

Reduction–melting behaviors of boron-bearing iron concentrate/carbon composite pellets with addition of CaO

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Abstract: Although the total amount of boron resources in China is high, the grades of these resources are low. The authors have already proposed a new comprehensive utilization process of boron-bearing iron concentrate based on the iron nugget process. The present work describes a further optimization of the conditions used in the previous study. The effects of CaO on the reduction–melting behavior and properties of the boron-rich slag are presented. CaO improved the reduction of boron-bearing iron concentrate/carbon composite pellets when its content was less than 1wt%. Melting separation of the composite pellets became difficult with the CaO content increased. The sulfur content of the iron nugget gradually decreased from 0.16wt% to 0.046wt% as the CaO content of the pellets increased from 1wt% to 5wt%. CaO negatively affected the iron yield and boron extraction efficiency of the boron-rich slag. The mineral phase evolution of the boron-rich slag during the reduction–melting separation of the composite pellets with added CaO was also deduced.

Keywords: iron concentrate; boron; ore reduction; composite pellets; calcium oxide

1. Introduction

Mineral resources are the foundation for the sustainable development of human society. Boron is well known to be one of the most important elements; it is used widely in hundreds of industries, including the chemical, ceramics, glass, metallurgy, medicine, defense, aerospace, and nuclear energy industries [1]. The total boron resources in China are abundant; China ranks fifth in the world in boron resources. However, most of the boron mineral resources in China are low grade. With the depletion of the traditional high grade szaibelyite ore and increase in the demand for boron products because of China's growing economy, the comprehensive utilization of the domestic low-grade boron resources has become the main task confronting the Chinese boron industry to guarantee sustainable development. Liaoning and Jilin provinces contain 0.28 billion tons of low-grade paigeite deposits; these deposits account for 57.88% of the boron reserves and 1% of the iron reserves in China and are regarded as the main alternate resource of szaibelyite ore [2].

Paigeite is a complex iron ore rich in iron, boron, and magnesium. The key factors in the comprehensive utiliza-

tion of paigeite as a resource are the achievement of a high degree of separation of boron and iron and the high yield and good quality of the separation products. At present, the combined ore dressing–pyrometallurgical separation two-step flowsheet for the utilization of crude paigeite has been generally recognized. The main issue is the boron and iron separation of the boron-bearing iron concentrate to achieve a high total yield of boron. We have previously proposed a novel comprehensive utilization flowsheet of boron-bearing iron concentrates by carbon-bearing composite pellet reduction and melting technology, i.e., the iron-nugget process [3–5]. This new technology has the merits of being coke free, having a short flowsheet, providing a high degree of separation of boron and iron, and resulting in a high grade of boron content in the boron-rich slag, among other advantages. However, the sulfur content in the separation iron nugget is high because of the relatively high content of pyrite, which is a detriment to its further utilization.

Calcium oxide (CaO) is the most widely used desulfurizing agent in the pyrometallurgical process. It is an economical raw material that is easily acquired. In the present

work, the effects of CaO on the reduction–melting behaviors of boron-bearing iron concentrate/carbon composite pellets and on the properties of the iron nuggets and boron-rich slag were studied. A better understanding of the mechanism of the new process was obtained from the experimental results.

2. Experimental

2.1. Raw materials

The boron-bearing iron concentrate used in this study was obtained from Dandong, Liaoning Province, China. The chemical composition of the complex ore sample is shown in Table 1. Most of the iron ore concentrate particles (98wt%) were less than 0.074 mm in size. Mineralogical analysis of the concentrate was performed using X-ray diffraction (XRD). The results are given in Fig. 1, which indicate that the main crystalline phases are magnetite (Fe_3O_4), szaibelyite ($\text{Mg}_2(\text{OH})[\text{B}_2\text{O}_4(\text{OH})]$), and chrysotile ($\text{Mg}_3[\text{Si}_2\text{O}_5](\text{OH})_4$). The chemical composition of the reducing agent is listed in Table 2. As evident from the results in the table, the reducing agent is a kind of anthracite with high fixed-carbon and low sulfur contents. The fineness of the reducing agent is 100%, passing 0.5 mm. The reactivity of the pulverized coal was assessed on the basis of its chemical reaction rate with carbon dioxide (30 mL/min) using a thermogravimetric method with a heating rate of $10^\circ\text{C}/\text{min}$. The results are shown in Fig. 2. The Boudouard reaction proceeded at a viable rate when the temperature was greater than 1150°C . The CaO used in the experiments was of analytical reagent (AR) grade.

