

# Effects of CaO and Na<sub>2</sub>CO<sub>3</sub> on the Reduction of High Silicon Iron Ores

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**Abstract:** The effects of CaO and Na<sub>2</sub>CO<sub>3</sub> on the reduction of high silicon iron ores at 1 250 °C were studied. The experimental results showed that the metallization rate was significantly hindered by the addition of CaO and Na<sub>2</sub>CO<sub>3</sub>, particularly at the early stage of roasting, compared to the rate without additives. In the absence of additives, iron oxides were quickly reduced to metallic iron, and fayalite was difficult to form. When CaO and Na<sub>2</sub>CO<sub>3</sub> were added, the low reducible iron-containing silicate compounds formed and melted, subsequently retarding the metallization process. The inhibition of Na<sub>2</sub>CO<sub>3</sub> was more noticeable than that of CaO, and higher Na<sub>2</sub>CO<sub>3</sub> doses resulted in stronger inhibition of the increased metallization rate. However, when Na<sub>2</sub>CO<sub>3</sub> was added prior to CaO, the liquid phase formed, which facilitated the growth of the metallic phase. To reinforce the separation of the metallic phase and slag, an appropriate amount of liquid phase generated during the reduction is necessary. It was shown that when 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub> were added, a high metallization rate and larger metallic iron particles were obtained, thus further decreasing the required Na<sub>2</sub>CO<sub>3</sub> dosage.

**Key words:** high silicon iron ores; metallization rate; liquid phase; metallic iron; growth

## 1 Introduction

The rapid development of the iron and steel industry in China in the past 30 years has resulted in the total accumulation of iron ore tailings greater than seven billion tons, which still contains approximately 8%-20% iron<sup>[1]</sup>. For countries like China that have a shortage of iron resources, recovering iron from iron ore tailings has positive economic effects and social benefits. In a previous study, the utilization of high silicon iron ore tailings from the Anshan region of Liaoning province was analysed. Due to the complex mineralogical relationships among iron minerals and gangues, it is difficult to obtain a high grade concentrate with high recovery by physical processing methods<sup>[2]</sup>. Direct reduction technology is an effective method to recover iron from iron ore tailings. However, due to the low content of iron, the cost of direct

reduction is high. Thus, beneficiation of the iron ore tailings is necessary, and high silicon iron ores can be obtained by grinding and magnetic separation. Due to the high content of impurities such as SiO<sub>2</sub>, its recovery has become increasingly difficult. Additives such as Na<sub>2</sub>CO<sub>3</sub> and CaO can be used to reinforce the reduction of iron oxides.

In previous studies, several researchers have analysed the influence of Na<sub>2</sub>CO<sub>3</sub> and CaO on the reduction of different types of iron ores<sup>[3-8]</sup>. It has been suggested that the reduction of iron oxides can be enhanced by an appropriate amount of Na<sub>2</sub>CO<sub>3</sub> and CaO. The reinforcement reduction mechanism can be explained by the functions of freeing FeO from fayalite or spinel and the improvement of the reducing reaction activity of FeO. Other studies indicated that Na<sub>2</sub>CO<sub>3</sub> can also facilitate the growth of the metallic phase<sup>[3,7,9]</sup>. The temperature in those studies was approximately 800-1 150 °C, and little attention was paid to these effects at temperatures higher than 1 250 °C. At higher temperatures, the liquid phases are readily generated by the addition of Na<sub>2</sub>CO<sub>3</sub> and CaO, and the effects of the liquid phases and the reduction of iron oxides should be considered. Currently, there are only a few systematic efforts focused on the influence of Na<sub>2</sub>CO<sub>3</sub> and CaO on the metallization and growth of the metallic phase of

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reduced high silicon iron ores that are pre-concentrated from iron ore tailings. Due to the high content of  $\text{SiO}_2$  and relatively low content of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in the high silicon iron ores, the reduction behaviour resulting from the addition of  $\text{Na}_2\text{CO}_3$  and  $\text{CaO}$  is different from what was observed in the previous studies. The current study will be beneficial for the recovery of iron from iron ore tailings with similar ore properties.

## 2 Experimental

### 2.1 Materials

High silicon iron ores used in the present work were pre-concentrated from Qidashan iron ore tailings, owned by Qidashan Ore Dressing Plant, Liaoning Province, China. The chemical composition of the high silicon iron ores is illustrated in Table 1 and the XRD pattern of it is shown in Fig.1. The high silicon iron ores contained 36.34% total iron, 41.71%  $\text{SiO}_2$  and relatively low content of  $\text{CaO}$ ,  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ . The main iron phases were hematite and magnetite and the gangue minerals included quartz, chlorite and hornblende. The pulverized coal used in this study was bitumite with a particle size  $<1$  mm and its proximate analysis is listed in Table 2. Analytical grade lime and sodium carbonate were used in this study as additives.

Table 1 Chemical compositions of the products/wt%

| $\text{Fe}_{\text{total}}$ | $\text{Fe}_2\text{O}_3$ | $\text{FeO}$ | $\text{SiO}_2$ | $\text{CaO}$ | $\text{MgO}$ | $\text{Al}_2\text{O}_3$ |
|----------------------------|-------------------------|--------------|----------------|--------------|--------------|-------------------------|
| 36.34                      | 42.83                   | 8.18         | 41.71          | 1.82         | 1.69         | 1.82                    |
| $\text{Na}_2\text{O}$      | $\text{K}_2\text{O}$    | $\text{MnO}$ | $\text{TiO}_2$ | S            | P            |                         |
| 0.41                       | 0.27                    | 0.14         | 0.072          | 0.1          | 0.02         |                         |

