Marra Mamba Ore, Its Mineralogical Properties and Evaluation for Utilization

Jun OKAZAKI and Kenichi HIGUCHI

Environment & Process Technology Center, Nippon Steel Corporation, Futtsu, Chiba 293-8511 Japan.

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This paper provides an overview of chemical and physical properties of Marra Mamba ores as well as their influence on sintering performance. Evaluation tests focusing on basic characteristics, granulation ability and melting behavior have been conducted by using Ore W, a newly shipped bland of Marra Mamba ore. Although the amount of gangue minerals in Marra Mamba ores is smaller than that of other Australian ores, they have high combined water content and high fraction of fine particles. They have inferior granulation ability and required high moisture content in granulation due to their porous structure. Cohesive strength of fine ores is still low level even at high moisture content due to small kaolinite content. Penetration behavior of melt from fine particles is superior due to their low gangue mineral content, while assimilation behavior of coarse ores is inferior, resulting in poor agglomeration despite favorable behavior during heating-up in term of crack formation. Pot test results performed by BHP Billion showed decrease of strength and product yield with large amount of use. Improvement of strength was achieved by increasing moisture content during granulation. Intensification of granulation with pre-treatment or palletizing of Marra Mamba ores must be one of the key technologies for utilization of them.

KEY WORDS: agglomeration; iron ore sinter; Marra Mamba; mineralogy; porosity microstructure; assimilation.

1. Introduction

In Australia, mines of Marra Mamba ores which contains high combined water have been developed in order to make up for the depletion of reserves of low phosphorous Brockman ores. Firstly West Angelas, represented as Ore W in the present paper, was shipped in 2002, followed by MAC (mining area C) in 2003 as a single bland of Marra Mamba ores. At the beginning, Marra Mamba ores have started to be mixed into conventional low phosphorous Brockman ore-bland. On the other hand Pisolite ores with high combined water content are still main ore sources in Japan, resulting in the accelerated increase of combined water content in Australian import ores. These situations derive that Marra Mamba ores will be the second dominant resources in Australia following Pisolite ores, thus the fundamental understand and utilization of Marra Mamba ores are important item for sintering process in Japan.

Although the fundamental characteristics of Marra Mamba ores have been reported in several literatures, further research on the mineralogical characteristics and sintering behavior of the ores is essential for further increase of blending ratio of Marra Mamba ores with keeping use of Pisolite ores.

This paper provides the summary of property of Marra Mamba ores including the basic characteristics, granulation ability and melting behavior, based on the measurement results of several fundamental tests.

2. Fundamental Evaluation of Marra Mamba Ores

2.1. Test Materials and Analytical Method

2.1.1. Analyzed Ores

Drum-sample of Ore W was used as Marra Mamba ores in the present study. The sample 350 kg in weight was dried and sieved to obtain certain sizes of ore sample by using Ro-Tap shaker. For comparison, other different types of ores having wide variety of property were analyzed as well. Ore A of dense ore and Ore B of porous ore were chosen as typical Brazilian ores. Ore C of porous ore and Ore D, which was denser than Ore C, were chosen as Australian low phosphorous Brockman ores. Ore E with high Al₂O₃ content and Ore F with low Al₂O₃ content were chosen as Pisolite ores. Ore G of high-goethite ore was chosen as Indian ores.

2.1.2. Basic Characteristics of Ores

1) Chemical Composition

Chemical compositions of coarse ores 2.0–2.8 mm and fine ores –0.5 mm in diameter were analyzed. These two classes of size correspond to the size behaving as nuclei and as adhering fine of pseudo-particles, respectively. TFe, SiO₂, CaO and Al₂O₃ were analyzed by X-ray fluorescence. Combined water (CW) was measured by Karl Fischer method.

2) Microscopic Observation

Oxide mineral structures of ores 0.25–0.5 mm, 0.5–
1.0 mm, 1.0–2.0 mm and 2.0–2.8 mm in size were observed by an optical microscope. Ore particles were mounted in resin and polished, then 120 ore particle of classes were observed for classification by 4 types of mineralogy of iron oxide, 1. Goethite, 2. Goethite accompanied with less hematite, 3. Hematite accompanied with less goethite and 4. Hematite.