Table 1. Chemical composition of the boron-bearing iron concentrate wt%

B_2O_3	TFe	MgO	SiO_2	Al_2O_3	FeO	CaO	P	S	LOI
6.90	47.20	19.20	5.32	0.15	18.90	0.34	0.020	0.16	4.97

Note: TFe represents the content of total iron in the ore sample, and LOI represents loss on ignition.

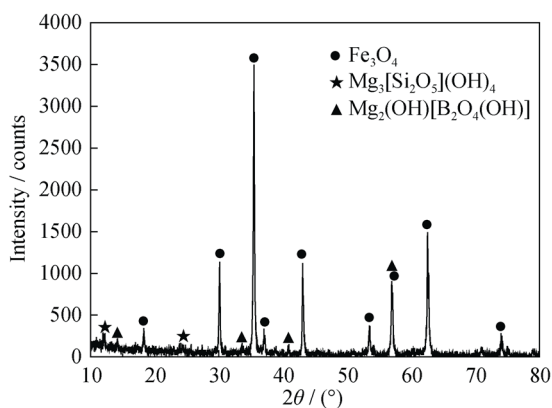


Fig. 1. XRD pattern of the boron-bearing iron concentrate.

Table 2. Proximate and ash analysis of the reducing agent

Proximate analysis				Ash analysis				
FC_d	V_d	A_d	S	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
81.40	6.40	11.10	0.34	46.10	32.16	9.51	4.26	0.65

Note: FC_d represents the fixed carbon (dry basis), V_d is the volatile matter (dry basis), A_d is the ash (dry basis), and S is the total sulfur.

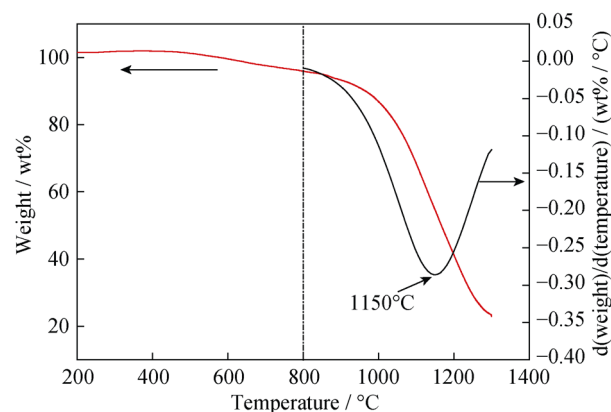


Fig. 2. Reactiveness thermogravimetric curve of the pulverized coal.

2.2. Experimental procedure

The boron-bearing iron concentrate, reducing agent, CaO, and organic binder were thoroughly mixed together. The mole ratio between the fixed carbon in the reducing agent and the oxygen in iron concentrate was 1.2. The amount of organic binder was 2wt% of the weight of iron concentrate and reducing agent. The amount of CaO was set as 0wt%, 1wt%, 3wt%, and 5wt% of the weight of the iron concentrate and reducing agent. The moisture of the mixer was controlled to be 7wt%. The prepared mixer was pelletized in a horizontal twin roller machine. The size of the pillow-shaped pellets was $40\text{ mm} \times 30\text{ mm} \times 20\text{ mm}$. The wet green pellets were dried for 12 h at 120°C .

