

INFLUENCE OF GANGUE EXISTING STATES ON THE HIGH-TEMPERATURE CHARACTERISTICS OF IRON ORE IN SINTERING PROCESS¹

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Abstract

High temperature characteristics reflecting the performance of iron ores in sintering process play very important role on the sinter strength. Previous researches mainly concerned about the influence of chemical composition on the high temperature characteristics of iron ores, but rare researches covered the influence of gangue existing state on the high-temperature characteristics of iron ores. Experiments were conducted to study the influence of SiO₂ and Al₂O₃ existing states on the assimilation characteristic, fluidity of liquid phase, and bonding strength of sinter body using micro-sintering equipment. The results are as follows: (1) Iron ores with different gangue content had different LATs and IFLs, with the increase of gangue, LAT decreased, IFL increased. (2) Dense gangue could increase the gangue content of local reaction interface and then led to low assimilation temperature. Moreover, compared to the Kaolin-type-SiO₂, Quartz-type-SiO₂ was more conducive to the assimilation reaction. (3) Low-Al₂O₃-SFCA with low viscosity could be formed when the gangue existed as Quartz-type-SiO₂, but High-Al₂O₃-SFCA with high viscosity would be formed when the gangue existed as Kaolin-type-SiO₂. (4) Existing state of SiO₂ and Al₂O₃ influenced the bonding strength of sinter body further through their influence on assimilation and fluidity of iron ores, low assimilation temperature and high fluidity of liquid phase was conducive to the bonding strength.

Key words: Iron ore; Sintering; Gangue existing state; High-temperature characteristics.

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1 INTRODUCTION

Strength of sinter plays more important role on the running-condition of BF with the development of high-grade burden and large-scale of blast furnace, and the improvement of sinter quality should be based on the study of properties of sintering raw materials, especially the high temperature characteristics of iron ores. WU's research indicated that 5 kinds of high temperature characteristics of iron ores could reflect the behavior and role of iron ores in the sintering process well.⁽¹⁻³⁾ Differences of assimilation characteristics between various iron ores has been also studied,^(4,5) in addition, Kasai e Saito⁽⁶⁾ and Kasai, Wyu e Omori⁽⁷⁾ studied the influence of Al_2O_3 content, particle size of iron ores and limestone on the melt-formation phenomena. Machida and Nushiro and Ichkawa⁽⁸⁾ studied the viscosity of melts during iron ore sinter, Hsien and Whiteman⁽⁹⁾ studied the effect of raw material composition on the mineral phases in iron ore sinter. However, rare study on the influence of gangue existing states on the high temperature characteristics of iron ores in sintering process was carried out.

Therefore, in the present research, firstly, high temperature characteristics of different kinds of iron ores were carried out. Secondly, simulating tests of fluidity of liquid phase were conducted. Thirdly, reaction mechanism of different gangue in sinter process was discussed, and the further influence of fluidity of liquid phase on bonding strength of sinter body was also analyzed.

2 EXPERIMENTS

2.1 Samples

5 kinds of iron ores were used in this research, in addition, Fe_2O_3 , CaO , SiO_2 , Al_2O_3 and kaolin pure reagent were also used. Ore-A was limonite iron ores from Australia, Ore-B was mixed iron ores from Australia, Ore-C was hematite iron ores from Australia, Ore-D and Ore-E were hematite iron ores from Brazil. Table 1 shows the chemical composition of iron ores used in this study.

Table 1. Chemical composition of iron ores/mass%

	TFe	SiO_2	CaO	Al_2O_3	PPC
Ore-A	58.07	5.30	0.03	1.55	10.18
Ore-B	60.84	3.96	0.03	2.26	6.30
Ore-C	62.44	4.43	0.03	2.37	3.35
Ore-D	64.62	4.69	0.03	0.79	1.47
Ore-E	65.26	1.92	0.03	1.27	2.08

2.2 Assimilation

To clarify the influence of gangue existing state on assimilation characteristic of the iron ores, assimilation tests were carried out. Figure 1 shows the schematic

representation of the micro-sinter equipment, and Figure 2 shows the temperature system and atmosphere of the assimilation reaction test. Figure 3 shows the schematic diagram of the assimilation tests, the reaction temperature when iron ore reacted with CaO pure reagent forming a little liquid phase was defined as the Lowest Assimilation Temperature (LAT). Iron ores with different particle size were grinded to -0.15 mm by using a sealed crusher. Materials were shaped into tablets with different diameters by using two steel moulds under a pressure of 15 Mpa. The weight of CaO tablet and iron ore tablets were 2.0 g and 0.8 g respectively. Then tablets were sintered in the micro-sinter equipment.

