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Development of the Process for Producing Pre-reduced Agglomerates†

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Abstract:

The Japanese steel industry, accounting for more than 11% of total energy consumption in Japan, addresses the Voluntary Action Program for Environmental Protection, which targets reducing 9% CO_2 *emissions in 2010 compared with 1990. Especially, the approaches of ironmaking process, consuming the largest energy in steel works, have become important. From the above background, the production process of pre-reduced agglomerates (PRA), which are reduced simultaneously with agglomeration on existing sintering machine, was proposed. It can be expected that the use of PRA on the blast furnace reduce total* CO_2 *emissions from the ironmaking process by more than 10%. In laboratory tests, a 45% reduction was achieved by examining suitable conditions for the coke breeze size, oxygen partial pressure in the suction gas and the granulated particle structure. Appling a briquette made by compression, reduction degree of 60% in the briquette was achieved and 70% reduction was achieved when the briquette was coated with a melt-retarding material. In addition, it was found that the pressure drop of the blast furnace using PRA was lower than that of conventional sinter, and decreases with an increase in the reduction degree in the PRA.*

1. Introduction

The steel industry, which accounts for 11% of Japan's final energy consumption, has established a Voluntary Action Plan with the aims of reducing energy consumption and CO_2 emissions and is implementing efforts toward the construction of a sustainable society[1)]. Under these circumstances, the development of a process which satisfies both the need to reduce environmental loads and the requirements of mass production by adding new functions to existing equipment as a base is desired.

Many fundamental studies have been conducted on PRA that were produced by reducing a position of oxidized iron to metallic iron. Sharma[2)] and Misra et al[3)]. studied the production of a partially reduced pellet by heating a composite pellet with inner coke in air. Iguchi et al[4)]. reported a carbon reduction process by heating a single pellet in oxygen containing a gas atmosphere, by utilizing the combustion heat generated by a composite pellet, with inner coke for heating.

However, these studies employed pellets of different structures from those used for conventional iron reduction processes and partially reduced iron was obtained in a controlled atmosphere only in the basic study, without proceeding to the process development.

Against the background, process development was carried out to realize a drastic reduction in CO_2 emissions and energy consumption by the conventional blast furnace process, and thereby contribute to solving global environmental problems such as global warming, by developing a new sintering process based on the existing sintering process which simultaneously achieves agglomeration and partial reduction and establishing a technology for using the pre-reduced agglomerates (PRA) produced by this process in the blast furnace.

2. Outline and Effect of PRA Production Process

Conventionally, reduction of sinter ore is mainly per-

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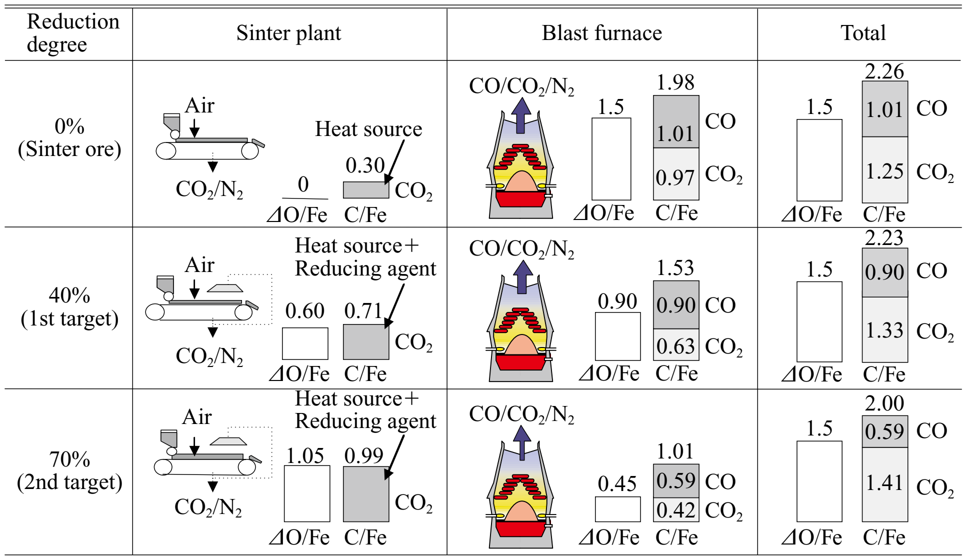