Reduction–melting experiments were performed in a closed MoSi_2 box muffle resistance furnace to simulate the iron nugget production process involving carbon composite pellets in a rotary hearth furnace. In each experiment, the dry green pellet was placed into a graphite crucible and then heated at 1400°C and 1450°C in the furnace. The crucible had already been heated to the target temperature before the reduction experiment. It would protect the furnace from being corroded by the formed slag. After the reduction experiment was completed, the sample was removed from the furnace and cooled to ambient temperature under the protection of nitrogen. The pellets, which were not smelted and became metalized pellets, were characterized by the index of metallization degree (η). The η was calculated by the fol-

lowing formula:

$$\eta = (\text{MFe}/\text{TFe}) \times 100\% \quad (1)$$

where TFe is the total iron content after reduction and MFe is the metallic iron content after reduction.

The chemical compositions of the separation slag and iron nugget were analyzed to reveal the effect of CaO addition on the reduction–melting behaviors. XRD and SEM–EDS analyses were also conducted to characterize the mineral phase composition and the microstructure of the slag. The normal-pressure alkaline leaching method, which is described elsewhere [3], was used to assess the efficiency of extraction of boron (EEB) of the boron-rich slag.

3. Results and discussion

3.1. Effect of CaO on the reduction of composite pellets

The reduction behaviors of composite pellets containing different contents of CaO at 1400°C are shown in Fig. 3. As evident in the figure, the metallization degree gradually increased with increasing reduction time. However, the metallization degree increased when the CaO content was increased from 0wt% to 1wt% and then maintained the standard level, i.e., approximately the same as that achieved with the 0wt% CaO content pellet, when the content of CaO was increased to 3wt% and 5wt%. The metallization degree of pellets containing 1wt%, 3wt%, 5wt%, and 0wt% CaO were 83.9%, 74.6%, 74.7%, and 73.3%, respectively, when the pellets were heated at 1400°C for 6 min. These experimental results indicate that CaO improves the reduction rate when its content is low and restrains the reduction when its content is high.

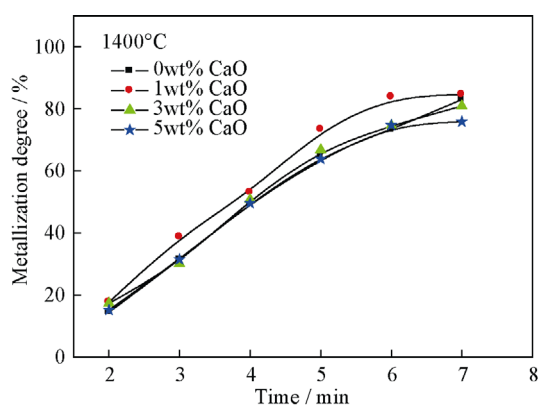


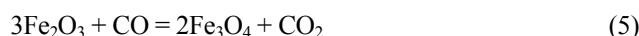
Fig. 3. Variation of the metallization degree of composite pellets with different CaO contents.

The reduction reactions of iron oxide in the carbon composite pellet are listed as follows [4].

Direct reductions:



Indirect reductions:



Boudouard reaction:



At the initial stage, the carbothermic reduction is dominated by the direct reduction. With increasing temperature and CO pressure, the indirect reduction will dominate the total reduction reaction. The Boudouard reaction is highly dependent on the temperature, and the CO₂ produced from the indirect reduction will be consumed by the solid carbon through the Boudouard reaction. The total reduction reaction is represented by the equation $\text{FeO}_x + x\text{C} = \text{Fe} + x\text{CO}$ and proceeds through the gaseous intermediates CO and CO₂.

CaO may catalyze the Boudouard reaction [6]. Hence CaO will improve the reduction of carbon composite pellets [7]. Under the present experimental conditions, the CaO can improve the reduction when the CaO content is low, such as 1wt%. As the iron oxide reduction progresses, Fe₃O₄ transform into FeO under the present experimental conditions. An increase in the CaO content during the reduction of Fe₃O₄ may decrease the melting point of the FeO-rich slag [8]. The morphology of the surface of the pellet reduced at 1400°C for 5 min is shown in Fig. 4. The surface of the reduced 1wt% CaO pellet exhibited little melting. The melting phenomenon occurred on the surface of the reduced 3wt% CaO pellet, and the area of the melting zone increased when the CaO content increased to 5wt%. FeO is difficult to reduce into metallic iron if it forms a melting slag phase with other gangue oxides. However, the melting slag phase may slow the mass transfer rate during the reduction process. Therefore, the reduction rate of the pellet decreased with increasing CaO content under the investigated conditions.