3) Pore Structure
Porosity and pore size distribution of ores 2.0–2.8 mm diameter were measured by mercury intruding porosimetry (Shimazu Autopore III).

4) Thermal Cracks
Primary melt of CaO–Fe₂O₃ system forms at a temperature near 1 200°C during sintering. Therefore the change of pore structure and crack formation of ores during heating up to 1 200°C have large influence on sintering reaction via a change in reaction area. In addition, decrepitation of ores affects physical stability of pseudo-particles, influencing permeability of sintering bed.

The structural change of ores with heating-up was observed. Figure 1(a) shows a schematic diagram of heat treatment method of ores. Ores having 2.0–2.8 mm in size were charged in a Ni vessel whose diameter and height were 20 mm and 15 mm, respectively, subsequently heated under air stream in a vertical electric furnace. Temperature of ores was increased from room temperature to 1 200°C for 4 min. After cooled, ores were mounted in resin and polished. Cracks formed within ores after heating were observed by optical microscopy.

5) Identification of Gangue Minerals
Gangue mineral type in ores was identified by TEM (Transmission Electron Microscope) with EDS (Energy Dispersive Spectrometry). Firstly ultra-fine particles were collected by catching floating materials after washing of ores whose diameter was less than 2 mm. The ultra-fine particles were identified as gangue minerals and oxide by using spot analysis of EDS. Morphology and chemical composition of 30 particles of gangue mineral particles were analyzed.

2.1.3. Granulation Ability
1) Cohesive Strength of Fine
Granulation of ores is rather complex phenomenon and difficult to describe by using fundamental parameters. Granulation ability of ores seems to depend on the surface structure of coarse ores acting as nuclei. Nevertheless, once fine particles adhere the surface of nuclei ores, further development of granulation seemed to be controlled by cohesive ability among fine particles within adhering layer in pseudo-particles. Therefore in the present study, cohesive strength of fine ores was measured to estimate one of the properties concerning granulation ability of ores.

Cohesive strength was measured by adopting the method for tensile strength measurement of fine packed bed. The packed bed of fine ores composed of equivalent mass ratio of 5 classes of size –1.0 mm, i.e., 0.063 mm, 0.063–0.125 mm, 0.125–0.25 mm, 0.25–0.5 mm and 0.5–1.0 mm. Cohesive strength was measured as a function of moisture of the packed bed ranging between 0 and 15 mass%. High cohesive value represents superior granulation ability and the moisture content at which cohesive value showed a maximum is optimum moisture content of each ore.

2) Water Absorption Capacity
Water absorption capacity of ores was measured by using ‘centrifugal moisture equivalent method’. Ores 2.0–2.8 mm and –1.0 mm in size were measured. Ores having a high value of centrifugal moisture equivalent require high moisture content during granulation to attain available water.

2.1.4. Melting Characteristics
1) Penetration of Melt from Fine
To simulate behavior of melt from fine within adhering layer in pseudo-particles, sintering tests of 2-layer tablet composed of ores and primary melt materials were carried out (Fig. 1(b)). Ore tablet was made from mixture of two classes of ore size, –0.25 mm and 0.25–0.5 mm, in equivalent mass ratio. The mixed fine was pressed into a cylinder tablet whose diameter and height was 15 mm and 5 mm, respectively. As a primary melt source, a cylinder tablet consisting of chemical reagent of CaO and Fe₂O₃ was used. Contents of CaO and Fe₂O₃ was fixed as 26 mass% and 74 mass%, respectively, near the eutectic composition of CaO–Fe₂O₃ system as Phillips et al. reported. The two chemical reagents were mixed for 20 min, subsequently pressed into tablet whose diameter and height was 5 mm. The two kinds of tablets were produced by using iron mould under a pressure of 4 Mpa.