Table 2 Proximate analysis of the coal/wt%

| Ingredient | Fixed carbon | Volatiles | Ash   | Moisture |
|------------|--------------|-----------|-------|----------|
| Content    | 45.16        | 28.76     | 16.20 | 9.88     |

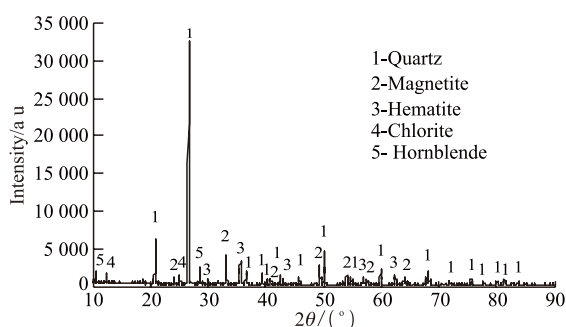


Fig.1 XRD pattern of the high silicon iron ores

### 2.2 Methods

Reduction experiments were performed in a muffle furnace (model CD-1400, made in China). Twenty grams of feed concentrate were mixed with

25% bitumite (mass percent of bitumite to feed concentrate) and 20% additives (mass percent of additives to feed concentrate) for every experiment. The additives used here included  $\text{Na}_2\text{CO}_3$  and  $\text{CaO}$ . The overall dosage of additives was held constant and the amounts of single additives were varied. The mixtures of 20%  $\text{CaO}$ , 15%  $\text{CaO}$  and 5%  $\text{Na}_2\text{CO}_3$ , 10%  $\text{CaO}$  and 10%  $\text{Na}_2\text{CO}_3$ , 5%  $\text{CaO}$  and 15%  $\text{Na}_2\text{CO}_3$ , and 20%  $\text{Na}_2\text{CO}_3$ , and without additives were heated (heating rate  $10$  °C/min) to  $1\ 250$  °C and then roasted for a set period of time. After roasting, reduced samples were removed, immediately quenched with water and then dried at  $80$  °C in a baking oven. Afterwards, the reduced samples were crushed and then milled for 20 min in a XMB- $\phi 65$  mm  $\times$  76 mm rod mill at a pulp density of 65% solids. The pulp was then separated via a CXG- $\phi 50$  magnetic tube with a magnetic field intensity of 191.2 kA/m. The iron content of the magnetic concentrate was analysed by a chemical method and the recovery of iron was calculated based on the mass balance during magnetic separation.

At the same time, the reduction degree was characterized by the index of the metallization rate ( $\eta$ ), and the formula can be calculated as follows<sup>[10]</sup>:

$$\eta = (W_{\text{MFe}} / W_{\text{TFe}}) \times 100\%$$

where  $W_{\text{MFe}}$  is the mass percent of metallic iron of the reduced samples and  $W_{\text{TFe}}$  is the mass percent of total iron after reduction. Both values were determined by chemical analysis. The XRD patterns of the reduced samples were investigated through X-Ray diffraction (RigakuDmax-RD12kW diffractometer with copper target, scanning speed  $10$  °/min, scanning angle  $10^\circ$ - $90^\circ$ ). The microstructures of reduced samples were also studied with a scanning electron microscope (German Carl Zeiss EVO18).

## 3 Results

### 3.1 Effects of $\text{CaO}$ and $\text{Na}_2\text{CO}_3$ on the metallization of reduced samples

#### 3.1.1 Metallization analysis

The effects of  $\text{CaO}$  and  $\text{Na}_2\text{CO}_3$  on the metallization of reduction of high silicon iron ores at  $1\ 250$  °C for different roasting times are given in Fig.2. Fig.2 shows that without additives, the metallization rate reached 91.07% at the beginning of roasting and increased within a narrow range as the reduction continued. The addition of additives had different levels of negative effects on the metallization rate,

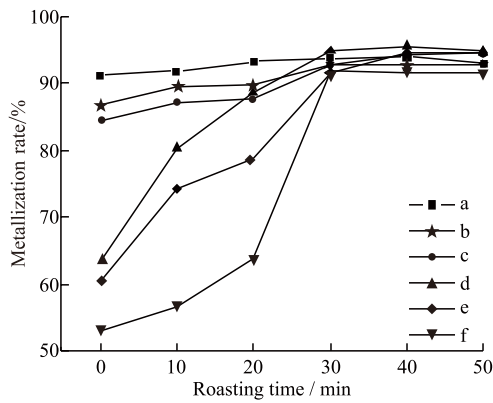


Fig.2 Metallization rate of reduced samples: (a) without additives, (b) with 20% CaO, (c) 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub>, (d) 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub>, (e) 5% CaO and 15% Na<sub>2</sub>CO<sub>3</sub>, and (f) 20% Na<sub>2</sub>CO<sub>3</sub>

particularly in the previous stage of roasting. Increased dosages of Na<sub>2</sub>CO<sub>3</sub> resulted in stronger inhibition of metallization rate increase. It was also observed that at the early stage of roasting, the metallization rate with 20% Na<sub>2</sub>CO<sub>3</sub> was greatly inhibited compared to the rate with 20% CaO, which indicates that the inhibition of Na<sub>2</sub>CO<sub>3</sub> was greater than that of CaO. As the roasting progressed, the metallization rate with additives increased rapidly, and the metallization rate with Na<sub>2</sub>CO<sub>3</sub> and CaO as additives was higher than that with a single additive after 30 min. The experimental data demonstrate that incorporation of Na<sub>2</sub>CO<sub>3</sub> and CaO as additives is a better way to enhance the reduction of high Silicon iron ores.