3.2. Effect of CaO on the melting separation behaviors of composite pellets

The morphologies of composite pellets containing CaO reduced at 1400°C for different times are shown in Fig. 5. As evident in the figure, the CaO content strongly influenced the melting behaviors. The 1wt% CaO pellet began to melt at 10 min and exhibited clean separation at 12 min. Its separation result is even better than that of pellets without CaO added. However, the melting separation worsened with increasing CaO content. The pellets containing 3wt% and 5wt% CaO did not melt separate when they were reduced for 20 min. The separation results of 1wt% CaO pellet reduced at 1400°C for 15 min are listed in Table 3.

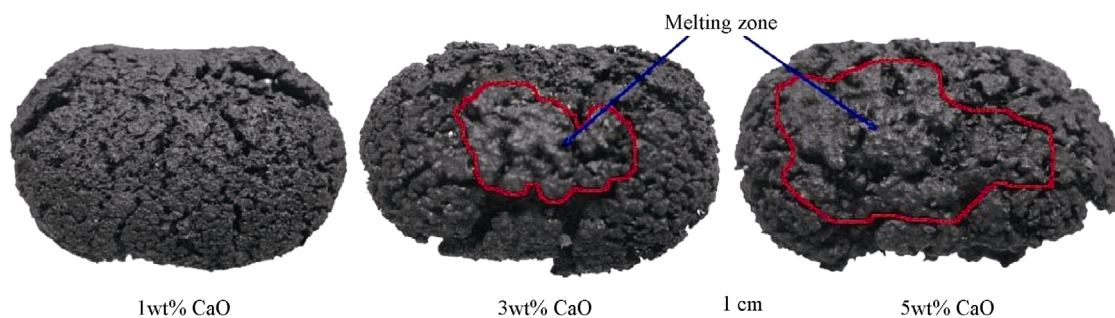


Fig. 4. Morphology of the surface of reduced pellets with different contents of CaO (1400°C, 5 min).

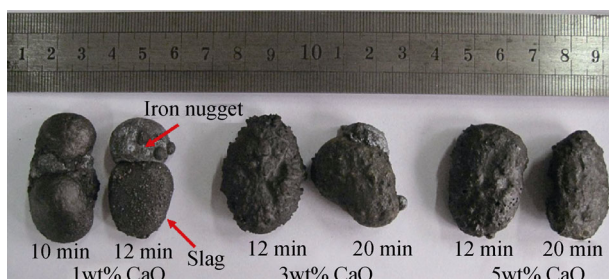


Fig. 5. Morphologies of the reduced pellets (1400°C).

Table 3. Separation results of the pellet with 1wt% CaO (1400°C, 15 min)

Slag/wt%			Iron nugget/wt%		
TFe	MFe	FeO	B ₂ O ₃	[S]	Iron yield
5.38	2.75	3.38	20.1	0.31	98.33

In general, the melting separation of the pellet was improved when the reduction temperature was increased. The morphology of composite pellets containing CaO reduced at 1450°C for 20 min are shown in Fig. 6. As evident in the figure, the separation behaviors of the pellets containing 3wt% CaO and 5wt% CaO improved compared to the behaviors of the pellets reduced at 1400°C. On the contrary, the pellet with 1wt% CaO exhibited worse separation behavior and the reduced iron formed some smaller iron nuggets rather than an integral larger nugget. The 5wt% CaO pellet still did not separate well because the slag melted