⊿O/Fe: Reduced oxygen (Mol-O/mol-Fe)
C/Fe: Carbon consumption (emission)(mol-O/mol-Fe)
Bonding agent ratio: 46 kg/t-sinter

Fig. 2 Influence of reduction degree of PRA on CO_2 emission in sinter plant and blast furnace

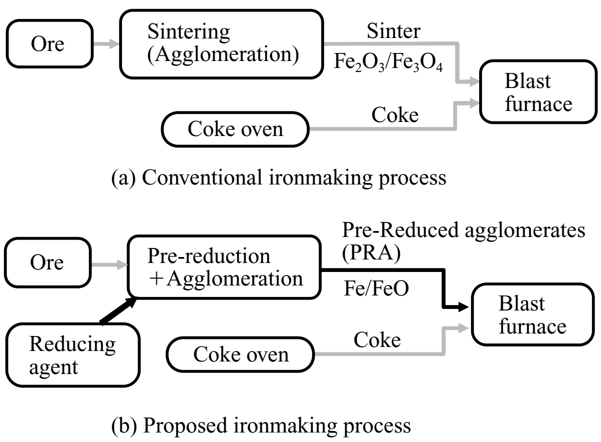


Fig. 1 Flow diagram in conventional process and new process

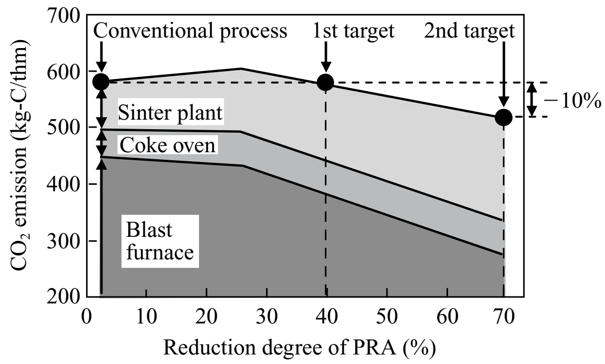


Fig. 3 Relationship between estimated CO_2 emission and reduction degree of PRA

formed by indirect reduction in the blast furnace. Thus, reduction behavior in the blast furnace is controlled by reduction equilibrium. However, with the newly developed process, in addition of agglomeration of fine ore, direct reduction by a reducing agent is performed simultaneously in the sintering machine. This enables reduction free from equilibrium restrictions of CO/CO_2 gas reaction.

Figure 1(a) shows the process flow diagram of a conventional ironmaking process and Fig. 1(b) shows that of the new process. In the conventional process, sinter is produced by the agglomeration of charging material, such as iron ore, by utilizing coke breeze as a heat source. On the other hand, the new process simultaneously performs the agglomeration and reduction of the reducing agent, in addition to the conventional sintering ore, and produces PRA that contains partially metallic iron and FeO. Both the sinter and PRA are used to produce pig iron in the blast furnace.

Figure 2 shows a comparison of the reduction degree and the carbon consumption of sinter and PRA in a sinter plant and a blast furnace[5]. It indicates that the carbon (C/Fe) required in a sinter plant increases from 0.30 to 0.71 and to 0.99 according to the increase in the reduction degree of PRA from 0% to 40% and to 70% respectively; however, it decreases from 1.98 to 1.53 and to 1.01 in a blast furnace. Therefore it is estimated that the combined carbon consumption of a sinter plant and a blast furnace can be reduced. In addition, it was found that total CO emissions decreased with the partial reduction of PRA in a sinter plant and contributed significantly to an improvement in carbon utilization efficiency.