3.1.2 Phase

The XRD patterns of reduced samples at 1 250 °C

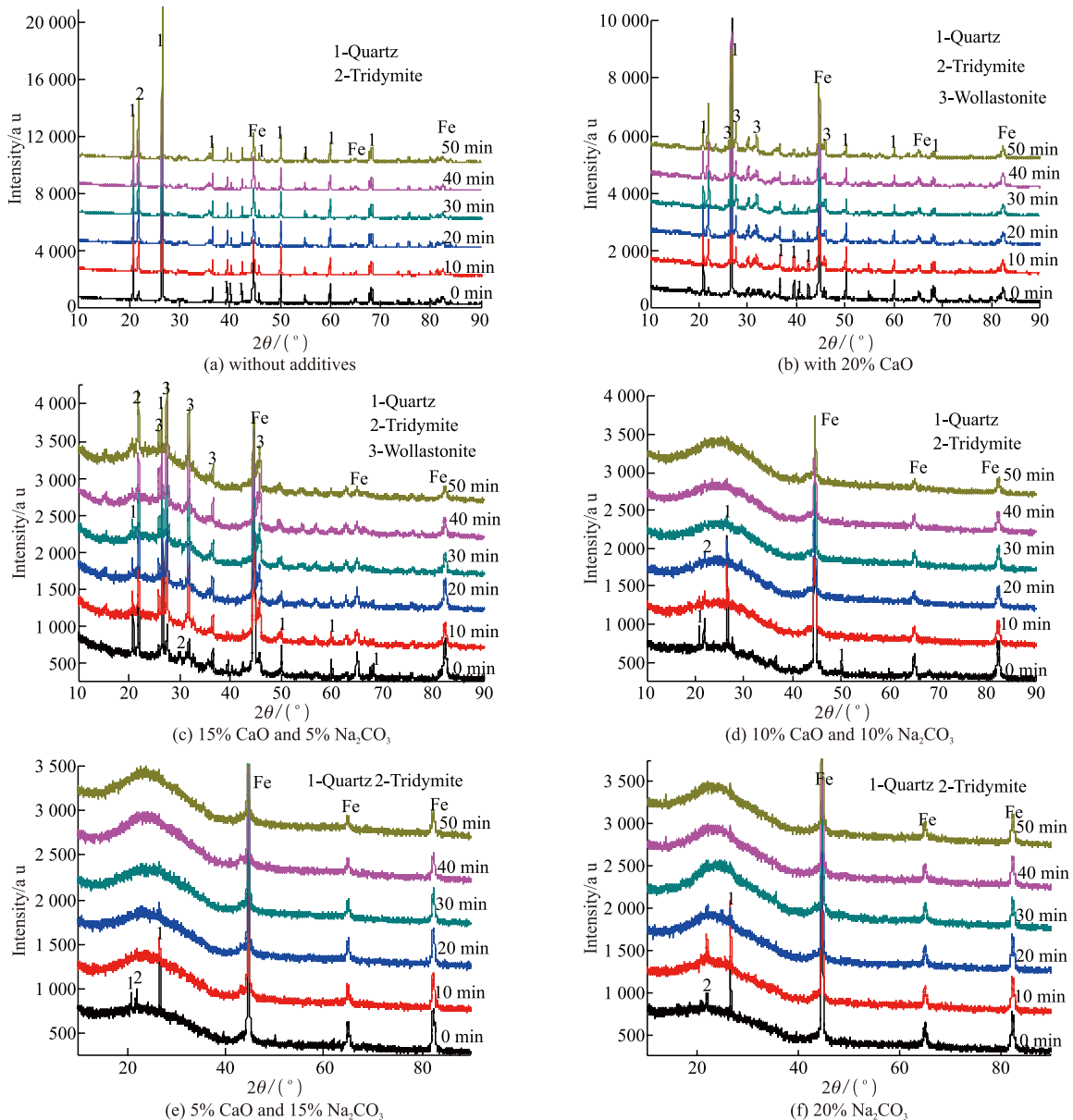


Fig.3 XRD patterns of reduced samples

for different roasting times are given in Fig.3. Fig.3(a) shows that without additives, the main crystalline minerals were quartz, tridymite and metallic iron, and no other types of iron-containing mineral peaks were detected. Therefore, it can be concluded that iron oxides were nearly completely reduced to metallic iron, which is demonstrated by the higher metallization rate of reduced samples at the beginning of roasting. When 20% CaO was added, the peak of wollastonite appeared at 10 min and then increased with prolonged roasting due to the reaction of CaO and SiO<sub>2</sub> in gangue (Fig.3(b)). When 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub> were added, the baseline of the XRD pattern from 0° to 40° was more noticeably elevated compared to that with the addition of 20% CaO, and the peak of wollastonite appeared at the beginning of roasting and then increased (Fig.3(c)). This result indicated that the melting point of slag phases was reached and the formation of wollastonite was catalysed because of the Na<sub>2</sub>CO<sub>3</sub> additive. This phenomenon likely occurred because the appropriate Na<sub>2</sub>CO<sub>3</sub> additive improved the melting behaviour of the slag and increased the chances of the reaction between CaO and SiO<sub>2</sub><sup>[7]</sup>. Due to the earlier and more rapid formation of wollastonite, the reaction between FeO and SiO<sub>2</sub> was impaired and the metallization rate was expected to be impacted slightly more by the addition of Na<sub>2</sub>CO<sub>3</sub>. A big change occurred when the dosage of Na<sub>2</sub>CO<sub>3</sub> was greater than 10%, as shown in Figs.3(d)-3(f). In Figs.3(d)-3(f), the peaks of quartz and tridymite were present at the beginning of roasting and then disappeared after 20 min. The arch of the XRD pattern between 20° and 30° indicated that a large amount of low melting point amorphous compounds were generated. This result shows that the addition of Na<sub>2</sub>CO<sub>3</sub> promoted the formation of low melting point compounds<sup>[11,12]</sup>. Combined with the previous metallization analysis, it can be concluded that a substantial amount of iron in iron oxides would be readily absorbed in those amorphous compounds, hindering the increase of the metallization rate.

