even more difficult.¹⁵⁾ In addition, the indirect reduction enjoys priority and the direct reduction of iron oxides is auxiliary in coal-based direct reduction process, it will lead to the stagnation of reduction when the contact between iron oxides and reducing agent is interrupted. So,

Fig. 6. Microstructure and XRD pattern of reduced ore.

catalyzing the reduction of fayalite is the key to the improvement of metallization of reduced ore and the separation of iron from slag.

3.3. Catalyzing Reduction of Siderite Ore with High Content of Phosphorus by Adding Sodium Carbonate

Sodium carbonate was added in the course of reduction to reinforce the reduction of siderite. The effect of Na_2CO_3 dosage on the reduction of siderite was investigated through experiments conducted at a temperature of 1050°C, a reducing time of 150 min and a mass ratio of pulverized coal to ore of 1:5. The experimental results are shown in Fig. 7.

It can be seen from Fig. 7 that (1) the grade of iron concentrate increases and the content of phosphorus in iron concentrate decreases with the increase of Na_2CO_3 dosage. Specifically, an iron concentrate with 60.54% of Fe and 0.32% of phosphorus is obtained without Na_2CO_3 additive. The grade of the iron concentrate can be improved by 13.19% with a mass ratio of Na_2CO_3 to ore of 1:5, while the content of phosphorus decreases from 0.32% to 0.16%; (2) the iron recovery increases with the increase of Na_2CO_3 dosage within the range of 0:50 to 1:10. The iron recovery percentage is 68.96% without Na_2CO_3 additives, while the iron recovery can be increased by 5.42 and 5.55% respectively at a mass ratio of Na_2CO_3 to ore of 1:20 and 1:10. With a further increase in Na_2CO_3 dosage, the iron recovery percentage starts to decrease. Na_2O may be dissociated from Na_2CO_3 in the liquid phase, as the result of the hindrance for internal diffusion of reducing gas in the indirect reduction process. What's more, obviously, the dissociation of CO_2 from Na_2CO_3 decreases the ratio of CO/CO_2 in the crucible which restricts the reduction of iron oxide. It can therefore be concluded that Na_2CO_3 dosage has a great influence on the reduction of siderite, no or excessive Na_2CO_3 additive cannot help the reduction of siderite, and only an appropriate Na_2CO_3 dosage can catalyze the reduction of siderite. The recommended Na_2CO_3 dosage corresponds to a mass ratio of Na_2CO_3 to ore of 1:20.

3.4. Characteristics of Reductive Ore Catalyzed by Na_2CO_3

SEM and XRD were employed to identify the phase transition of iron minerals in the process of reducing siderite catalyzed by Na_2CO_3 , while the thermodynamic calculation of the phase change of phosphorus compounds was conducted to provide the theoretical guidance for the subsequent dephosphorization.

Fig. 7. Effect of Na_2CO_3 dosage on reduction of siderite ore with high phosphorus content.

Fig. 8. Microstructure of reduced sample catalyzed by sodium carbonate. Reducing at 1050°C, for 150 min and at mass ratio of pulverized coal to ore of 1:5 (a) mass ratio of Na_2CO_3 to ore of 1:20, (b) mass ratio of Na_2CO_3 to ore of 1:10, (c) mass ratio of Na_2CO_3 to ore of 3:20, (d) mass ratio of Na_2CO_3 to ore of 1:5.

As shown in Figs. 8 and 9 respectively, the iron particle size in the reduced ore catalyzed by Na_2CO_3 is coarser and more aggregated than the reduced ore without Na_2CO_3 additive (Fig. 6). What's more, the iron particle size in reduced

Fig. 9. XRD pattern of reduced sample catalyzed by sodium carbonate.

ore increases with the increases of Na_2CO_3 . The separation of iron from slag can be improved by adding Na_2CO_3 to make the liberation of single irons from slag more easy and create a favorite condition for the magnetic separation. It can be seen from the XRD pattern of reduced ore that the diffraction peak of metallic iron increases markedly with the ratio of Na_2CO_3 to ore increased to 1:20 and 1:10 compared with the reduced ore without Na_2CO_3 additive (Fig. 6). Meanwhile, the diffraction peak of fayalite reduces significantly and the hedenbergite disappears. With a further increase of Na_2CO_3 dosage, the diffraction peak of metallic iron starts to drop, and the diffraction peak of fayalite increases obviously. This is due to the fact that the Na_2O dissociated from Na_2CO_3 can replace the FeO from fayalite, which increases the reducing reaction activity of FeO , and as a result, the reduction of iron oxide can be promoted.¹⁶⁾ Moreover, the mass and heat transfer during the reducing reaction can be optimized by adding Na_2CO_3 additive because the carbon gasification reaction can be accelerated.^{17,18)} However, excessive Na_2CO_3 cannot help the reduction of iron oxide. Maybe the abundant Na_2O dissociated from Na_2CO_3 will appear in the liquid phase because of its low melting point, which results in a hindrance for the internal diffusion of reducing gas, while the dissociation of CO_2 from Na_2CO_3 decreases the ratio of CO/CO_2 in the crucible which restricts the reduction of iron oxide. So, the reduction of siderite can only be catalyzed by adding an appropriate amount of Na_2CO_3 additive.