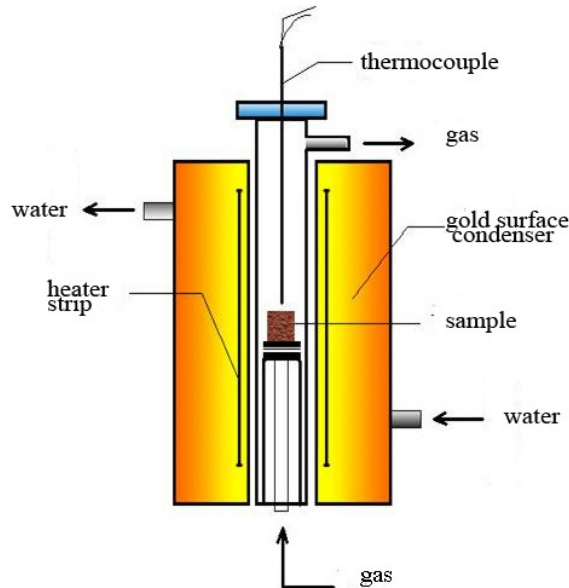


Figure 1. Schematic representation of the micro-sinter equipment

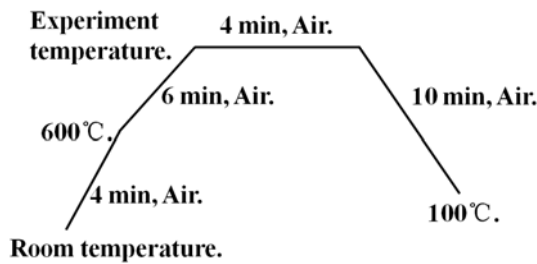


Figure 2. Temperature system and atmosphere of the assimilation test.

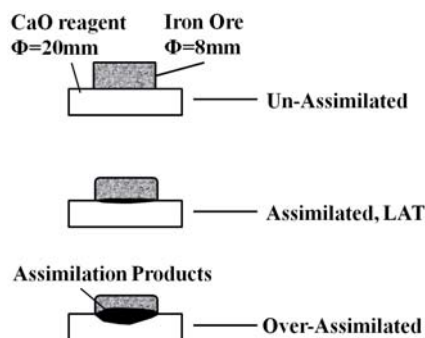


Figure 3. Schematic diagram of the assimilation tests.

2.3 Fluidity of Liquid Phase

To clarify the influence of gangue existing state on the fluidity of liquid phase in the sintering process, fluidity characteristic tests were carried out by the fluidity of liquid phase tests method. 5 kinds of iron ores and CaO pure reagent were used. Each kind of iron ore was mixed with CaO pure reagent, and the binary basicity of each mixture was 4.0. Fine mixture about 0.8 g was shaped into tablet by using steel mould under a pressure of 15 Mpa. The equipment, temperature and atmosphere of fluidity characteristic tests were almost same to the assimilation tests, except that the experiment temperature of fluidity tests was 1280 °C, and the air atmosphere was changed to N₂ after 600 °C. Figure 4 shows the schematic diagram of fluidity of liquid phase. Index of Fluidity of Liquid phase (IFL) was achieved by comparing the area of the liquid phase before and after sinter tests. As shown in Eq. (1), IFLs were calculated.

$$IFL = (FA - OA) / OA \dots \dots \dots (1)$$

In which, IFL is Index of Fluidity of Liquid phase, FA is Flowing Area after sinter test, mm², and OA is Original Area before sinter test, mm².

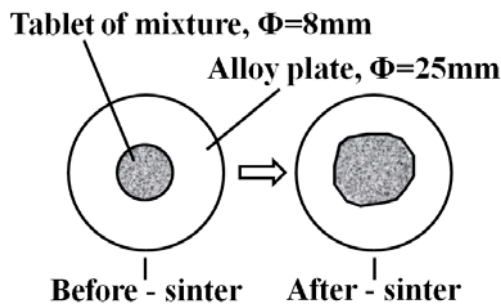


Figure 4. Schematic diagram of fluidity of liquid phase.