### 3.1.3 Microstructure

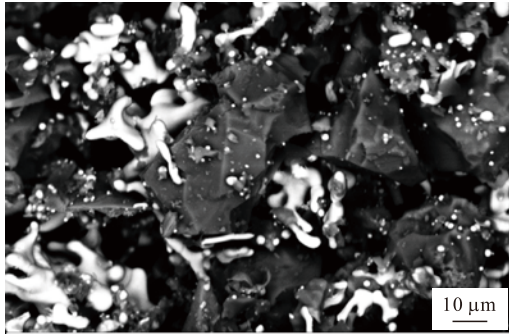
In our experiment, no iron containing minerals were detected by XRD analysis. Combined with the metallization analysis, it is likely that some iron in iron oxides were transferred into the slag. Thus, the microstructures of reduced samples at the beginning of the roasting time were studied using SEM, and the composition of the slag was analysed by EDS as shown in Fig.4.

Fig.4(a) shows that the ore structure was not

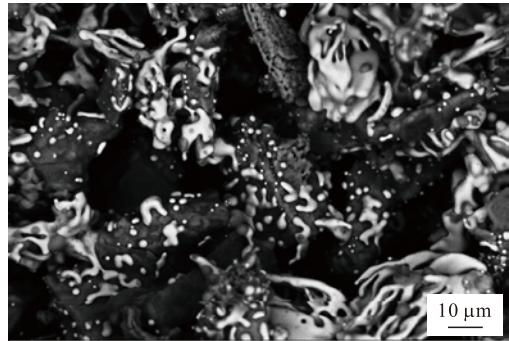
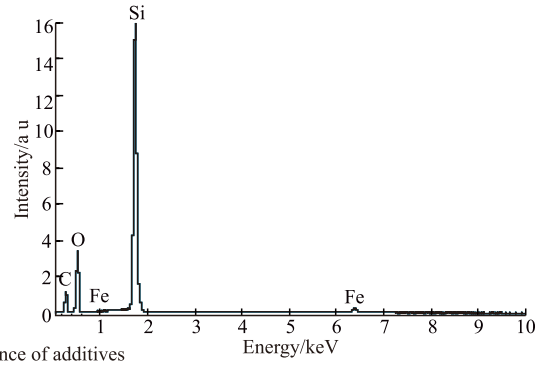
changed in absence of additives and a small amount of metallic iron formed at the ore interface. The composition of the ore surface was detected by DES analysis, and the result revealed that a small amount of fayalite formed on some ore surfaces. As a result, a high metallization rate can be achieved at the beginning of the roasting, which differs from the result published by Bai *et al*<sup>[3,4]</sup>. Their results revealed a substantial fayalite formation in the absence of additives. The differences between these results could be due to the different mineral compositions and reduction conditions. In our experiments, the sizes of most of the high silicon iron ore particles are less than 0.038 mm, and the contact area between iron oxides and coal particles is large. Thus, iron oxides can be quickly reduced to the metallic phase owing to the good reducing gas diffusion conditions, shortening the contact time of FeO and SiO<sub>2</sub><sup>[6]</sup>. As a result, the large fayalite formation was impeded within the experimental range and conditions.

Fig.4(b) shows that the ores were generally covered with a product layer that changed the surface morphology of the ore structure. Several fine vermicular metallic iron products grew in the product layer. The EDS analysis shows that the product was composed of FeO-CaO-SiO<sub>2</sub> compounds that contained 3%-15% iron in different areas. It is observed that the iron-containing product layer was much thicker than the fayalite product layer without additives. In our experiments, FeO-CaO-SiO<sub>2</sub> compounds formed more readily and no fayalite phase was detected when CaO was added. This result shows that adding CaO inhibited the generation of fayalite, but FeO-CaO-SiO<sub>2</sub> compounds formed readily. At a temperature of 1 250 °C, a wide liquid phase area appeared according to the FeO-CaO-SiO<sub>2</sub> phase diagram<sup>[13]</sup>. The liquid phase within the product should be considered in certain regions of the product where there is a locally high concentration of FeO, which is demonstrated by the baseline of the XRD pattern from 0° to 40° that is noticeably increased obviously in Fig.2(b). Then, the compounds would melt and wet the ores. Because of the mildly reducible compounds, the metallization rate with 20% CaO was lower than it was without additives.

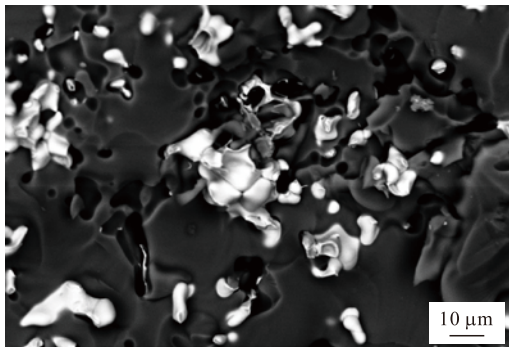
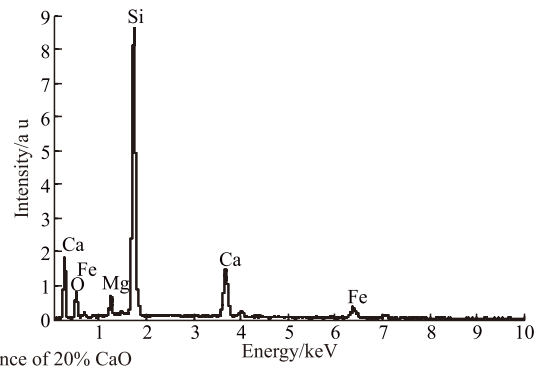
Different from the reduced samples without additives or with 20% mass CaO, when Na<sub>2</sub>CO<sub>3</sub> was added, the ore structure was destroyed, as shown in Figs.5(c)-5(f). When 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub> were added, a large number of 0-10 μm micropores could be observed in the slag, and metallic iron particles were becoming coarser and aggregating in the pores. When