It can be seen from the binary phase diagram of $\text{CaO}-\text{SiO}_2$ that the reduction reaction of fluorapatite during the Na_2CO_3 catalyzing reductive roasting can be given.¹⁹⁾

The calculation of Gibbs free energy of Eq. (1) is as follows:²⁰⁾

$$\Delta G^\theta = 3\Delta G_{(2)}^\theta - \Delta G_{(1)}^\theta + 5\Delta G_{(3)}^\theta = 1\,464\,300 - 977.85T \quad \text{J} \cdot \text{mol}^{-1} \quad (5)$$

The minimum reduction temperature of fluorapatite can be obtained by calculating the balance temperature of Eq. (5), and the temperature is about 1 224°C. So, fluorapatite is not reduced to P_2 at the temperature of 1 050°C. It can be seen from the previous research as well that phosphorus compounds are not reduced in the low temperature reduction process of iron minerals with high content of phosphorus and remain in the form of oxides in the gangue phases.²¹⁾ As we know, once the phosphorus compounds is reduced, phosphorus is prone to enter into metallic iron phase and make the separation of iron from phosphorus even more difficult.²²⁾ So, phosphorus still exists as fluorapatite, which will enter into slag phase. The microstructure of reduced ore indicates that the iron grain is combined with the slags closely without Na_2CO_3 additive because it is dif-

Fig. 10. Effect of grinding fineness on magnetic separation.

difficult for iron grain to grow and aggregate due to the high content of SiO_2 , which makes the separation of iron phase from slag phase very difficult. While the iron grain is coarse and aggregated with Na_2CO_3 additive. This is due to the fact that the Na_2O dissociated from Na_2CO_3 can replace the FeO from fayalite, which increases the reducing reaction activity of FeO and the reduction of iron oxide can be promoted. Moreover, Na_2O dissociated from Na_2CO_3 will appear in the liquid phase and is benefit for the metallic iron to diffuse and aggregate. This will make the liberation of single irons from slag easier, which is of benefit to the removal of fluorapatite by magnetic separation. The separation of iron phase from slag phase is thus improved by adding Na_2CO_3 additive, which may be the main reason why the content of phosphorus decreases in the iron concentrate as the dosage of Na_2CO_3 increases. Moreover, dephosphorization can be realized completely by magnetic separation if fluorapatite can be fully separated from the magnetic minerals. Ultrafine grinding is therefore an efficient way to obtain qualified iron concentrate.

3.5. Effect of Grinding Fineness on Magnetic Separation

As shown in Fig. 10, the iron concentrate grade increases from 58.84% to 68.45%, and the content of phosphorus in the iron concentrate reduces from 0.32% to 0.08%, when the grinding fineness is raised from 78.5%-74 μm to 89.7%-26 μm , but the iron recovery percentage sharply goes down to 68.53% until the grinding fineness is about 89.7% below 26 μm . When the grinding fineness is 90.45% below 45 μm , a concentrate with 65.85% Fe can be obtained, at a recovery percentage of 75.63%, and a content of phosphorus 0.21%. Ultrafine grinding is therefore an efficient way to remove phosphorus, and the increase in the recovery percentage of fine particles of magnetic minerals is the key to obtain a good result of magnetic separation.

It can be seen from Fig. 11 that the qualified iron concentrate by magnetic separation consists of predominantly metallic iron and a small quantity of magnetite and very little gangue minerals. Typical chemical composition of iron concentrate by magnetic separation is presented in Table 4. It can be concluded that the gangue mineral is mainly quartz.

Fig. 11. XRD pattern of iron concentrate by magnetic separation.

Table 4. Typical chemical composition of iron concentrate by magnetic separation.

Components	TFe	SiO_2	Al_2O_3	CaO	MgO	P	S
wt(%)	65.85	8.75	1.75	1.65	1.4	0.21	0.28

4. Conclusions

The experimental results obtained in the present study lead to the following conclusion:

(1) The iron minerals are mainly siderite, and the phosphorous mainly exists as fluorapatite. It is a challenging task to process this ore to produce a qualified iron concentrate because the ore is of a low grade and it has a complex mineral composition, a disseminated particle size and a high content of phosphorus.

(2) High temperature, long reducing time and strong reducing atmosphere are required to fulfill this challenging task. It is inevitable that a series of reactions between FeO and SiO_2 lead to the formation of a new phase fayalite ($2\text{FeO} \cdot \text{SiO}_2$). Fayalite is difficult to reduce to metallic iron and it is prone to be separated from the reducing agent. The formation of fayalite is therefore the main hindrance to rapid the reduction of siderite.

(3) The reduction of siderite can be catalyzed by adding an appropriate amount of Na_2CO_3 to the raw ore before reductive roasting. The diffraction peak of metallic iron increases markedly while the diffraction peak of fayalite reduces significantly. Excessive Na_2CO_3 cannot help the reduction of siderite.

(4) Fluorapatite is not reduced to P_2 and does not enter into metallic iron phase on the temperature of 1050°C. Ultrafine grinding is the key to the acquisition of high grade of iron concentrate with low content of phosphorus. When the reduced ore catalyzed by Na_2CO_3 is grinded to 90.45% below 45 μm , after the magnetic separation, a qualified iron concentrate with 65.85% Fe, and 0.21% P, can be obtained at a recovery percentage of 75.63%.

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