2.4 Bonding Strength

To clarify the influence of gangue existing state on the strength of sinter, bonding strength tests were carried out. 5 kinds of iron ores were used, and Fe₂O₃, SiO₂, Al₂O₃ and CaO pure reagent were also used. Figure 5 shows the schematic diagram of sinter body in bonding strength tests. About 200 quasi-particles made in a disc pelletizer were put into a quartz crucible. The nuclei-particles used in these tests were Ore-F from Brazil, and the adhesive powders were consisted of each kind of iron ore and pure reagent. To achieve the influence of assimilation temperature of iron ore on the bonding strength of sinter body clearly, the chemical composition of quasi-particles were maintained constant, *i.e.* Fe₂O₃ = 60.8 mass%, SiO₂ = 3.5 mass%, CaO = 7.1 mass%, Al₂O₃ = 1.6 mass%, basicity was 2.0, by adjusting the proportion of pure reagent. The equipment, temperature and atmosphere of bonding strength tests were same to the fluidity tests. After sinter, measured the weight (original weight) of the sinter body, and then free fell the sinter body from 2 m high, and screened the pieces with 5 mm perforated screen, first shatter index was achieved by calculating the ratio of the weight of pieces above 5 mm and the original weight of the sinter body. Then sequentially free fell the above 5

mm pieces from 2 m high and screened, second shatter index was achieved by calculating the ratio of the weight of pieces above 5 mm and the original weight of the sinter body. The third to ten shatter indexes were achieved similarly.

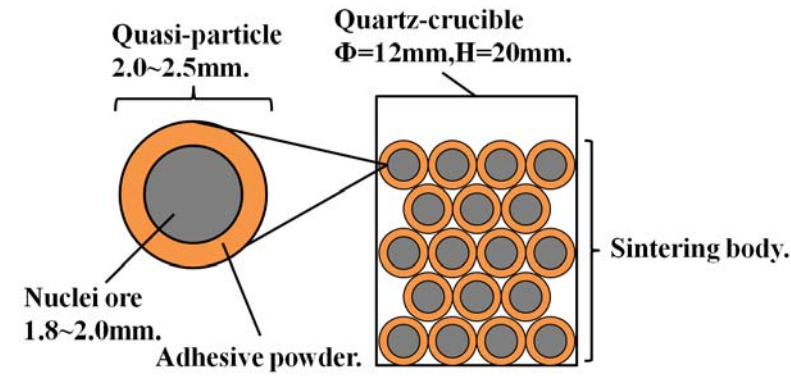


Figure 5. Schematic diagram of sinter body in bonding strength tests

3 RESULTS

3.1 Assimilation

Figure 6 shows the LAT of 5 kinds of iron ores. Australian limonite Ore-A had lowest LAT, then Australian mixed fines Ore-B and hematite iron ore Ore-C, Brazilian hematite iron ores had higher LAT, especially Ore-D.

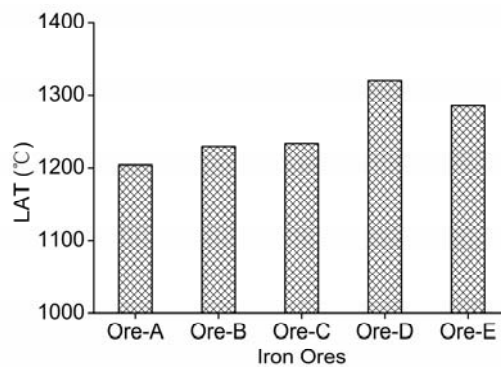


Figure 6. Assimilation temperature of iron ores.

3.2 Fluidity of Liquid Phase

Figure 7 shows the IFL of 5 kinds of iron ores. Australian limonite Ore-A had highest IFL, then Ore-C, Ore-B and Ore-D, Ore-E had lowest IFL.

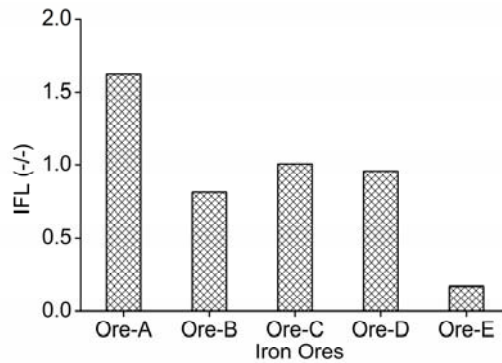


Figure 7. Fluidity of liquid phase of iron ores

3.3 Bonding Strength

Figure 8 shows the BS (5 times for falling) of 5 kinds of iron ores. Australian limonite Ore-A and Brazilian hematite Ore-D had higher BS, Ore-C, Ore-B and Ore-E had lower BS.