The tablets were put in Ni vessel and heated under air stream. Sample was heated from 1 100 to 1 290°C for 1 min, subsequently cooled down to 1 100°C for 3 min, simulating the heating condition in plants. After cooled down to below 1 100°C, sample was taken out from the furnace and cooled in air, subsequently mounted in resin and polished to show a vertical section of the sample. Penetration length of melt was defined as the distance between the upper rim of
the ore tablet and a tip of reaction zone and measured by image analysis method using macro image photos in 5-times magnification. Penetration length of fine ore has strong correlation with strength of sinter and product yield in plant operation.16)

2) Assimilation Behavior

To evaluate melting characteristics of coarse ores acting as nuclei, sintering tests of small packed bed consisting of pseudo-particles, coarse ores coated by fine limestone,18) were conducted (Fig. 1(c)). The psudo-particles were made from ores 2.0–2.8 mm in diameter as nuclei and limestone less than 0.5 mm in diameter as adhering layer, at which the mass fraction of CaO/Ore was 0.1 to meet the blending condition of materials in plants. They were made by hand-granulation with adding moisture, subsequently charged in Ni vessel to form a packed bed. Sample was heated under air stream from 1 100 to 1 300°C for 1 min, subsequently cooled down to 1 100°C for 3 min. Polished samples were made to observe a horizontal cross-sectional plane of sintered sample at 5 mm above from the bottom of the vessel. Assimilation behavior and microstructure were observed by optical microscope. In addition, void fraction (ε) of samples was defined as shown in Eq. (1) and measured with image analysis by using macro image photos in 5-times magnification.

\[
\varepsilon = \left( \frac{A_S - A_V}{A_V} \right) \times 100
\]

where \( \varepsilon \) : Void fraction (Area\%)

\( A_V \) : Area of Ni vessel (cm\(^2\))

\( A_S \) : Area of sintered sample (cm\(^2\))

2.2. Results

2.2.1. Basic Characteristics of Ores

Figure 2 shows mass fraction of \(-0.125\) mm of ores. Ore A and Ore G had large amount of fine particles. It was noteworthy that Marra Mamba ore (Ore W) contained much fine particles than other ores.

Figure 3 shows chemical compositions of coarse ore (2.0–2.8 mm) and fine ores (\(-0.5\) mm). The extent of difference of chemical composition by particle size was similar among ores except for Ore A. Marra Mamba ore (Ore W) had relatively large amount of CW, however T:Fe content of Ore W was comparable with that of low phosphorous Brockman ores (Ore C and Ore D). The content of SiO\(_2\) and Al\(_2\)O\(_3\) in Ore W was 2.5 mass\% and 1.6 mass\%, respectively, representing that the content of gangue minerals was small compared with that of other Australian ores.

Figure 4 shows microstructures of ores with 2.0–2.8 mm diameter. Hematite grains of Ore A exhibited large by 50–100\(\mu\)m and dense structure (Fig. 4(b)). Microstructures of Ore C consisted of fine hematite grains, representing microlat hematite. Ore D had similar structure as Ore C. Ore E had the most featured structure showing pisolithic hematite cores surrounded by relatively dense goethite (Fig. 4(d)). Ore F had similar structure as Ore E.

On the other hand, Ore W had hematite grains (in this case, martite grains) 20–50\(\mu\)m in size surrounded by ochreous goethite and contained many pores (Fig. 4(a)). It was observed that some particles of Ore W consisted of sin-
gle phase of goethite.

Figure 5 shows the analytical result of mineral type ratios of iron oxide of coarse (2.0–2.8 mm) Marra Mamba ore compared with that of low phosphorous Brockman ores (Ore C, D). Ore W contained particles of single phase of ‘goethite’ and co-existing phases of ‘goethite and martite’ by 60%. In contrast, Ore C and Ore D contained particles of single phase of ‘hematite’ by 60%. This tendency was the same in the case of other particle sizes. This difference in mineralogy of iron oxide phase between Australian ores was reported to be ascribed a difference in supergene enrichment process after BIF (Banded Iron Formation).1)

Figure 6 shows measurement result of porosity less than 200 μm in pore diameter. Porosity of Ore W was 0.085 cm$^3$/g. This value was higher than those of Ore C and Ore D and comparable with those of Pisolite ores (Ore E, Ore F) and Indian ore (Ore G). However, pore size distribution of ores was different by ore types.

Figure 7 shows microstructure of coarse ores (2.0–2.8 mm) after heating up to 1,200°C. Goethite turned into hematite after dehydration. Many cracks were found in goethite region in Pisolite ore (Ore F) containing high CW content (Fig. 7(b)). On the other hand, no crack was found in microstructure of Ore W despite its high CW content (Fig. 7(a)).