Figure 3 shows the relationship between the reduction degree of PRA and estimated CO_2 emissions in the ironmaking process[5]. This figure indicates that when the reduction degree of PRA increases, the reduction ratio in a blast furnace decreases and carbonization energy in a coke oven decreases; however, CO_2 emissions in a sinter plant increase with the increase in coke used for the reduction of PRA. Therefore, it is estimated that total CO_2 emissions in the ironmaking process gradually increase when the reduction degree of PRA reaches 30%, and then starts decreasing and reaches the same level as the conventional process when the reduction degree of PRA reaches 40%, and decreases further to 70%, which is 10% lower than that of the conventional process. Based on this estimation, the goal for the reduction degree of PRA was first set at 40% and then at 70% in this study.

3. Basic Study of the PRA Production Process

3.1 Sintering Test Conditions

A pot test was conducted to evaluate the basic PRA production process. An iron ore, with a high grade pellet feed of less than 125 μm in diameter was used as charging material. Burnt lime of less than 1 mm in diameter was used as the auxiliary charging material. Coke breeze with a particle size of less than 1 mm was used, and the particle size was adjusted as necessary. The mixture of charging material was composed of 92% of iron ore and 8% of burnt lime, and 12% of coke breeze was used as a reducing agent by granulating it into granulated particles, with 3% coke breeze was used as bonding agent by coating the granulated particles. Granulation was performed using a disc pelletizer. The granulated particle diameter was set at 8 to 11 mm. The granulated particles were packed into a test pot with a 300 mm inner diameter and a bed height of 300 mm, and then ignited and sintered. In the final period of sintering, nitrogen gas at room temperature was introduced into the packed bed to prevent re-oxidization of the PRA.

As basic conditions for a pot test, coke breeze of less than 1 mm in diameter and suction gas with a partial oxygen pressure of 21% were used. Pre-reduction was achieved with granulated particles of a uniformly mixed structure of iron ore, burnt lime and coke breeze.

3.2 Test Results

3.2.1 Effects of fine coke size

One effective means of promoting the reduction of iron ore by coke breeze is use of an increased contact area between the two materials. Therefore, use of finer coke breeze was studied. **Figure 4** shows the relationship between the sinter reduction degree and production ratio when the size of the inner coke was 1 mm, 125 μm, 44 μm, and 10 μm or less, respectively. In all cases, these are results when the inner coke ratio was 12% (theoretical amount of coke for reducing) and the coating coke of −1 mm ratio was 3%. The sinter reduction

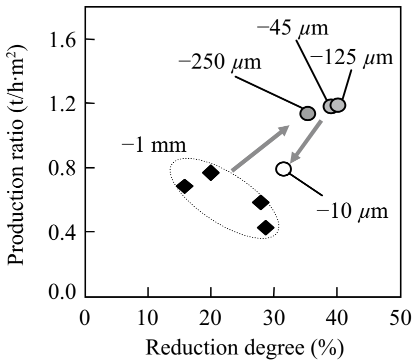


Fig. 4 Influence of coke breeze size on productivity and reduction degree[6)]

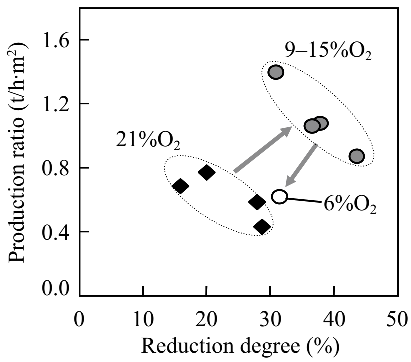


Fig. 5 Influence of O_2 content in suction gas on productivity and reduction degree[6)]

degree was maximum between −45 μm and −125 μm, and the production ratio also showed its maximum value in the same size range. If the particle size is reduced further, both the reduction degree and the production ratio decrease. This is considered to be because finer coke burns rapidly, and simultaneously with this, the granulated particles are melted excessively, resulting in a lower reduction degree.