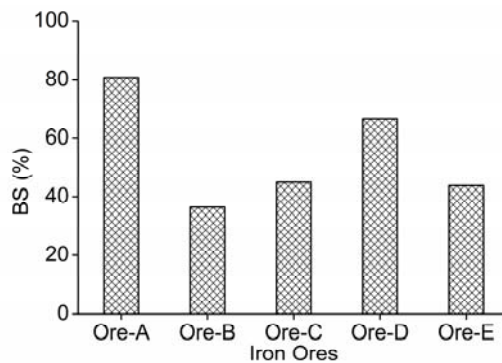


Figure 8. Bonding strength of sinter body

4 DISCUSSION

4.1 Influence of Gangue Existing State on Assimilation Temperature

Figure 9 shows the relationship between gangue content and LATs of iron ores. According to the previous research,^(10,11) it could be speculated that low-melting-point eutectic mixtures would be formed with the coexistence of iron oxide with gangue such as SiO_2 and Al_2O_3 , and with the increase of gangue (SiO_2 and Al_2O_3 in the present study) content, LAT decreased, so the LATs of Ore-A to Ore-C were lower than that of Ore-D and Ore-E. Moreover, LAT of Ore-D was higher than LAT of Ore-E even Ore-D's gangue content was higher than Ore-E, and the reason could be because the gangue distribution which was shown as Figure 10. Dispersive gangue was discovered in Ore-D, and the gangue size was nearly 20 μm , on contrast, dense gangue was discovered in Ore-E, and the gangue size was almost 100 μm . In the assimilation tests, all the iron ores were crushed to -150 μm , so all the gangue could be still combined with hematite for the Ore-D, but gangue of Ore-E might be separated with hematite, and in the assimilation reaction process, topo-high gangue content in Ore-E could lead to lower LAT.

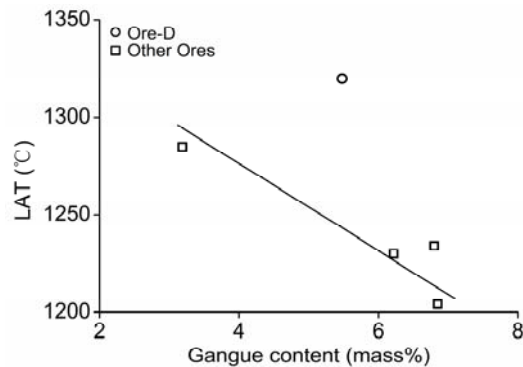


Figure 9. Relationship between gangue content and LATs of iron ores.

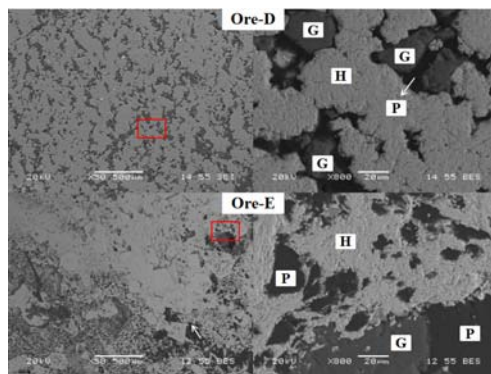


Figure 10. Gangue distribution of Ore-D and Ore-E. G: gangue, H: hematite, P: pore.

To clarify the influence of gangue existing state on assimilation temperature, XRD of iron ore and pure reagent simulating tests were also carried out. Figure 11 shows the results of XRD of iron ores. Gangue of Ore-A and Ore-D were mainly quartz and gibbsite, and gangue of Ore-B, Ore-C and Ore-E were kaolin, quartz and gibbsite. Table 2 shows the mixing condition of pure reagent simulating tests of assimilation, SiO_2 and Al_2O_3 were used in Sch 1 to Sch 3, which simulated the gangue existing state of quartz and gibbsite, and the ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$ were 2, which was same to the chemical composition of kaolin used in Sch 4 to Sch 6. Figure 12 shows the LAT of each scheme. All the LATs of samples in which gangue was existed as Quartz-type- SiO_2 were lower than that the gangue existing state as Kaolin-type- SiO_2 , so for the high gangue (total content of SiO_2 and Al_2O_3 was higher than 6 mass%) iron ores, such as Ore-A with gangue of quartz and gibbsite had lowest LAT.