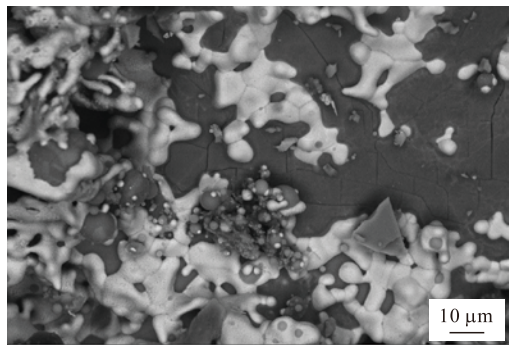
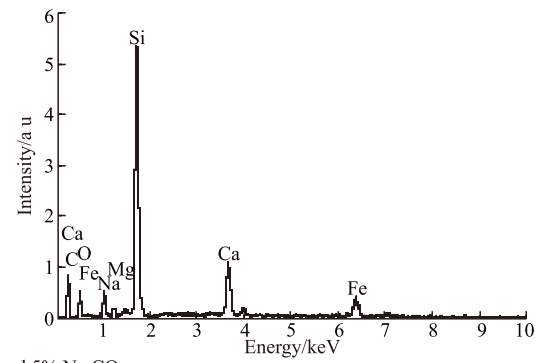
(a) in the absence of additives



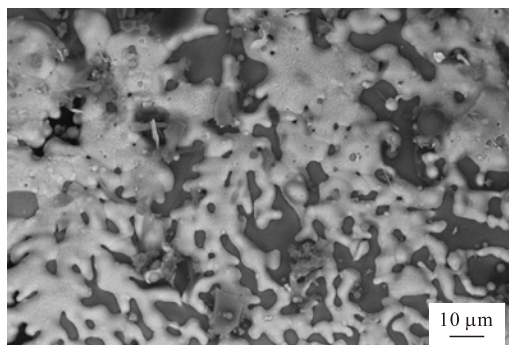
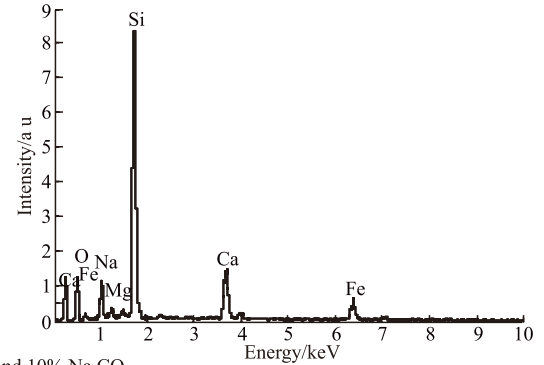
(b) in the presence of 20% CaO



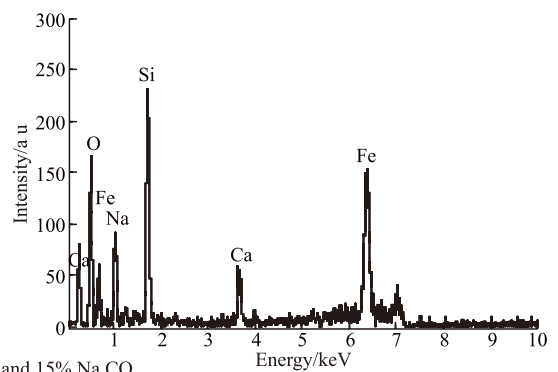
(c) 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub>



