Coke Breeze-less Sintering of BOF Dust and Its Capability of Dezincing

Masanori NAKANO, Tsutomu OKADA, Hiroshi HASEGAWA and Michiaki SAKAKIBARA

Steel Research Laboratories, Nippon Steel Corporation, Shintomi, Futtsu, Chiba, 293-8511 Japan.
1) Kyozai Kougyo Limited, Kanda-Nishiki-machi, Chiyoda-ku, Tokyo, 101-0054 Japan.

(Received on June 29, 1999; accepted in final form on September 6, 1999)

In order to promote recycling of basic oxygen furnace (BOF) dust, sintering of the dust without coke breeze (fuel) has been researched by pot test method and the possibility of dezinving during the sintering has been evaluated.

Typical BOF dust, containing about 20% of metallic iron (M. Fe), is agglomerated without fuel and dezinved by about 50% during sintering. The agglomeration is caused by heat generation due to oxidation of the metallic iron. The dezinving takes place by the reaction: ZnO + M. Fe → Zn(gas) + FeO at elevated temperature. Secondary dust emitted during sintering mainly consisted of ZnO containing 40 to 50% of zinc. The ratio of dezinving is improved by blast furnace (BF) dust addition and up-draft sintering method. The carbon in BF dust produces metallic iron and CO gas from "FeO" melt, then they accelerate ZnO reduction. The up-drafting makes a melt pool in the lower layer, where the melt remains longer at high temperature, resulting in increase in the ratio of dezinving.

KEY WORDS: agglomeration; BF dust; BOF dust; dezinving; dust recycling; coke breeze-less sintering; up draft sintering; zinc.

1. Introduction

In integrated steelworks in Japan, flue dust from basic oxygen furnaces (BOF dust) is mainly recycled as a raw material for cold bond pellet or a desiliconizing agent for pig iron, since BOF dust is a useful iron resource containing about 64% of total iron. The processes to handle the dust pose some problems: dust emission in the course of drying in the yard, extra energy requirement for final drying in a kiln or that for adding cement in pelletizing, and occasional discarding due to zinc restriction in the blast furnace. For the recycling of the dust, an alternative is needed that can process the dust more economically without pollution.

BOF dust contains about 20% metallic iron (M. Fe). The metallic iron should be able not only to agglomerate the dust by acting as fuel in the sintering process, but also to dezinve the dust during the sintering by the reduction of ZnO by the metallic iron. Such dezinving by the use of metallic iron has already been proposed by Ito and Azakami1–3) as “Zn removal method by metallic iron reduction”.

This work aimed to evaluate if BOF dust can be sintered without coke breeze and how much it can be dezinved during the sintering, consisting of two series of experiments. First experiments concerned the basic behavior of coke breeze-less sintering of BOF dust. Second experiments concerned improvement in the ratio of dezinving, where blast furnace dust (BF dust) was sintered together with BOF dust.

2. Experimental

2.1. Experimental Apparatus and Items of Measurement

The experimental apparatus was the common one for sintering pot test [Fig. 1]. The sintering pot was 210 mm in diameter and 250 mm in bed height, into which three thermocouples were inserted at 50 mm, 100 mm and 200 mm from the bottom. In down-draft sintering, the air was supplied from the top of the pot by a blower after measuring its pressure and flow rate, and exhausted from the bottom of the pot before gas analysis for O2, CO, CO2, NO, SO2. In up-draft sintering, the route of gas flow was reversed.

After sintering, sintercake was sieved by 5mm. Defining over-5mm size as product (sinter), the index of yield was calculated as weight percentage of the product to the sinter-
cake, meaning the ability of the dust to agglomerate. The ratio of dezincing was also evaluated as zinc percentage in sinter of $1\over 5$ mm divided by that in raw mix, the index meaning the amount of dezincing of the dust during sintering.

2.2. Experimental Conditions

The pot test consisted of two series of experiments [Table 1]. The first experiments were planned to reveal the basic behavior of coke breeze-less sintering of BOF dust, where three samples different in metallic iron content were sintered to compare yield and the ratio of dezincing.