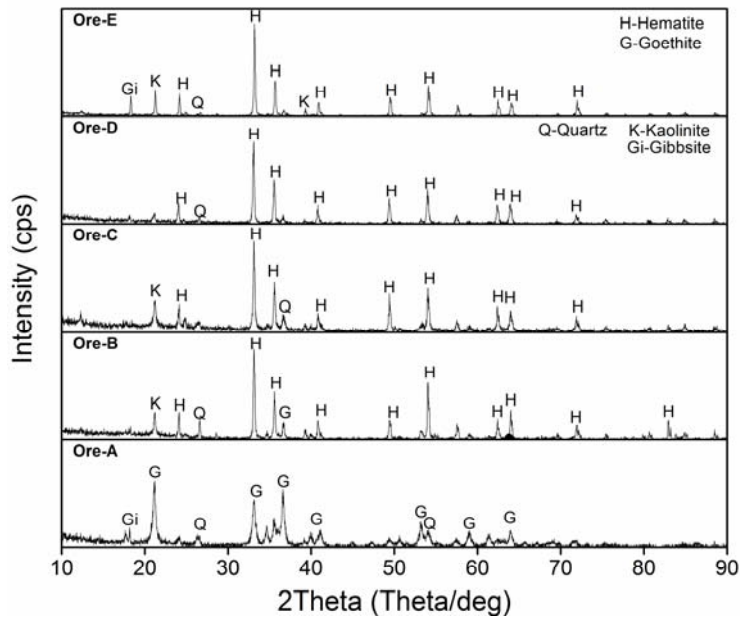


Figure 11. Results of XRD of iron ores.

Table 2. Mixing condition of simulating tests of assimilation/mass%

Schemes	Fe ₂ O ₃	2SiO ₂ - Al ₂ O ₃	Kaolin	Total
Sch 1	98	2	0	100
Sch 2	96	4	0	100
Sch 3	94	6	0	100
Sch 4	98	0	2	100
Sch 5	96	0	4	100
Sch 6	94	0	6	100

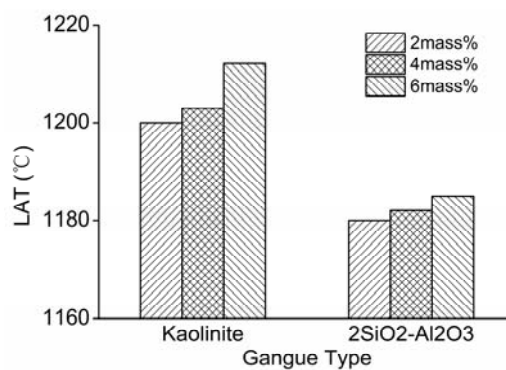


Figure 12. Results of pure reagent simulating tests.

4.2 Influence of Gangue Existing State on Fluidity of Liquid Phase

Figure 13 shows the relationship between gangue content and IFLs of iron ores. More low-melting-point eutectic mixtures would be formed with the increase of gangue,