3.2.2 The effects of controlling oxygen partial pressure[7)]

To determine the optimum oxygen partial pressure for reduction of PRA, the effects of reducing the partial pressure of oxygen were studied. As a result, as shown in **Fig. 5**, coke combustion was constrained when the oxygen partial pressure was between 9 and 15%, and high productivity and a high reduction degree could be obtained. Iron ore melted excessively when the partial pressure of oxygen was 21%, and conversely when it was 6%, coke combustion could not be sustained and un-reacted carbon remained after sintering.

3.2.3 Problem in the reduction process and investigation of the structure of a granulated particle[8)]

To improve the reduction degree, we analyzed the reducing behavior in the height of sinter cake when sin-

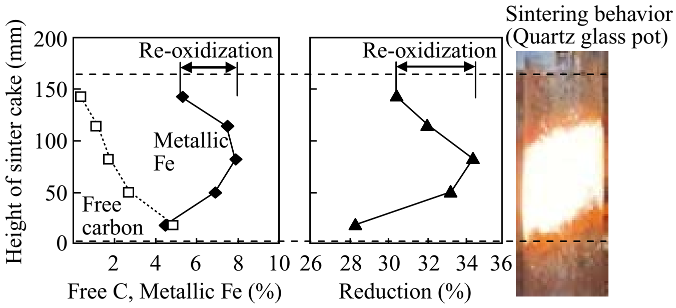


Fig. 6 Reducing behavior of PRA in sintering

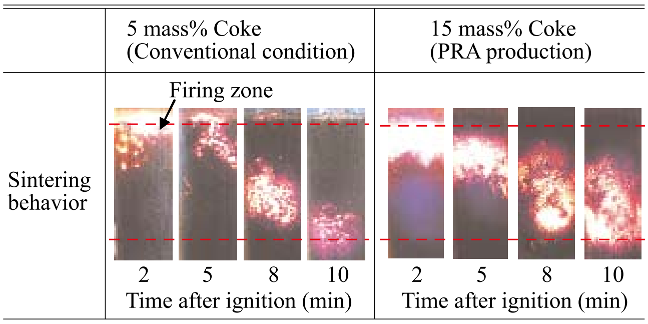


Fig. 7 Influence of coke breeze mixing ratio

tering was interrupted while in progress. The results are shown in **Fig. 6**. The highest metallic Fe content ratio and reduction degree occur near the middle position in the firing zone. Then, maximum reduction degree was 34%. It was understood that the reduction reaction proceeded in the lower position and it was confirmed that re-oxidation occurred in the upper position, resulting in a lower metallic Fe and reduction degree.

Next, the movement of the combustion zone from upper to lower during the sintering process was observed using a silica glass tube in the pot test. **Figure 7** shows the time-dependent change and progress of the movement of the combustion zone during the sintering. When the ratio of inner coke breeze was high, enlargement of the width of the combustion zone was observed, compared to the conventional condition, whereas movement and cooling of the combustion zone were delayed. In addition, an excessive melting was occurred due to the longer detention time at a higher temperature.

In order to establish countermeasures against these two problems, the structure of a granulated particle was studied. **Figure 8** shows the three granulated particle