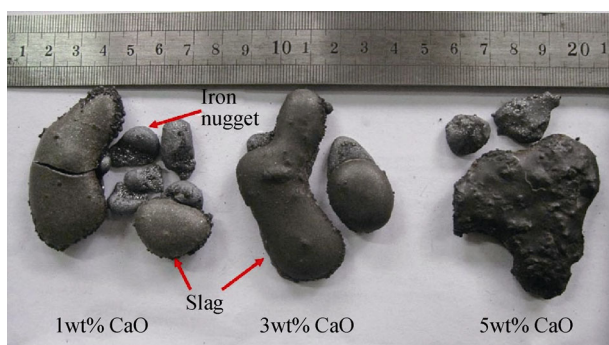


Fig. 6. Morphology of the reduced pellets (1450°C, 20 min).

extensively. The chemical compositions of the slags separated from the pellets with 1wt%, 3wt%, and 5wt% CaO are given in Table 4. These results show that the FeO content in the slag was relatively low and the residue metallic iron in the slag increased remarkably with increasing CaO content in the pellets.

Table 4. Chemical compositions of separation slags (1450°C, 20 min)

Pellet	MgO	B ₂ O ₃	SiO ₂	CaO	Al ₂ O ₃	MFe	FeO
1wt% CaO	53.4	20.0	16.9	4.3	2.3	2.3	0.4
3wt% CaO	45.4	15.6	14.3	9.3	2.0	11.8	1.9
5wt% CaO	36.3	14.8	11.5	11.8	1.6	25.3	2.5

The process of forming an iron nugget from a carbon composite pellet generally includes four stages: the heating stage, the reduction stage of iron ore, the carburization of reduced iron, and the melting separation stage of carburized iron and slag. The most important stages are the carburization and iron–slag melting separation. Many previous literature reports have indicated that the slag composition affects not only its own melting, but also affects the carburization and, consequently, the melting separation of molten slag and iron–carbon alloy [9–12]. The melting points of the separation slags were measured; the results are listed in Fig. 7. As evident in the figure, the melting point of the slag first decreased as the CaO content in the pellet was increased from 0wt% to 1wt% and then increased as the CaO content was increased from 1wt% to 5wt%. The main components of the separation slag are MgO, B₂O₃, SiO₂, and CaO, which illustrates the main properties of the slag to some extent. The melting point of B₂O₃ is the lowest among the components of the present slag system and is approximately 450°C. Although the addition of CaO changed the composition of the slag, the mass ratio of MgO, B₂O₃, and SiO₂ remained the same. The variation of the melting properties of the separation slag is illustrated qualitatively to some extent in the

MgO–CaO–SiO₂ phase diagram [8]. The liquidus temperature of the MgO–CaO–SiO₂ slag gradually increased with increasing CaO content, and the melting point at which the slag separated from the pellet gradually increased correspondingly. Therefore, the melting separation of the 1wt%, 3wt%, and 5wt% CaO pellets became increasingly difficult.

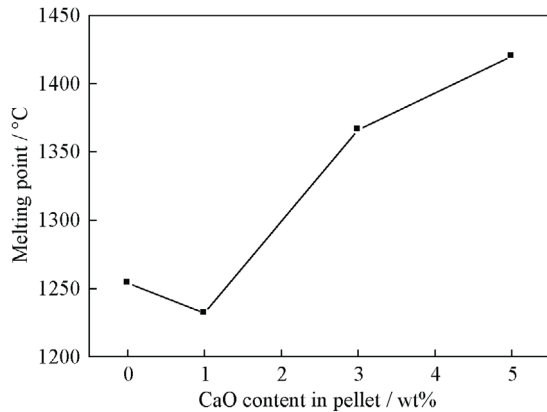


Fig. 7. Effect of CaO addition on the melting point of the separation slag.

The properties of the separation iron nuggets are shown in Fig. 8. The sulfur content of the iron nugget gradually decreased from 0.16wt% to 0.046wt%. The iron nugget that separated from the pellet containing 5wt% CaO or slightly less than 5wt% would be a good raw material for steel making. A high CaO content in the slag resulted in a melting difficulty and a high viscosity of the slag at the experimental temperature. Thus, the metallic iron could not aggregate sufficiently, and some iron particles remained in the slag. The morphology of the residual metallic iron particles in the separation slag (3wt% CaO) is shown in Fig. 9. In the end, the yield of iron in iron nugget form decreased with increasing CaO content.