(d) 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub>



(e) 5% CaO and 15% Na<sub>2</sub>CO<sub>3</sub>



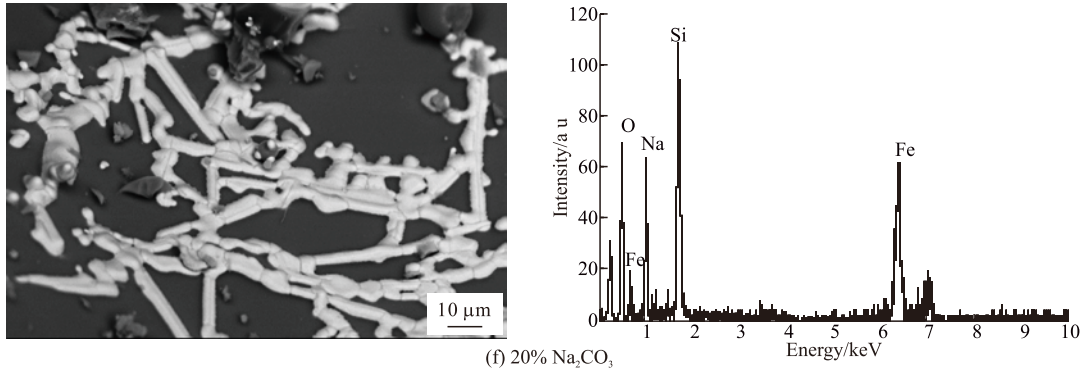


Fig.4 SEM images of reduced samples at the beginning of roasting

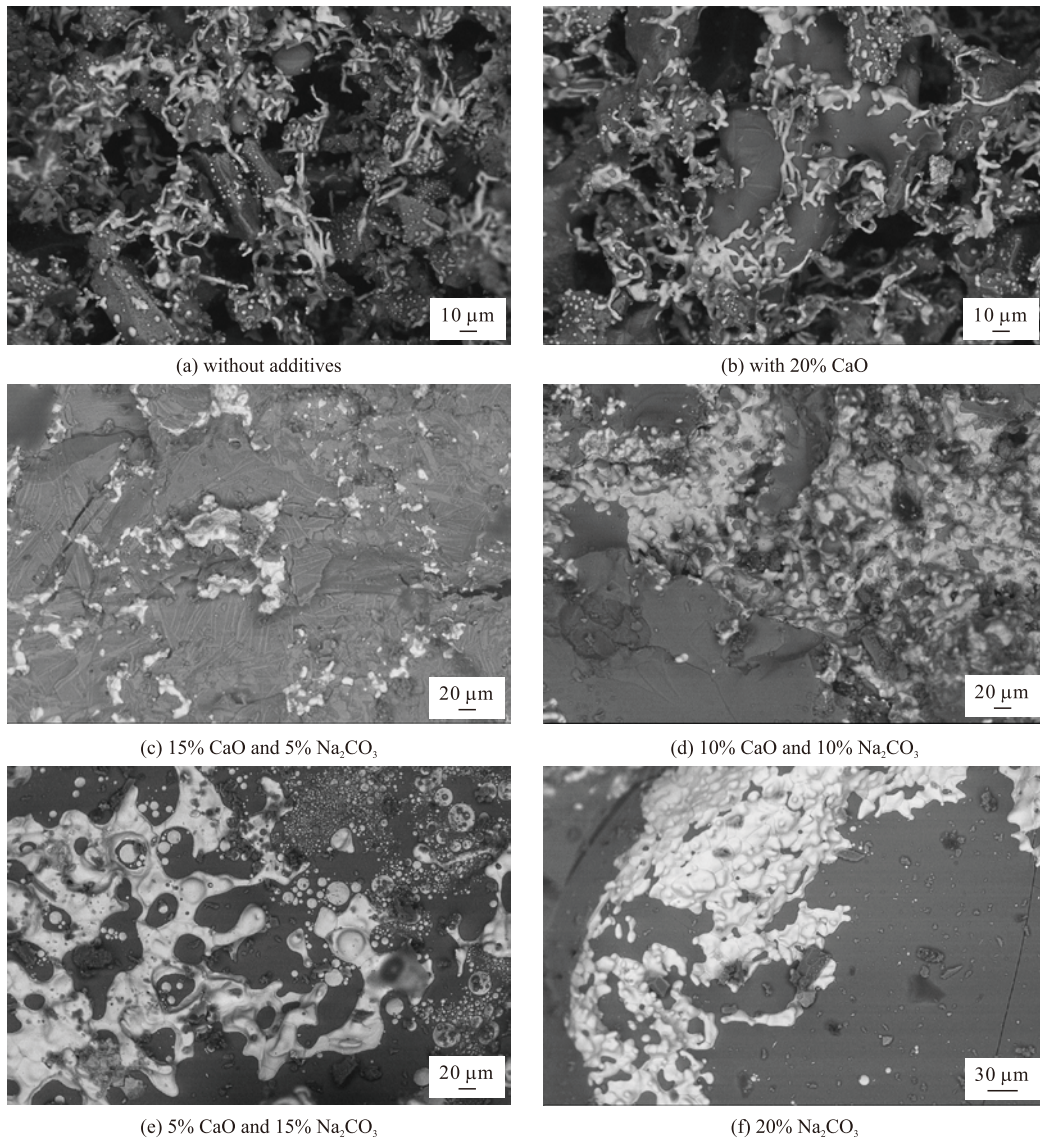


Fig.5 SEM images of the reduced samples at 1250 °C for 30 min

the dosage of  $\text{Na}_2\text{CO}_3$  was more than 10%, a denser slag phase was obtained and metallic iron formed at the slag's interface. The elemental composition of those slags was detected by EDS, and the results show that the slags were mainly composed of  $\text{FeO-CaO-Na}_2\text{O-SiO}_2$  ( $\text{FeO-Na}_2\text{O-SiO}_2$ ) compounds. These silicate

compounds are amorphous based on their identification from the XRD analysis in Figs.3(c)-3(f). The iron content in the slag was proportional to the  $\text{Na}_2\text{CO}_3$  ratio, and the iron content in the slag with 20%  $\text{Na}_2\text{CO}_3$  can reach 10%-30%.

When  $\text{Na}_2\text{CO}_3$  was added,  $\text{Na}_2\text{O}$  was dissociated

from Na<sub>2</sub>CO<sub>3</sub> at 851 °C and appeared in the liquid phase. Then, Na<sub>2</sub>O reacted with SiO<sub>2</sub>, FeO and CaO to form low melting point compounds. These compounds melted and generated a large amount of liquid phase which further corroded the gangue and iron oxides. Greater Na<sub>2</sub>CO<sub>3</sub> dosages resulted in increased liquid phase formation. As a result, a large amount of iron was transferred from iron oxides to the slag which caused a lower metallization rate. The metallization rate did not noticeably improve when the roasting time was less than 20 min. This phenomenon could have occurred because the liquid phase hindered the internal diffusion of reducing gases and then restricted the reduction process, causing more iron ions to be absorbed in the slag and lowering the metallization rate<sup>[3, 14]</sup>.

It should be noted that when 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub> were added, the porous slag occurred as a result of the breakdown of the initial slag because of the interior reducing gas diffusion pressure that was caused by the subsequent reaction of the carbon in the reductant with the oxygen in the iron oxides. These small pores were considered to act as nucleating points with the resulting growth of metallic iron at the pores' interface, which had a positive effect on the interior reducing gas diffusion. In addition, an appropriate liquid phase in the slag prevented more iron ions from being transferred from iron oxides into the slag according to the previous analysis. When the dosage of Na<sub>2</sub>CO<sub>3</sub> was more than 10%, excessive liquid phase formation occurred, and the porous slag was difficult to shape.