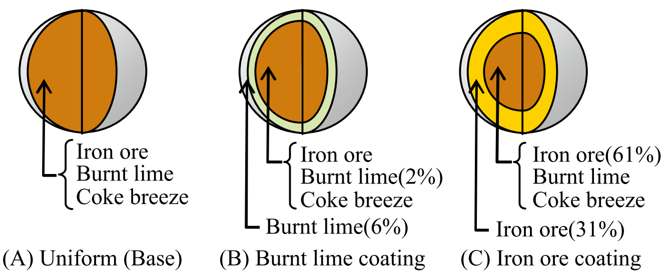


Fig. 8 Quasi-particle structure

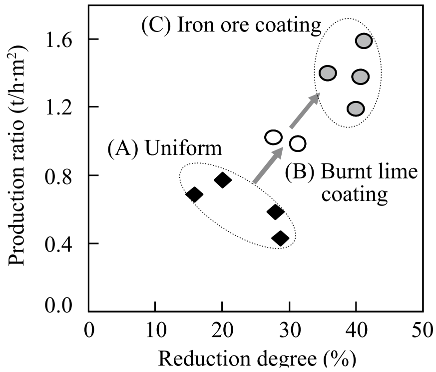
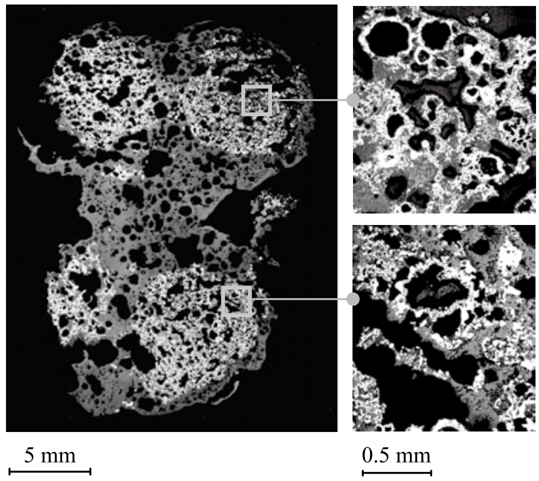


Fig. 9 Influence of quasi-particle structure on productivity and reduction degree[6]



Quasi-particle structure: Iron ore coating

Photo 1 Cross section of PRA

structures that were investigated. These are a uniform type (A), a burnt lime coated type (B) which is coated on the outside with partially burnt lime, and an iron ore coated type (C) which is coated on the outside with partial iron ore. For types (B) and (C), different granulated particle structures were designed, with the aim of restraining melting and preventing the outflow of the melt from the granulated particle. **Figure 9** shows the experimental results for these structures. In case of using type (B) with a burnt lime coating, both a higher reduction degree and productivity were achieved. By using type (C) with an iron ore coating, a much higher reduction degree and productivity was achieved. In particular, a 45% reduction was achieved, which exceeds the first target of the study.

Photo 1 shows cross sectional photographs of PRA that were sintered with granulated particles of the iron ore coated type (C). It was observed in the photographs that the shape of granulated particles is maintained, and white metallic iron remains inside. Based on this observation, an optimum granulated particle structure was developed. Furthermore, the prevention of the particle collapsing and the re-oxidation of Fe content were successfully achieved, as initially intended.

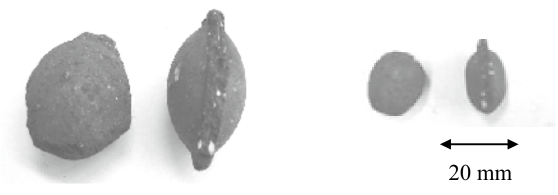
4. Effects of Adding Compressed Particles and Coated Particles

4.1 Study of Reduction Conditions of Compressed Particles Using Electric Furnace

According to the result obtained in the previous section, upper limit of reduction degree is 40% in the production of PRA by the sintering of granulated particles. Therefore, means to prevent the burning of coke breeze added in the granulated particles and over melting of materials is necessary to improve the reduction degree. It is expected that the reason of oxygen entering into the granulated particle is generation of crack in the particle by the pressure increase the inside of the particle by CO and CO_2 gas generated by the reducing reaction. Therefore, it was considered that the increase of the particle strength by the tight contact of iron ore with coke breeze would be effective measures. **Photo 2** shows briquettes made by compressing the mixed raw materials. The briquettes had an almond shape and were formed into two different volumes: 6 m*l* and 1.2 m*l*.

The briquettes were charged into the sintering bed along with the conventional granulated particles for sinter, because the heat is required in sintering. The optimum heating conditions were studied by using an electric furnace before conducting a sintering pot test.