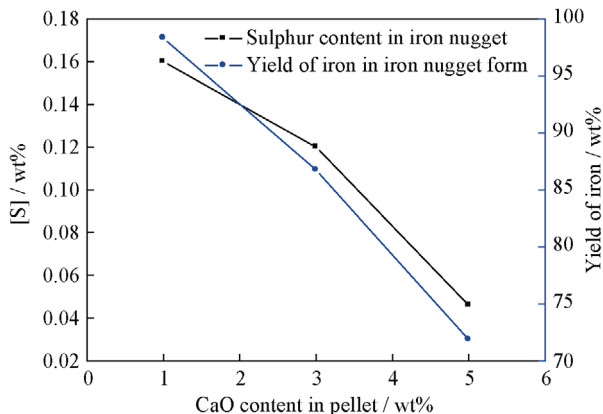


Fig. 8. Properties of the separation iron nuggets (1450°C, 20 min).

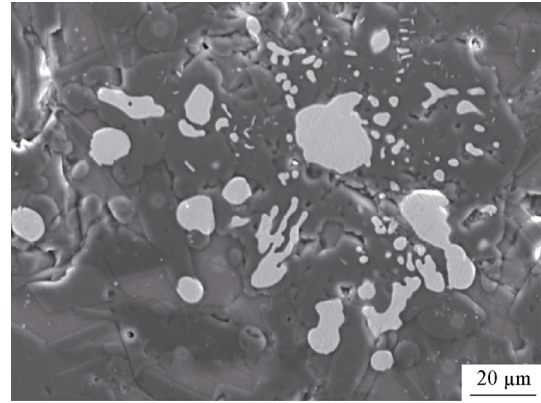


Fig. 9. Morphology of the residual metallic iron particles in the separation slag (3wt% CaO).

3.3. Properties of the separation boron-rich slag

The pellets containing 1wt%, 3wt%, and 5wt% CaO were reduced at 1450°C for 20 min; the furnace was then shut down to allow the slag to slowly cool in the furnace. The XRD patterns of the slow-cooled boron-rich slag are shown in Fig. 10. The main crystalline phases in the slag separated from the 1wt% CaO pellet were suanite (Mg₂B₂O₅), kotoite (Mg₃B₂O₆), olivine (Mg₂SiO₄), and metallic iron (α-Fe). The amounts of suanite and kotoite were approximately the same. The main crystalline phases in the slag separated from the 3wt% CaO pellet were kotoite (Mg₃B₂O₆), olivine (Mg₂SiO₄), metallic iron (α-Fe), and periclase (MgO). The only boron-containing crystalline phase was kotoite; the suanite phase disappeared. The new phase, periclase, formed in small quantities. The main crystalline phases in the slag separated from the 5wt% CaO pellet were kotoite (Mg₃B₂O₆), olivine (Mg₂SiO₄), metallic iron (α-Fe), periclase (MgO), and calcium borate (Ca₃B₂O₆). The amounts of periclase and metallic iron increased, and a new phase,