so the fluidity of liquid phase increased with the increase of gangue. In addition, pure reagent simulation tests were also carried out for the fluidity of liquid phase. Table 3 shows the mixing condition of pure reagent simulating tests of fluidity of liquid phase. SiO_2 and Al_2O_3 were used to simulate quartz and gibbsite, the chemical composition was constant, *i.e.* $\text{Fe}_2\text{O}_3 = 75.1$ mass%, $\text{SiO}_2 = 4.5$ mass%, $\text{CaO} = 18.0$ mass%, $\text{Al}_2\text{O}_3 = 2.3$ mass%, $\text{MgO} = 0.1$ mass%, basicity was 4.0. Figure 14 shows the results of pure reagent simulating tests of fluidity of liquid phase. IFL decreased along with the gradual replacement of kaolin to SiO_2 and Al_2O_3 pure reagent, in other words, fluidity of liquid phase increased with the increase of gangue in the case of Quartz-type- SiO_2 , on contrast, decreased in the case of Kaolin-type- SiO_2 , and the reason could be that High- Al_2O_3 -SFCA might be formed when the SiO_2 and Al_2O_3 were existed as kaolin. SEM and energy spectrum analysis were carried out for the samples after pure reagent simulating tests of fluidity of liquid phase. Figure 15 and Table 4 show some results of the analysis. B was bonding phase, and P was pores in the bonding phase. It could be found that Low- Al_2O_3 -SFCA was discovered in Sch 1 using quartz and gibbsite as gangue, the highest Al content in Sch 1 was below 1.9 mass%, and a part of Al_2O_3 was formed in slag, such as potion 5. On the contrary, High- Al_2O_3 -SFCA was discovered in Sch 3 using kaolin as gangue, the lowest Al content in Sch 3 was above 2.2 mass%, and rare Al_2O_3 was discovered in the slag. So the reaction mechanism of different gangue with iron oxide and CaO could be described as Figure 16. Fe_2O_3 , SiO_2 , Al_2O_3 , CaO were defined as F, S, A, C respectively. For the case (a) using SiO_2 and Al_2O_3 pure reagent as gangue, the SiO_2 and Al_2O_3 were physical separated, in the liquid formation process, part of Al_2O_3 defined as A_1 attended the reaction with Fe_2O_3 , SiO_2 , CaO and formed SFCA, or Al_2O_3 fused into SFCA and formed Low- Al_2O_3 -SFCA, another part of Al_2O_3 defined as A_2 might attend other reaction, such as slag formation reaction. On contrast, for the case (b) using kaolin as gangue, the SiO_2 and Al_2O_3 were chemical combined, in the liquid formation process, all the Al_2O_3 attended the reaction with Fe_2O_3 , SiO_2 , CaO, excess Al_2O_3 fused into the SFCA and formed High- Al_2O_3 -SFCA. According to the research of Lu⁽¹²⁾, high Al_2O_3 in the liquid phase led to high viscosity of liquid phase, so the fluidity of liquid phase of case (b) using kaolin as gangue was lower than that of case (a) using SiO_2 and Al_2O_3 pure reagent as gangue.

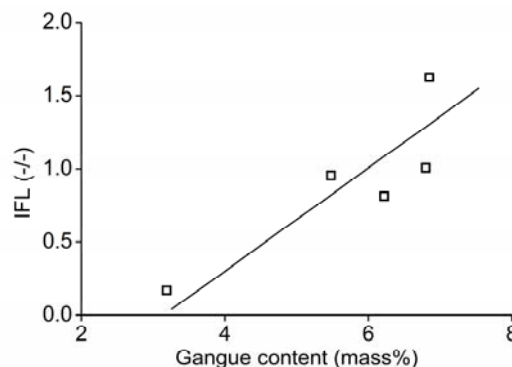


Figure 13. Relationship between gangue content and IFLs of iron ores.

Table 3. Mixing condition of simulating tests of fluidity /mass%

	Sch 1	Sch 2	Sch 3
Fe ₂ O ₃	75.10	74.74	74.38
CaO	18.00	17.92	17.84
MgO	0.10	0.10	0.10
SiO ₂	4.50	3.08	1.64
Al ₂ O ₃	2.30	1.16	0
Kaolin	0	3.00	6.04

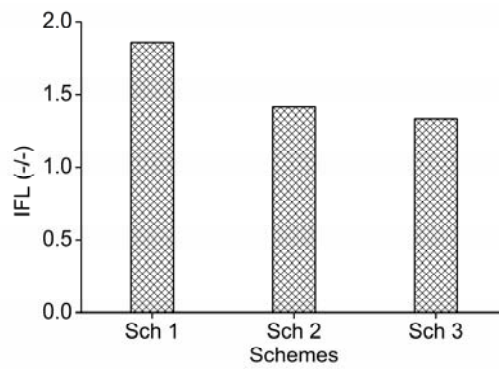


Figure 14. Results of pure reagent simulating tests.