Figure 10 shows the heating conditions of the briquette in an electric furnace. Particles of 3 mm in diameter for the conventional sintering were packed in a crucible of 34 mm diameter and 45 mm height, and then a sample briquette was placed in the center. In this heating



(a) 6 m*l* briquette (size: 35 × 23 × 16 mm)
(b) 1.2 m*l* briquette (size: 19 × 14 × 8 mm)

Photo 2 Appearance of used briquette

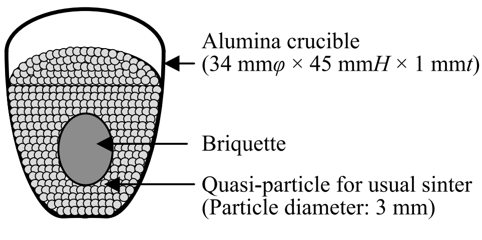
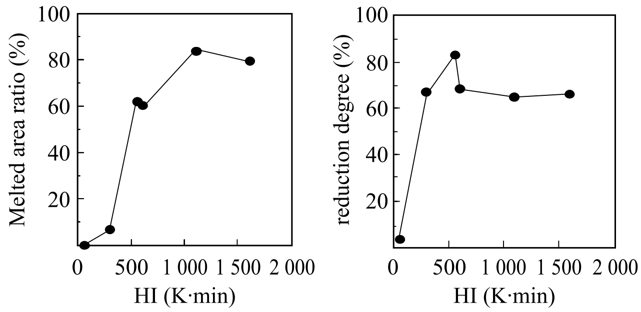


Fig. 10 Heating condition of briquette in electric furnace test



(a) Relation between HI and malted area ratio
(b) Relation between HI and malted area ratio

Fig. 11 Influence of HI on melted area ratio and reduction degree of briquette

experiment, a new heating index HI (K·min) expressed in Eq. (1) was defined as the integration of temperature difference between the heating temperature and 1 468 K over heating time. Here, 1 468 K indicates the melting point of calcium ferrite.

$$\mathrm{HI} = \int_0^t (T - 1\,468)\mathrm{d}t \quad \cdots\cdots (1)$$

where, T: Heating temperature (K)
t: Heating time (min)

In the conventional sintering process, HI is 300 K·min. when the sintering temperature is 1 300°C and heating time is 3 min.

The results of the electric furnace test are shown in **Fig. 11.** Figure 11 (a) shows the change in melted area ratio of the briquette on HI after heating. The melted area ratio reached 60% of 500 K·min. at HI. It is estimated that the briquette is unable to keep its original shape at this temperature, therefore an optimum HI would be less than 500 K·min. Figure 11 (b) shows the change in the reduction degree of the briquette on HI. The reduction degree reached its maximum value of 82% at around HI of 500 K·min, however, even at 300 K·min it was 67%. It was confirmed that a high reduction degree could be achieved, even under conventional sintering conditions.

4.2 Laboratory Sintering Test by Adding Compressed Particles

Figure 12 shows the concept of charging condition of briquettes in sintering bed in the sintering pot test. The sintering test was conducted by packing the briquettes in the middle and bottom layers, where the holding time at a high temperature is longer.

Figure 13 shows the comparison of chemical analysis of the granulated particle discussed in previous section and the briquette after the sintering by the relation between reduction degree and metallic iron content.