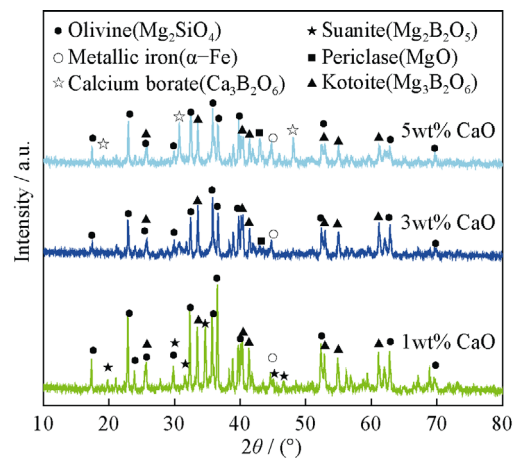


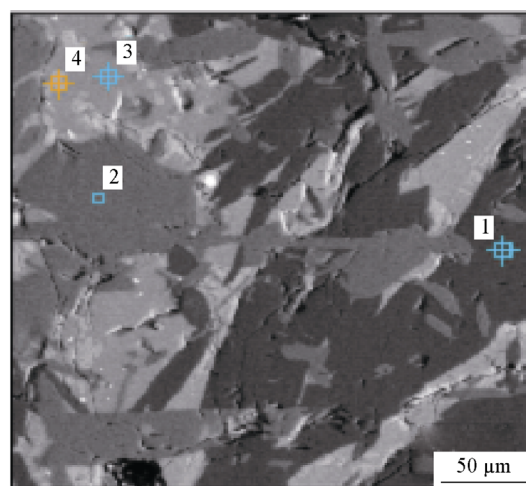
Fig. 10. XRD patterns of slow-cooled boron-rich slag (1450°C, 20 min).

calcium borate, formed. The total amount of boron-containing crystalline phase increased compared to that in the slag separated from the 3wt% CaO pellet. In general, the slag separated from the 3wt% CaO pellet contained the least amount of boron-containing crystalline phase according to the experimental results. However, the precipitation of the periclase increased the viscosity of the separation slag.

The SEM–EDS analysis of the slow-cooled boron-rich slag separated from the pellet containing 3wt% CaO is shown in Fig. 11. The SEM image reveals that the slag was composed of three main phases: a dark-gray, a gray, and a light-gray phase. The three phases clearly separated from each other. According to the EDS analysis results, the dark-gray phase was the mineral kotoite, the gray phase was the mineral olivine, and the light-gray phase was a complex CaO-rich phase. The CaO-rich phase also contained the islet of free lime, which indicates that the amount of CaO added was excessive. The EDS maps of Mg, Si, and Ca are shown in Fig. 12. The compositions and relations of the mineral phases in the slag are clearly recognized through the EDS mapping images.

The EEB of the slow-cooled boron-rich slag that separated from the composite pellet is shown in Fig. 13. The EEB closely depends on the species of boron-containing crystalline phases and their amount. The EEB of suanite was the highest in the present slag system. According to our previous work, the main boron-containing crystalline phase in the slow-cooling slag separated from the pellet without additive is suanite and the EEB of the slag is as high as 86.46% [3]. All of the EEB values in the present study were lower than 86.46%. The EEB first decreased when the CaO

content in the pellet was increased from 1wt% to 3wt% because of the suanite transforming into kotoite. The EEB then increased when the CaO content was increased to 5wt% because of the increase in the total amount of boron-containing crystalline phases. The change in content of residual B₂O₃ in the leached slag exhibited the opposite trend to the change in the EEB.



Position	Element content/at%								Phase
	O	Mg	Al	Si	Ca	Ti	Mn	Fe	
1(dark gray)	59.86	38.96	—	0.83	0.13	—	—	0.22	Kotoite
2(gray)	53.56	29.60	—	16.66	0.17	—	—	—	Olivine
3(light gray)	61.57	10.52	4.23	5.64	16.12	0.08	0.65	1.17	CaO-rich phase
4	59.92	0.43	—	0.20	39.44	—	—	—	Lime

Fig. 11. SEM–EDS analysis results for slow-cooled boron-rich slag (3wt% CaO, 1450°C, 20 min).