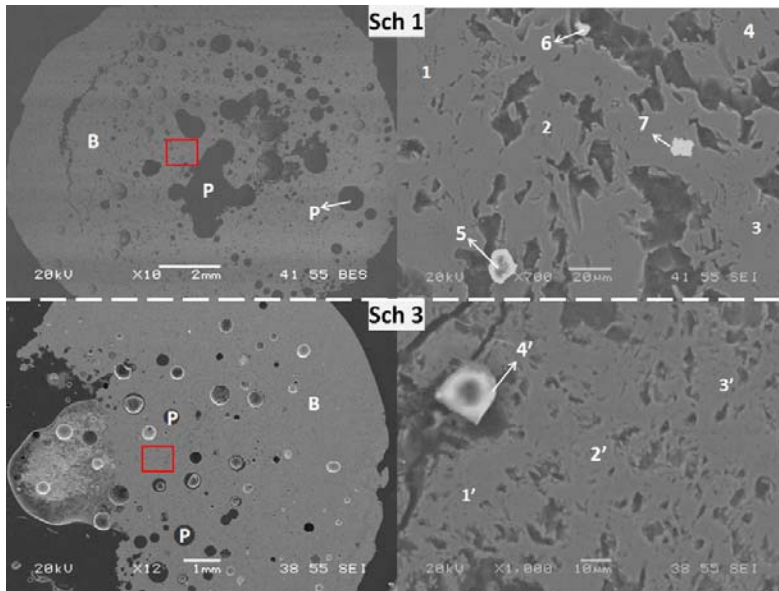
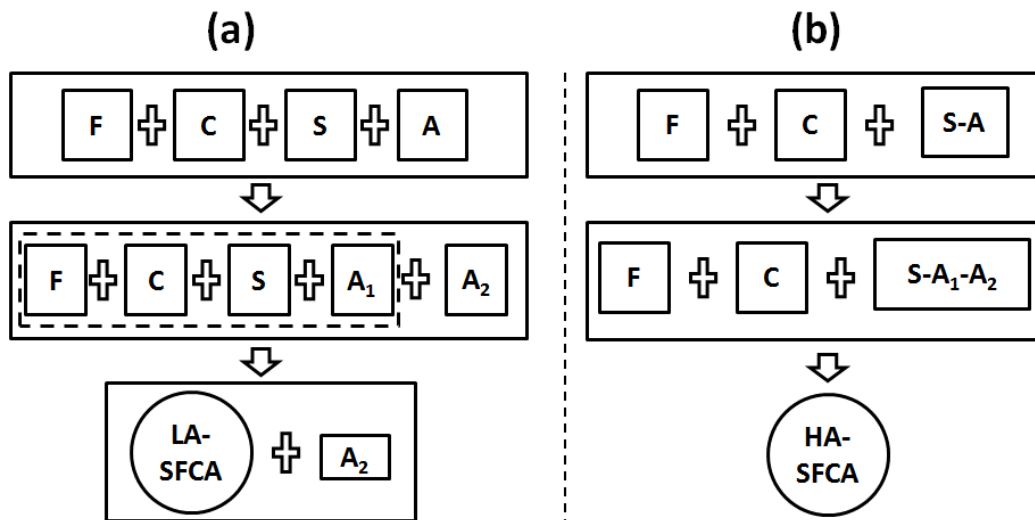


Figure 15. Identified phase of Sch 1 and Sch 3.

Table 4. Identified phase of Sch 1 and Sch 3 /mass%

Schemes	Portion	Identified phase	O	Al	Si	Ca	Fe	Total
Sch 1	1	SFCA	27.38	0.70	0.35	10.19	61.38	100
	2	SFCA	27.91	1.32	0.36	9.48	60.93	100
	3	SFCA	29.35	1.90	0.64	8.47	59.64	100
	4	SFCA	28.18	1.80	1.08	8.46	60.48	100
	5	Slag	40.55	7.84	24.06	7.02	20.53	100
	6	Slag	0	0	1.11	21.86	77.03	100
	7	Slag	59.84	0.26	4.15	30.15	5.60	100
Sch 3	1'	SFCA	25.01	2.95	1.00	11.03	60.01	100
	2'	SFCA	26.75	2.33	2.02	8.40	60.50	100
	3'	SFCA	26.34	2.22	1.42	9.86	60.16	100
	4'	Slag	53.02	0.24	5.93	17.94	22.87	100

**Figure 16.** Reaction mechanism of different gangue.

4.3 Influence of Fluidity of Liquid Phase on Bonding Strength

To clarify the further influence of fluidity of liquid phase on bonding strength of sinter body, relationship between influence of fluidity of liquid phase and bonding strength of sinter body was analyzed. Figure 17 shows the analysis results. Bonding strength of sinter body increased with the increase of fluidity of liquid phase. Liquid phase having high fluidity could bond the sinter body units together perfect, which led to high bonding strength of sinter body further.

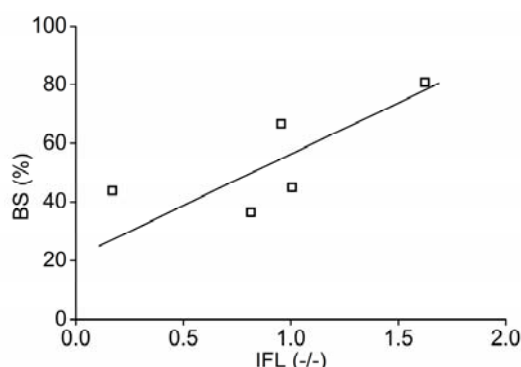


Figure 17. Fluidity of liquid phase and bonding strength.