In summary, the addition of CaO and Na<sub>2</sub>CO<sub>3</sub> had a negative influence on the reduction of iron oxides at the early stage of roasting under the selected reducing conditions. This result primarily occurred because the sequence of the reduction of iron oxides was changed. Without additive, iron oxides can be quickly reduced to the metallic phase by stepwise reduction<sup>[15]</sup>, and few iron oxides are reduced by the FeO→fayalite→Fe sequence. When CaO and Na<sub>2</sub>CO<sub>3</sub> were added, many iron oxides were reduced by the FeO→iron-containing silicate compounds→Fe pathway, and these compounds are more difficult to reduce than FeO to the complicated structure. The reduction process was slightly more impacted by the addition of CaO, and the negative influence was strengthened by increasing the Na<sub>2</sub>CO<sub>3</sub> dosage. After 30 min, the incorporation of CaO and Na<sub>2</sub>CO<sub>3</sub> appeared to increase the metallization rate compared to the rate without additives. In this mechanism, it is readily apparent that the liquid phase

promoted the migration and accumulation of iron ions to the reduction reaction interface and accelerated the transfer of iron ions to the metallic phase<sup>[16]</sup>.

### 3.2 Effects of CaO and Na<sub>2</sub>CO<sub>3</sub> on the growth of metallic phase

The effects of CaO and Na<sub>2</sub>CO<sub>3</sub> on the growth of the metallic phase at 1 250 °C for 30 min are shown in Fig.5. Figs.5(a) and (b) indicate that the metallic iron particles with sizes of 0-10 μm were not combined with one another fully and were still closely associated with the slag, which led to the more difficult mineralogical separation of metallic iron particles and slag. When Na<sub>2</sub>CO<sub>3</sub> was added, it can be seen from Figs.5(c)-5(f) that most of the metallic iron particles aggregated together and exhibited noticeable growth. The results showed that the growth of the metallic phase can be improved by the addition of Na<sub>2</sub>CO<sub>3</sub>; thus, the liberation of metallic iron from slag will become easier.

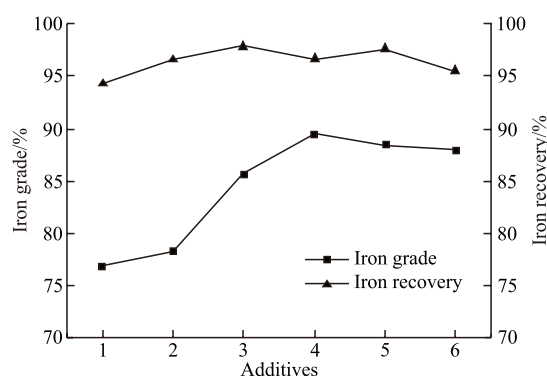


Fig.6 Effects of CaO and Na<sub>2</sub>CO<sub>3</sub> on the iron grade and iron recovery of reduced samples (The numbers 1 to 6 on the abscissa axis represent no additives, 20% CaO, 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub>, 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub>, 5% CaO and 15% Na<sub>2</sub>CO<sub>3</sub>, and 20% Na<sub>2</sub>CO<sub>3</sub>, respectively)

Grinding and magnetic separation were used for indirect evaluation of the effect of CaO and Na<sub>2</sub>CO<sub>3</sub> on the growth of the metallic phase by the determination of iron grade and iron recovery in magnetic concentrates. Reduced samples were comminuted for 20 min and then separated by low magnetic intensity, and the results are shown in Fig.6. It can be seen from Fig.6 that the iron grade of the magnetic concentrate with 20% CaO only increased slightly compared to the iron grade without additives. This result indirectly indicated that only adding CaO did not noticeably promote the growth of metallic iron particles. The iron grade in the magnetic concentrate was noticeably improved when 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub> were added, and the best index was apparently obtained when 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub> were added. This result shows that adding Na<sub>2</sub>CO<sub>3</sub> can considerably improve the growth of the

metallic phase. However, the iron grade decreased slightly as the  $\text{Na}_2\text{CO}_3$  dosage was more than 10%. The reasons for this decrease require further study. It is apparent that the iron recovery of magnetic concentrate was not noticeably affected by the addition of CaO and  $\text{Na}_2\text{CO}_3$ .

## 4 Discussion

The reduction of iron oxides involves two process: the chain of reduction reactions to form a metallic phase and the growth of the metallic phase from small particles to larger particles that are amenable to separation. For high grade iron ores that contain low levels of impurities, whether the iron ore can be completely reduced into metallic iron is the key factor for evaluating the quality of the direct reduction iron product. However, low grade iron ores or iron-containing materials contain many impurities. A high metallization rate alone is inadequate to remove the impurities. The growth of the metallic phase is considered to be equally important because the mineralogical separation of metallic iron particles and the slag is imperfect through conventional grinding if the particles are very small. In our studies, high silicon iron ores contain many impurities, especially  $\text{SiO}_2$ ; therefore, the growth of the metallic phase and the liberation of metallic iron from the slag need to be considered.

Without additives or with 20% CaO added, the quantity of fayalite or FeO-CaO- $\text{SiO}_2$  compounds generated at the surface of gangue was limited and the reduced samples almost did not sinter due to the lack of a liquid phase. It is difficult for metallic iron particles to grow and aggregate through the solid phase at 1 250 °C because the particles were fine and dispersed in the reduced samples. It is difficult to separate the metallic phase from the slag, although the metallization rate of over 90% without additives can be obtained at the beginning of the roasting. In addition, the metallization rate increase with 20% CaO was restricted because of the FeO-CaO- $\text{SiO}_2$  compounds, compared to the absence of additives, which indicated that only adding CaO is insufficient to reduce the high silicon iron ores at 1 250 °C or a lower temperature.