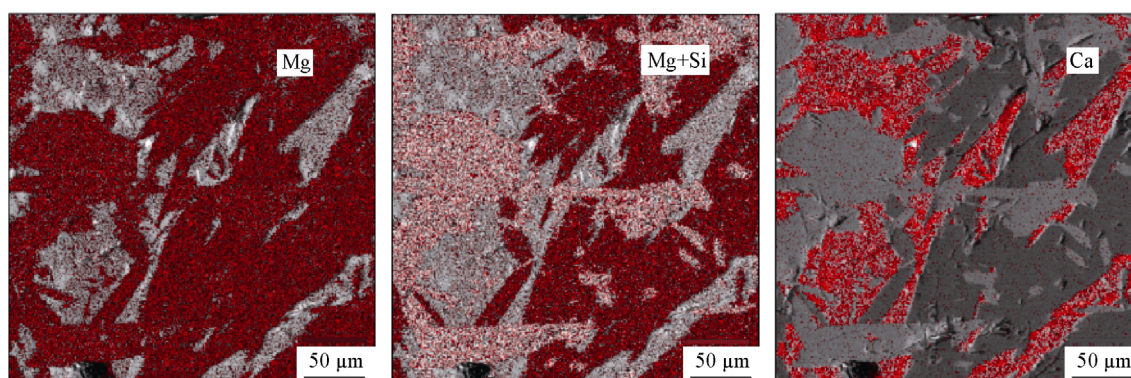
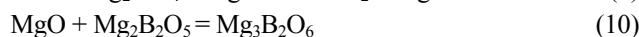


Fig. 12. EDS maps of Mg, Si, and Ca in slow-cooled boron-rich slag (3wt% CaO, 1450°C, 20 min).

According to the present results and our previous work, the addition of CaO negatively affects the EEB of boron-rich slag under the experimental conditions used in this study. The CaO improves the formation of kotoite instead of suanite when the CaO content is relatively low. The corre-

sponding reactions are listed as follows:



With the further increasing of CaO content in the slag, the boron contained in the glass phase will react with CaO

forming the calcium borate ($\text{Ca}_3\text{B}_2\text{O}_6$) during the slow cooling process.

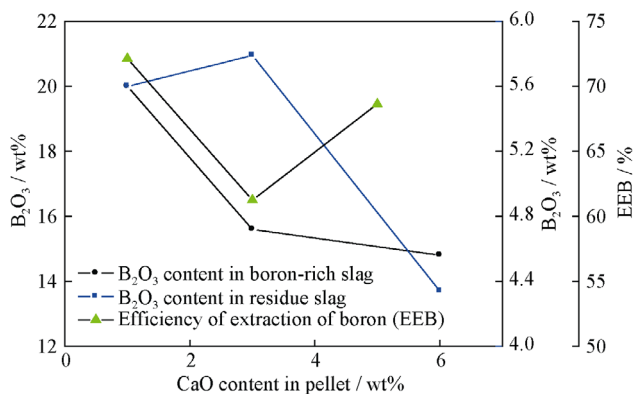
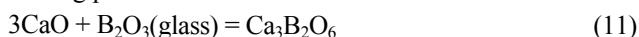


Fig. 13. Extractive properties of slow-cooled boron-rich slag.

4. Conclusions

(1) The metallization degree of boron-bearing iron concentrate/carbon composite pellets first increased when the CaO content was increased from 0wt% to 1wt% and then remained approximately the same as that of the 0wt% CaO content pellet when the content of CaO was increased to 3wt% and 5wt%. The addition of CaO may decrease the melting point of the FeO-rich slag during the reduction process, which will slow the mass transfer rate and restrain the reduction at a significant rate when its content is higher.

(2) The composite pellet underwent melt separation in a clean manner at 1400°C when the CaO content was 1wt%. However, the pellets containing 3wt% and 5wt% CaO did not undergo melt separation at 1400°C, and they partially melted when the heating temperature was 1450°C. The metallic iron could not sufficiently aggregate, and some small iron particles remained in the slag, which resulted in a gradual decrease in the iron yield. The sulfur content of the iron nugget gradually decreased from 0.16wt% to 0.046wt% when the CaO content in the pellet was increased from 1wt% to 5wt%.

(3) The addition of CaO improved the formation of kotoite instead of suanite when the CaO content was relatively low, and the boron contained in the glass phase reacted with CaO to form calcium borate ($\text{Ca}_3\text{B}_2\text{O}_6$) when the CaO content in the slag was increased further. Therefore, the EEB of the boron-rich slag decreased with as the CaO content in the pellet was increased from 1wt% to 3wt% and then increased when the CaO content was increased from 3wt% to 5wt%.

The addition of CaO negatively affected the EEB of the boron-rich slag under the experimental conditions used in this study.

Acknowledgements

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