Figure 8 shows morphology and chemical composition of gangue minerals of Ore W. Two kinds of crystal structure of gangue minerals, hexagon type and stick type, were
found. Previous investigation reported that most of gangue minerals in Ore C were hexagon type. The fractions of the former and the latter was 30% and 70%, respectively in the case of Ore W. The hexagonal crystal shape and the result of chemical composition showing Al and Si led the conclusion that the former gangue mineral was kaolinite. The latter consisted of Al and Si as well however different crystal shape indicates that the latter was another kind of gangue mineral.

2.2.2. Granulation Ability

Figure 9 shows measurement result of cohesive strength of ores as a function of moisture. Optimum moisture of Ore W at which cohesive strength showed a maximum was 10 mass%, while 5–6 mass% in the cases of other Australian ores. In addition, the maximum strength of Ore W was 14 g/cm², lower than those of other Australian ores and comparable with those of Brazilian ores.

Figure 10 shows measurement result of centrifugal moisture equivalent of coarse ores and fine ores. Ore W showed high centrifugal moisture value, in particular fine particles showed a significant value.

2.2.3. Melting Characteristics

Figure 11 shows measurement results of penetration length of melt from fine ores. Penetration length of Ore W was 3.0 mm and larger than those of other Australian ores.

Figure 12 shows macro images of cross section of samples after assimilation tests. Figure 13 shows measurement results of void fraction of samples with image analysis. Sintered structure of Ore W contained many pores by 50% in area (Fig. 12(a)), similarly as the structure of Ore E (Fig. 7).
This result implies that strength of sintered Ore W would be low.

2.3. Discussion

Summarizing the results of exploring fundamental characteristics, Ore W had much CW and fine particles compared with other Australian ores, while it contained small quantity of gangue minerals resulting in low SiO$_2$ and Al$_2$O$_3$ content. Thermal behavior of Ore W seems to be superior due to its high porosity despite its high CW content. This stable thermal behavior of Ore W is possibly due to its high porosity. H$_2$O gas, formed by dehydration of goethite during heating-up, was readily released though open pores. Cracks were found in dense goethite region even in Ore W as well, however, a fraction of the region was small.

As for granulation ability of Marra Mamba ores, fine particles of them had low value of cohesive strength, possibly due to small quantity of Kaolinite enhancing granulation. In addition, they had high capacity of water absorption. Figure 14 shows comparison of SEM images of ores surfaces. It was clearly shown that each ore had individual surface morphology. In particular, pores 20–30 $\mu$m in diameter were found on the surface of Ore W (Fig. 14(a)). Thus, high capacity of water absorption of Ore W was caused by readily intrusion of water thorough open pores from ore surface. Granulation in high moisture content is necessary to enhance granulation ability. However even in this case, granulation ability of fine ores would be still low as shown in Fig. 9. Summarizing those results with fine particle size, low permeability of sintering bed was inspected when Marra Mamba ores were used.

As shown in Fig. 12, Ore W had relatively high value of penetration length of melt from fine. Authors showed that penetration length increased with decreasing contents of SiO$_2$ and Al$_2$O$_3$.\textsuperscript{15} Thus, the higher value of penetration length of Ore W would be explained by its lower content of gangue minerals. On the other hand, the sintered sample
after assimilation tests of coarse Ore W was poorly agglomerated. The reasons for high void fraction of sintered Ore W are discussed as follows. Figure 15 shows macrostructures of Ore W after assimilation. Calcium ferrite melt was found to form within residual (un-reacted in macro scale) ores of Ore W (Figs. 15(a), 15(b)). This implies that formed melt readily intrudes into ores thorough open pores. In addition, assimilation of ore particles containing high SiO₂ content
above 5 mass% was suppressed, resulting in silicate melt covering ore surface (Figs. 15(c), 15(d)). This structure was possibly formed as a result of dissolution of SiO₂ in ores into calciumferrite melt, increasing melt fluidity. However, number of ore particles containing high SiO₂ content was rather small. Therefore a dominant factor showing high void fraction was porous structure, resulting in decrease of available melt to agglomerate. The results concerning melting characteristics of Marra Mamba ores, it could be necessary to improve the assimilation behavior of coarse ores acting as nuclei in pseudo-particles. Heating temperature above 1 300°C is required to maintain sufficient melt quantity to agglomerate. In contrast, melt penetration within adhering fine is faster than those of other Australian ores.