The second experiments were to improve the ratio of dezincing, as the ratio did not attain to a satisfactory value in the first experiments. In the second experiments, the following 4 factors: gas flow rate, granulator and the size of granules, blending ratio of BF dust, and direction of draft were evaluated one by one with other factors fixed at typical values. The first factor is a basic controlling factor in sintering process. The second is to improve the stability in the progress of the flame front. The third is to reinforce the reducing atmosphere. The fourth is previously reported to be a factor affecting the ratio of dezincing.

2.3. Raw Materials

BOF dust is the flue dust of BOF that is collected by wet scrubber and that is removed of large metallic-iron-rich particles by screw separator before the filter press of thickener sludge. In this work, partially-dried-in-the-sun specimens were sampled from the yard and sieved by 10 mm to reject coarse agglomerate before the sintering test. Three samples, A, B, C were examined, the metallic iron content of which ranged from 12 to 22% [Table 2].

BF dust is the flue dust of blast furnace that is collected by wet scrubber after the cyclone. Since this dust contains about 30% carbon [Table 2], it was added in the second experiments as a reductant to accelerate dezincing.

3. Results and Discussion

3.1. Behavior of Coke Breeze-less Sintering of BOF Dust

3.1.1. Experimental Results with Typical BOF Dust (Dust-A)

The heat pattern during sintering of BOF dust indicated that the maximum temperature attained $1300^\circ C$ to $1500^\circ C$ and that the intervals between times of the maximum temperature were often uneven [Fig. 2]. Since the maximum temperature reached the melting temperature of “FeO” ($1369^\circ C$), metallic iron was thought to be oxidized to form “FeO” melt. The unevenness in the time spaces implied that the progress of the heat front was not as stable as when iron-ore sintering.

The concentrations of SO$_2$ and NO of exhaust gas were about 40 ppm and about 30 ppm, respectively. These values were much lower than those of iron-ore sintering even though the carbon content of BOF dust,okes (chemically analyzed as carbon) are the origin of SO$_2$ and NO, is nearly same as that in raw mixture for iron-ore sintering. This fact
means that coke breeze-less sintering takes place under a more reducing atmosphere than iron-ore sintering.

The chemical composition of each class in size showed that Fe$^{3+}$ and zinc decrease and Fe$^{2+}$ increases as the size of class increases [Fig. 3]. As the ratio of Fe$^{2+}$/Fe$^{3+}$ basically corresponds to the sintering temperature, large particles hold high temperature, resulting in low zinc content. The zinc content of –1 mm class was 1.2%, more than that of the original dust. The reason for the concentration is discussed in Sec. 3.1.3.

When the size becomes larger, the product seems to contain fewer red particles and more blue well-sintered particles. Under the microscope, the red particles contained no melted structure and metallic-iron grains and fine dust grains as they were in raw mixture; the blue particles were melted entirely and consisted of wustite [Fig. 4].

Secondary dust, which was collected from the exhaust gas by JIS-8808 method, mainly consisted of ZnO according to XRD analysis, containing zinc percentage of 40–50% enough for the secondary dust to be available as zinc resource, for example, in the Weltz Kiln process.

3.1.2. Influence of Metallic Iron Content of the Dust

Yields of A, B and C were almost even and as high as that of iron-ore sintering [Fig. 5]. Therefore, 12% of metallic iron, that is the least value among them, is enough for BOF dust to agglomerate. This was confirmed by comparison of combustion heat per raw mixture in Table 1, which shows that even dust-C contains almost the same combustion heat as iron-ore-sintering mixture.

The ratio of dezincing of typical BOF dust, dust-A, was about 50%. Decrease in metallic iron content resulted in decrease in the ratio of dezincing [Fig. 5].