5 CONCLUSIONS

As the fundamental study for gangue existing state of iron ore on high temperature characteristics, experiments were conducted to study the influence of SiO_2 and Al_2O_3 existing states on the assimilation characteristic, fluidity of liquid phase, and bonding strength of sinter body. Moreover, the action mechanisms of gangue on the flow and bond of bonding phase were explored. The results obtained are follows:

1) Iron ores with different gangue content had different LATs and IFLs, and with the increase of gangue content in iron ores, LAT decreased, IFL increased.

2) Dense gangue in iron ores could increase the gangue content of local reaction interface between iron ore with CaO , which led to low assimilation temperature. Moreover, compared to the Kaolin-type- SiO_2 , Quartz-type- SiO_2 was more conducive to the assimilation reaction, and decreased the LAT.

3) Low- Al_2O_3 -SFCA with low viscosity and high IFL could be formed in the formation of liquid phase when the gangue existed as Quartz-type- SiO_2 , on the contrary, High- Al_2O_3 -SFCA with high viscosity and low IFL would be formed when the gangue existed as Kaolin-type- SiO_2 .

4) Existing state of SiO_2 and Al_2O_3 influenced the bonding strength of sinter body further through their influence on assimilation and fluidity of iron ores, low assimilation temperature and high fluidity of liquid phase was conducive to the bonding strength.

Acknowledgment

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REFERENCES

- 1 WU. S. L, LIU. Y, DU. J. X. New Concept of Iron Ores Sintering Basic Characteristics. *Univ. Sci. Technol. Beijing*, v. 24, p. 254-257, 2002.
- 2 WU. S. L, DU. J. X, MA. H. B. Fluidity of Liquid Phase in Iron Ores during Sintering. *Univ. Sci. Technol. Beijing*, v. 27, p. 291-293, 2005.
- 3 YAN. L. J, WU. S. L, YOU. Y. Assimilation of Iron Ores and Ore Matching Method Based on Complementary Assimilation. *Univ. Sci. Technol. Beijing*, v. 24, p. 298-305, 2002.

- 4 YANG. L. X, DAVIS. L. Assimilation and Mineral Formation during Sinter for Blends Containing Magnetite Concentrate and Hematite/Pisolite Sintering Fines. *ISIJ Int.*, 39(1999), NO. 3, 239.
- 5 WU. S. L, DAI. Y. M, OLIVEIRA. D. Optimization of Ore Blending during Sintering Based on Complementation of High Temperature Properties. *Univ. Sci. Technol. Beijing*, V. 32, P. 719-724, 2010.
- 6 KASAI. E, SAITO. F. Differential Thermal Analysis of Assimilation and Melt-formation Phenomena in the Sintering Process of Iron Ores. *ISIJ Int.*, v. 36, p. 1109-1111, 1996.
- 7 KASAI. E, WU. S. L, OMORI. Y. Factors Governing the Strength of Agglomerated Granules after Sintering. *ISIJ Int.*, v. 31, p.17, 1991.
- 8 MACHIDA. S, NUSHIRO. K, ICHIKAWA. K. Experiment Evaluation of Chemical Composition and Viscosity of Melts during Iron Ore Sinter. *ISIJ Int.*, v. 45, p. 513-521, 2005.
- 9 HSIEN. L. H, WHITEMAN. J. A. Effect of Raw Material Composition on the Mineral Phase in Lime-fluxed Iron Ore Sinter. *ISIJ Int.*, v. 33, p. 462-473, 1993.
- 10 XUE. M. S, GUO. X. M. Effect of Al_2O_3 and SiO_2 on Formation and Crystal Structure of Calcium Ferrite Containing Al_2O_3 and SiO_2 . *Journal of the Chinese Rare Earth Society*. v. 26, p. 205-209, 2008.
- 11 NICOLA. V. Y. S, MARK. I. P, IAN. C. M. Reaction Sequences in the Formation of Silico-Ferrites of Calcium and Aluminum in Iron Ore Sinter. *MMTB*, v. 35B, p. 929-936, 2004.
- 12 LU. L, HOLMES. R. J, MANUEL. J. R. Effect of Alumina on Sintering Performance of Hematite Iron Ores. *ISIJ Int.*, v. 47, p. 349-358, 2007.