3. Sintering Performances with Using Marra Mamba Ores

As mentioned in previous chapter, melting characteristics of Marra Mamba ore was inferior in coarse ores and superior in fine ores compared with low phosphorous Blockman ores. Currently, there is limited information on sintering performance when Marra Mamba ores are used. Therefore the influence of Marra Mamba ores on sintering performance is discussed based on the results of pot tests with using MAC, another bland of Marra Mamba ore, conducted by BHP Billiton\(^{21}\) (Fig. 16). Despite the different bland, fundamental characteristics of Ore W and MAC were similar.

A decrease of productivity and an increase of BAR (bonding agent rate) were found in the case of 30 mass% replacement of MAC from Mt. Newman (low phosphorous Brockman) in a constant moisture content (see blend 1 and 2). However, adjusting moisture content with using MAC resulted in sufficient productivity with only slightly increase of BAR (see blend 3 and 6). These results conclude that increasing moisture content of raw material mixture is essential if the mixed amount of Marra Mamba ores were increased. This conclusion agreed with the results of tests concerning granulation ability in the present study. Strength of sinter products was improved as well by adjusting moisture content, possibly due to uniform gas flow.

The results of plant trial using Marra Mamba ores were reported\(^{22}\). However, a clear influence of Marra Mamba ores on plant operation is still unknown. Changes in productivity with increasing the amount of Marra Mamba ores up to 100 kg/t-sinter showed large disagreement among trials due to their short estimation period. The reasons for unclear influence of Marra Mamba ores on current sintering operation are most likely following two facts. Marra Mamba ores with relatively high quality are currently shipped due to ‘hard-cap’ mined from the upper region of ore body. In addition, still small quantity of Marra Mamba ores, 20 kg/t-sinter in all Japan average in 2002, are used.

4. Past and Future of Utilization of Marra Mamba Ore

In Japanese mills, JFE (formerly named NKK) developed mini-pellet process for utilization of Marra Mamba ores in 1987\(^{23}\). Fukuyama No. 4 sintering plant could use Marra Mamba ores (BHP OB29\(^{24}\)) up to 10 mass% with this technique. Furthermore, HPS (Hybrid palletized sinter) processes\(^{25}\) developed at Fukuyama No. 5 sintering plant in 1988 enabled to use Marra Mamba ores up to 15 mass%. After these trials in plant, it was pointed out that Marra Mamba ores required an increase of moisture both for han-
dling and bed permeability due to their many fine particles and low density.

Similarly, the measures improving granulation ability of Mara Mamba ores have been reported. Pre-mixing treatment with Eirich mixer is effective for utilization of Marra Mamba ores. In addition, MEBIOS (Mosaic Embedding Iron Ore Sintering) proposed by Kasai have large possibility to utilize Marra Mamba ores by palletizing them. Simultaneously it must be noted that Marra Mamba ores contain less SiO$_2$. Further research should be going on to develop ‘low-slag sinter based on mineralogy of Marra Mamba ores’ with controlling the influence of their high CW and high fine particle fraction.

5. Conclusions

Evaluation of Marra Mamba ores using Ore W, a newly shipped bland, has been conducted. Following results were obtained.

(1) Marra Mamba ore had high combined water content, many fine particles and porous structure. The amount of gangue minerals was smaller than that of other Australian ores.

(2) Marra Mamba ores exhibited high water absorption capacity hence required high moisture content for granulation due to their porous structure. Cohesive strength of fine particles was still low level even at high moisture content due to small kaolinite content. Summarizing those results of fine particle size, low permeability of sintering bed was inspected when Marra Mamba ores are used.

(3) Penetration behavior of melt from fine particles of Marra Mamba ores acting as adhering fine in psudo-particles was superior due to their low gangue mineral content. In contrast, assimilation behavior of coarse Marra Mamba ores acting as nuclei was inferior, resulting in poor agglomeration. Thus, an improvement of behavior of coarser particles would be beneficial.

(4) Intensification of granulation with pre-treatment will be effective technique for utilization of Marra Mamba ores. In particular, palletizing of Marra Mamba ores must be one of the key technologies for utilization of the ores.

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