When  $\text{Na}_2\text{CO}_3$  was added, the original ore structure could be destroyed and a considerable quantity of the liquid phase formed. This liquid phase greatly improved the growth of the metallic phase, as shown in Fig.5. The metallic iron particle size in the

reduced samples was coarser and more aggregated than that without additives or with 20% CaO. This result occurred because the  $\text{Na}_2\text{O}$  dissociated from  $\text{Na}_2\text{CO}_3$  appeared in the liquid phase, which promoted the migration and aggregation of the metallic iron<sup>[7,8, 17]</sup>. The mechanism of growth of the metallic phase via the liquid phase can be explained by studies conducted by Weissberger *et al* and Nadiv *et al*<sup>[18,19]</sup>. Those authors suggested that iron was dissolved on the surface of smaller particles and migrated in the matrix and then deposited on the larger growing ones. The liquid phase generated in the slag created the bridges between metallic iron particles which promoted the diffusion of ions and enhanced mass transfer from the smaller to the larger iron particles.

However, the liquid phase formation resulted in a lower metallization rate at the beginning of roasting due to some iron being transferred from iron oxides to the slag. When only CaO was added, FeO-CaO- $\text{SiO}_2$  compounds formed, and when  $\text{Na}_2\text{CO}_3$  was added, more complicated iron containing silicate compounds were generated. The decomposition pressure of iron-containing silicate compounds is higher than that of iron oxides; Thus, these compounds are more difficult to reduce than iron oxides<sup>[20]</sup>. The subsequent reduction was more likely controlled by the reduction reactions of the compounds that were difficult to reduce. Furthermore, the liquid phase entrapped the gangue and iron oxides to form a denser slag phase and hindered the diffusion of the reducing gases, inhibiting the increase of the metallization rate.

Based on the above analysis, it can be inferred that the growth of the metallic phase was closely associated with the liquid phase generated during the reduction, and the appropriate amount of liquid phase can support the growth of the metallic iron particles. However, the liquid phase formation in the slag will retard the metallization process and the larger the liquid phase formed in the slag, which will increase the strength of the inhibition of the metallization rate, especially at the early stage of roasting. However, to obtain a better separation of metallic iron particles and the slag, the appropriate amount of liquid formation during the reduction is necessary, although it will retard the metallization process.

It is apparent that a higher metallization rate after 30 min and a better iron grade and iron recovery rate can be obtained when 10% CaO and 10%  $\text{Na}_2\text{CO}_3$  were added. This result shows that for the reduction of high silicon iron ores, incorporation of CaO and  $\text{Na}_2\text{CO}_3$



is better than that of CaO or Na<sub>2</sub>CO<sub>3</sub> individually. However, the metallization rate was lower at the early stage of roasting as the Na<sub>2</sub>CO<sub>3</sub> additive was more than 10%, which shows that the liquid phase formation was excessive. On the other hand, the excessive Na<sub>2</sub>CO<sub>3</sub> is easy to corrode industrial reduction equipments and the price of Na<sub>2</sub>CO<sub>3</sub> is more expensive than that of CaO. So Na<sub>2</sub>CO<sub>3</sub> additive should be further decreased.

It was observed that most of the sizes of metallic iron particles were greater than 10 μm as 15% CaO and 5% Na<sub>2</sub>CO<sub>3</sub> were added. According to the study conducted by Hu *et al.*<sup>[21]</sup>, the metallic iron particles with sizes >10μm can be recovered by ultrafine grinding and stage magnetic separation. Furthermore, the metallization rate was impacted slightly more compared to other excessive Na<sub>2</sub>CO<sub>3</sub> additive conditions. Thus, the quantity of the Na<sub>2</sub>CO<sub>3</sub> additive can be further decreased. The optimum reduction parameters will be studied further. However, due to the adding of Na<sub>2</sub>CO<sub>3</sub> and the low iron content of high silicon iron ores, it is difficult to make a profit under the depressed steel prices. Although at present the reduction of high silicon iron ores is not economically feasible, as a kind of national high-tech research and development program of China, it has important strategic and forward-looking significance for the utilization of high silicon iron ores. When China's steel market is relatively weak, this research results can be used as a technical reserve which would be used in the near future. As the steel industry is gradually warming, the research results can realize industrial production.

## 5 Conclusions

a) The metallization rate was significantly hindered by the addition of CaO and Na<sub>2</sub>CO<sub>3</sub>, especially at the early stage of roasting, compared to those without additives. This result occurred primarily because the additives CaO and Na<sub>2</sub>CO<sub>3</sub> promoted the formation of low melting point low reducible iron-containing compounds and made the iron transferred from iron oxides into slag.

b) The reduction process was slightly more impacted by only adding CaO, and the negative influence was strengthened with increased Na<sub>2</sub>CO<sub>3</sub> dosage. Increased Na<sub>2</sub>CO<sub>3</sub> dosage was associated with greater liquid phase formation, which caused the stronger inhibition of the increased metallization rate.

c) Na<sub>2</sub>CO<sub>3</sub> added prior to CaO facilitated the growth of the metallic phase because of the liquid

phase formation in the slag. To enhance the liberation of metallic phase from slag, an appropriate amount of liquid phase generated during the reduction was necessary, although it retarded the metallization process.

d) When 10% CaO and 10% Na<sub>2</sub>CO<sub>3</sub> were added, a higher metallization rate and better iron grade and iron recovery of magnetic concentrate were obtained after 30 min, and the optimal Na<sub>2</sub>CO<sub>3</sub> dosage will be determined in future studies.

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