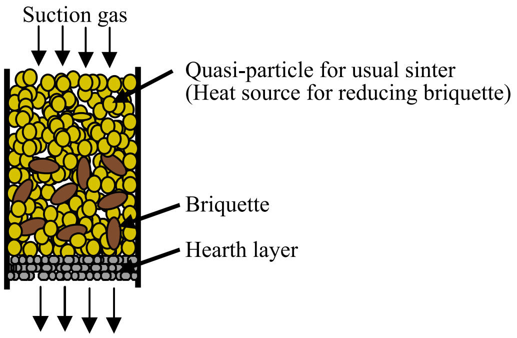


Fig. 12 Charging condition of briquette and quasi-particle in pot test

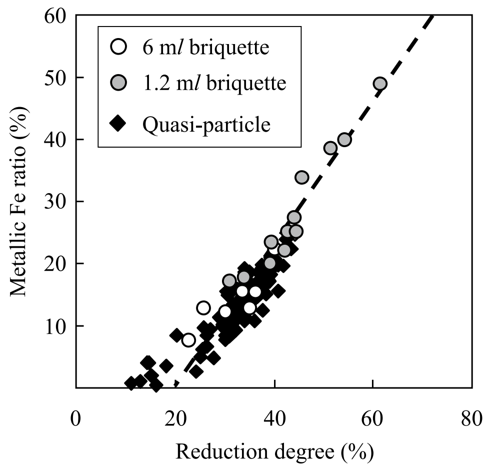


Fig. 13 Relation between reduction degree and metallic Fe in PRA

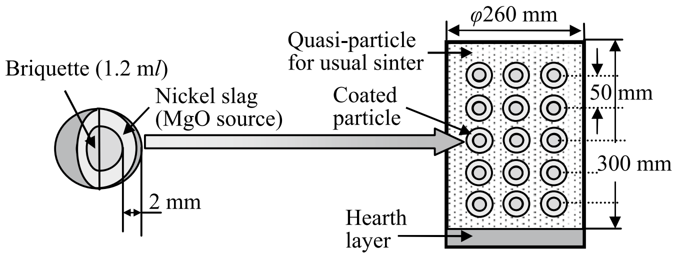


Fig. 14 Charging condition of coated particle and quasi-particle in pot test

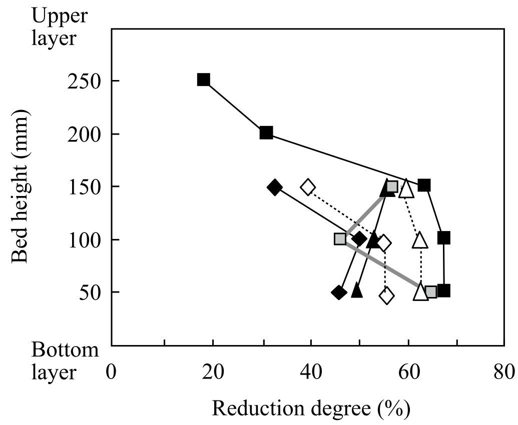


Fig. 15 Reduction degree of coated particle[6)]

These values of briquettes lie on the extrapolation line of correlation between metallic iron content and reduction degree for granulated particle. It is obvious that reduction degree and metallic iron content are remarkably improved.

However, when samples of the briquettes were removed from the sintered cake, several of them had melted. This is because the sintering temperature differed depending on the charged locations, and the briquettes melted when placed in a high temperature region.

4.3 Laboratory Sintering Test by Adding Coated Particles

As a countermeasure against the melting of the briquettes described in Section 4.2, a new method of applying a charging material coating to the briquette surface was used, which retarded melting.

Figure 14 shows the experimental conditions when using a coated particle. The 1.2 m*l* briquettes were coated with 2 mm of nickel slag as a MgO source which is a high melting temperature, and charged on the sintering bed to form five layers, each 50 mm apart in height. At each height level, four briquettes were arranged around a central briquette, each being 50 mm apart.

Figure 15 shows the experimental results. Although the reduction degree was less than 40% in the upper layers of the sintering bed, it reached a maximum of 68% in the lower layers. However, variations in the results caused a reduction degree of less than 50%, even in the lower layers.

It was needed to improve the firing technology to achieve a uniformly high reduction degree of the coated particles in the future.

5. Evaluation of Reducing Behavior of PRA in the Blast Furnace

A softening under load test was performed to investigate the behavior of PRA in the blast furnace. Sinters were packed into a graphite crucible or alumina crucible (70 mmφ × 150 mm) as the test apparatus, and changes in temperature and gas formation accompanying descent through the blast furnace were simulated by program control. Considering the wall effect, the particle size of the specimens was set at 6.5 mm, which is approximately 1/2 that of actual sinter.