3.1.3. Discussion

Dezincing during coke breeze-less sintering possibly proceeded as follows. First, metallic iron is oxidized to FeO, which increases the temperature of the dust, then the formed FeO becomes melts. Zinc must be dissolved as ZnO–FeO melt, according to the phase diagram of Zn–Fe–O that Ito and Azakami5) have surveyed. Second, if the temperature exceeds 1,450 K, which is the equilibrium temperature of the reaction: Fe$^0$+ZnO=FeO+$^0$Zn, the metallic iron particles remaining can reduce ZnO (in Wustite) to Zn vapor. Third, the Zn vapor moves to the gas stream, and re-oxidizes in the zone of raw mixture where the gas is cooled. Finally, the ZnO particles are carried outside suspended in the gas flow.

The ratio of dezincing of coke breeze-less sintering was around 50%, less than that of other dezincing processes. Some reasons for the limitation in the ratio of dezincing in the coke breeze-less sintering: one is generation of not-dezincing part (above-mentioned red agglomerate) due to instability in the progress of sintering, another is adhering of the re-oxidized ZnO (or zinc vapor) to the particles of raw mixture downstream. The adhesion of once-vaporized zinc can also explain the fact of high zinc concentration in –1 mm particles [Fig. 3]. That is, the adhering increases Zn content at the surface of the particles of raw mixture. In weakly-sintered regions, the particles are fired as their shapes as they were, thus the surface of sinter also remains rich in Zn, which likely to be broken into –1 mm pieces by sieving.

3.2. Improving the Ratio of Dezincing

3.2.1. Results

(1) Gas Flow Rate

As gas flow rate increases, FFS (flame front speed) increases but yield and the ratio of dezincing decrease due to the decrease in bed temperature, though the differences be-
tween 0.2 and 0.4 were not significant [Fig. 6]. This behavior was basically the same as that of iron-ore sintering.6)

(2) Granulation of Raw Material

As green pellet increases in size, FFS decreases; yield increases in spite of temperature decrease. The ratios of dezincing showed the maximum value when the pellet size is 6 mm in diameter. The pellet size of 6 mm was adopted as optimum condition because dezincing is more important than productivity and yield. Pelletizing of raw material is able to raise FFS and yield; but not the ratio of dezincing, comparing to mixing simply by Eirich mixer [Fig. 7].

The product sintered from 6 mm pellet was observed to contain many red agglomerates keeping its shape as pelletized, which were probably weakly sintered but strong enough to sieve over to product sinter. The fact that the size of green pellet was larger than the aperture of the sieve, therefore, contributed to the increase in yield, though the decrease in bed temperature usually results in the decrease in yield.

The decrease in the ratio of dezincing was also comprehended by the increase of the red agglomerates which were not dezinced as mentioned above.

(3) Addition of BF Dust

Addition of BF dust to BOF dust enhances the ratio of dezincing when the yield keeps almost constant. For example, the ratio increases from 50% to 70% by 25% BF dust addition [Fig. 8]. As the bed temperature did not increase with increasing BF dust, the carbon in BF dust must react endothermically with FeO melt, producing metallic iron and CO gas. Increase of metallic iron grain was actually observed in a sample of a preliminary test that was heated in the electric furnace in the air and quenched [Fig. 9].

Increase of generation of CO gas was also verified by gas analysis of the exhaust gas [Fig. 10]. In conclusion, the generation of metallic iron and CO gas accelerated zinc re-

---

**Fig. 6.** Influence of gas flow rate on yield, FFS and ratio of dezincing with 6 mm pellet composed of BOF:BF=1:1.

**Fig. 7.** Influence of granulation on yield, FFS and ratio of dezincing sintered at 0.2 Nm/s in down draft. Eirich: mixed by eirich mixer, 3mmP: press-formed through 3 mm die.

**Fig. 8.** Effect of BF dust addition on yield and ratio of dezincing as well as sintering temperature, when 6 mm pellet was sintered at 0.2 Nm/s in down draft sintering.

**Fig. 9.** Microscopic observation of 15 mm pellets fired at 1250°C in the air.
(a) BOF dust only, (b) BOF : BF = 1 : 1.
M: metallic iron, W: wustite, P: pore.

**Fig. 10.** Change of exhaust gas composition by 50% addition of BF dust.
(4) Direction of Draft

Compared to downdraft, updraft improves the ratio of dezincing; FFS and yield are almost unchanged [Fig. 11]. Takahashi et al. have already reported the same result without any comment on the reason.