Figure 16 shows the results of the softening under load test. The lower part of figure 18 shows the pressure drop relative to furnace temperature, while the upper part of figure 16 shows bed shrinkage of sample layer. PRA of high reduction degree obtain in the pot test was used as sample. It can be understood that starting temperature of shrinkage was approximately 100°C faster with the conventional sinter in comparison with the

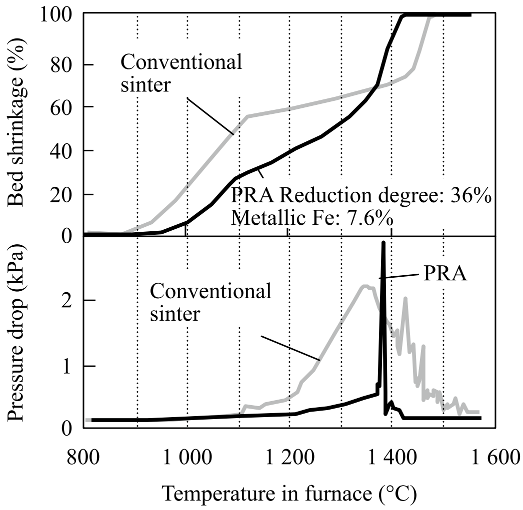


Fig. 16 Comparison of sinter and PRA in shrink behavior[6)]

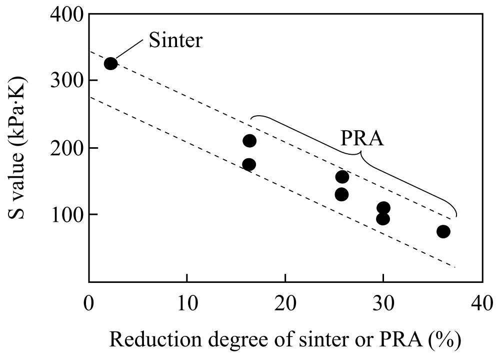


Fig. 17 Relationship between reduction degree and S value[6)]

PRA, and at the same time, the porosity of the specimen bed was reduced by shrinkage, resulting in an increase in pressure drop.

With the conventional sinter, shrinkage occurred gradually after reaching 1 150°C, and as a result, pressure drop was also high. Rapid shrinkage occurred when the temperature exceeded 1 400°C, and pressure drop decreased after meltdown. In contrast, with the PRA, shrinkage was relatively slight up to 1 400°C, and pressure drop was also small, but because shrinkage and meltdown occurred rapidly at the comparatively low temperature of 1 400°C, PRA has excellent high temperature properties. Therefore, when PRA is used in a blast furnace, it can be expected that the thickness of the blast furnace cohesive zone will be thinner and pressure drop will be reduced, making a substantial contribution to improved blast furnace productivity.

The area of the portion of graph bounded by the pressure drop curve and abscissa in the lower part of figure 18 corresponds to resistance to gas permeability until completion of meltdown, and is attributable to softening and melting of the sinter. An attempt has been made to evaluate sinter ores by defining this area as the *S* value[9)]. The relationship between the reduction degree and *S* value is shown in **Fig. 17**. A reduction in pressure drop with PRA in comparison with an actual sintering machine product was confirmed, as described previously. However, this study revealed that the S value, that is, resistance to gas permeability in the blast furnace, decreases as the reduction degree increases.

6. Conclusions

Production technologies of PRA and PRA behavior in the blast furnace were investigated with the following results:

(1) At the basic studies, appropriate conditions for producing PRA such as the particle size of coke breeze as reducing agent, the oxygen concentration and the structure of granulated particles during sintering were examined. Then to produce PRA with granulated particles by tumbling granulation, the maximum reduction degree of 45% was achieved.

(2) Adding briquette of compressed charging material to sintering bed, 60% reduction in the briquette was achieved and 70% reduction was achieved when the briquette was coated with melt retarding material. The development of firing technologies is necessary to prevent excess melting of briquettes and to improve the non-uniform reduction degree. Furthermore, technologies to increase the mixing ratio of the briquette are also necessary.

(3) From the results of estimations to use PRA at blast furnace, it was confirmed that permeability in blast furnace remarkably decreased as compared with conventional sinter ore.

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