A cross section of an updraft-sintered sintercake showed that there existed a large dense part at the lower part of the bed, accompanying porous part over it [Fig. 12]. Probably, melt dropped down to a pool, and kept high temperature longer, resulting in the increase in the ratio of dezincing. This is a result from one sample, so that it is not yet clear if the formation of dense layer is essential to updraft sintering. But Inazumi et al. have not found such densification in the downdraft-sintered iron-ore sintercakes.

3.2.2. Discussion

Additions of BF dust enhance the ratio of dezincing. Possibly, the ratio would reach to 80%, the same level for Weltz kiln process, in the combined condition of updrafting and addition of BF dust. The previous work of Takahashi et al. recorded over 80% by this combination. Note that the addition of BF dust has a disadvantage to increase sulfur content in product since de-sulfurization reaction scarcely takes place under coke breeze-less sintering. Takahashi et al. reported the ratio of de-sulfurization ranges from 10 to 30%.

The behavior of sulfur is discussed below from the thermodynamic point of view. The oxygen potential \(\frac{RT}{2} \ln P_{O_2}\) in iron-ore sintering is estimated to be about \(1 \times 10^{-19}\) at 1300°C under the equilibrium of hematite and magnetite as they are dominant iron-containing minerals in iron-ore sinter. And that in coke breeze-less sintering is \(1 \times 10^{-8}\) under the equilibrium of metallic iron and FeO. Since that under the equilibrium of S and SO2 is about \(1 \times 10^{-6}\), then the coke breeze-less sintering can not vaporize sulfur as SO2 though the iron-ore sintering can.

4. Conclusions

In order to promote the recycling of BOF dust, sintering of the dust without coke breeze (fuel) was investigated by sintering pot test and the possibility on dezincing during the sintering was evaluated. The results are:

1. Typical BOF dust containing about 20% of metallic iron is agglomerated without fuel, and dezinced by about 50% during sintering.
2. Secondary dust mainly consists of ZnO, containing 40 to 50% of zinc.
3. BF dust addition and up-draft sintering method improve the ratio of dezincing. The carbon in BF dust produces metallic iron and CO gas from “FeO” melt, then they accelerate ZnO reduction. The up-drafting makes a melt pool in the lower layer, where the melt keeps longer at high temperature, resulting in the increase in the ratio of dezincing.

The coke breeze-less sintering aims to closed-recycle the BOF dust in steel making division. That is, powder of the product is used as desiliconizing agent; lump of the product as coolant during smelting. A part of lumpy product is also available for BF under its zinc restriction. Re-sintering of powdery product probably enable to produce lumpy product only. How it will change yield and the ratio of dezincing needs further experiments.

The coke breeze-less sintering has an advantage in investment, as a sintering machine is more economical than a rotary kiln or other reduction facilities. We expect that the restriction of zinc income from scraps and the control of zinc input to blast furnace will enable to function the coke breeze-less sintering as a dezincing process in integrated steelworks, even though the ratio of dezincing is relatively low.

© 2000 ISIJ
REFERENCES

1) S. Ito and T. Azakami: Nihon-kogyo-kaishi, 104 (1998), 297.
2) S. Ito and T. Azakami: Nihon-kogyo-kaishi, 104 (1998), 543.
3) S. Ito and T. Azakami: Nihon-kogyo-kaishi, 104 (1998), 821.
4) Y. Fukagawa, K. Shida, T. Takahashi, K. Tsujihata and Y. Kimura: Tetsu-to-Hagan¯i, 61 (1975), S428.
5) S. Ito and T. Azakami: Shigen-to-sozai, 109 (1993), 185.
6) E. W. Voice, S. H. Brooks, W. Davies and B. L. Robertson: J. Iron Steel Inst., 174 (1953), 97.
7) T. Inazumi, M. Nakano and S. Kasama: Shigen-to-sozai, 111 (1995), 821.
8) J. E. Doodwill and D. E. Klesser: Steel Technol. Int., (1994/95), 91.