Note

Porosity of Sinter and Its Relation with the Sintering Indices

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1. Introduction

The performance of blast furnace depend, to a greater extent, on the physical and chemical characteristics of the burden materials and their consistency. Sinter constitutes 70–80% of the iron bearing burden material in the modern blast furnaces. An important aspect of the sinter, as ferrous burden, is that it could be tailor made. Its physical & chemical properties depend on the properties of individual components and on its micro-structure, especially on the size, shape distribution and the mutual interaction of the individual components. A thorough appreciation of the micro-structure of sinter is a basic necessity and the first step towards establishing structure–property relationship. The fact that calcium-rich ferrites impart beneficial properties of strength and reducibility to fluxed sinter has been accepted.¹⁾

Porosity of sinter is an important parameter which influence its property significantly, in particular its reduction properties. Bristow *et al.*²⁾ have studied the effect of porosity on reducibility of sinter and found that SFCA stabilised the fine pores produced during the reduction process leading to increased porosity and higher reducibility. Maeda *et al.*³⁾ reported that the reduction of sinter starts in its proportions in contact with micro-pores and that the proportion and structure of the micro-pores supplied by the reducing gas play an important role in determining the reducibility of the entire sinter. It is also reported that the reduction of magnetite to wustite markedly increases the number of pores of 0.1 to 10 μm in size and that when the melt starts to form at 1 423 to 1 473 K, the fine pores are sequentially closed.

Several factors most significantly, particle size of flux and coke breeze affect the sinter porosity. Yang *et al.*⁴⁾ have observed that:

- the number of pores increases with increasing lime content,
- the porosity of sinter increases with decreasing limestone particle size, and
- pores are produced in the sintermass after the combustion of coke breeze.

They concluded that the particle size and quantity of limestone and the particle size of coke breeze have a great effect on the formation of pores in sinter.

The influence of MgO addition on sinter mineralogy *vis-à-vis* the properties of sinter has been studied in detail by Panigrahy *et al.*⁵⁾ They observed that most significant effect of MgO addition was the suppression of hematite and Ca–ferrite phases and the increase in magnetite phase. Most of the MgO was picked by the magnetite phase to form mixed spinels of type $(\text{Fe}, \text{Mg})\text{O} \cdot \text{Fe}_2\text{O}_3$.

2. Materials and Methods

2.1 Raw Materials

Blended iron ore fines from two different sources A and B, as well as limestone, pyroxenite and coke breeze were used for the studies. Freshly calcined lime was used during the experiments. **Table 1** shows the sieve analysis of iron ore fines, coke breeze, anthracite, crushed limestone and pyroxenite. **Table 2** shows the chemical analysis of iron ore fines, non-ferrugeneous and carbonaceous mix ingredients.

X-ray diffraction of the ore fines from the sources, A and B shows that hematite was the major iron bearing mineral. The minerals, which were present in ore fines in minor to trace quantity, are goethite, hydrated iron oxide, gibbsite, kaolinite and quartz. Calcite is the major mineral phase present in limestone. The minerals, dolomite and quartz were present in minor amount. The pyroxenite sample consisted of magnesium silicate ($\text{MgO} \cdot \text{SiO}_2$) as major mineral phase.

2.2 Sintering

Sintering tests were carried out in a batch square shaped sintering unit of $30 \cdot 30 \text{ cm}^2$ cross sectional area with 400 mm high sinter box having removable grate bar at the bottom. The sinter mix prepared in a disc pelletiser was put into the pot up to the top layer level and ignited. Vacuum was maintained by operating the exhaust fan till the completion of sintering which was known from the temperature of the wind box (burn through point). The sinter was allowed to cool under suction till the temperature of exhaust gas reaches 100°C. The sinter cake was then dislodged and subjected to stabilisation/shatter test.

2.3. Parameters Studied

The parameters, which were held fixed are mentioned below against their level:

- Return fines in the sinter mix: 22%
- CaO/SiO_2 ratio of the sinter: 2.1; MgO in sinter: 1.5%

Table 1. Sieve analysis of raw mix ingredients.

Size in μ	Wt. % undersize					
	Ore A	Ore B	C/B	Anthra	L/S	Pyrox.
10,000	93.83	96.30				
6,000	77.84	72.67				
3,360	60.27	49.74	71.63	73.39	99.94	99.57
2,000	45.72	32.14	49.74	52.24	56.70	62.47
1,410	39.47	25.96	40.12	43.61	41.01	48.61
840	34.96	20.93	30.15	35.54	30.97	39.75
590	29.52	15.45	22.98	29.04	24.02	32.80
500	25.62	11.52	17.36	23.11	19.24	26.57
297	22.22	8.33	12.63	18.47	16.00	21.64
250	18.75	5.55	8.63	14.20	13.12	15.26
150	17.19	4.38	6.13	10.26	11.75	11.68

Table 2. Chemical analysis of raw mix ingredients.

Radical	Weight %						
	Ore A	Ore B	L/S	Pyrox.	Lime	C/B	Anthra
CaO			52.50	4.35	91.5		
MgO			0.18	28.03	1.72		
SiO_2	0.98	1.29	3.25	51.74	1.98	42.20#	42.3#
Al_2O_3	1.94	3.61	0.36	1.94	1.75	21.24#	20.26#
Fe_2O_3	97.29	94.86	3.57	5.43	0.51	20.52#	15.78#
LOI			40.4	3.85	2.31		
FC						75.39	76.88
VM						1.53	9.93
Ash						22.14	11.18

in ash

- Heat input for ignition: 24,000 kcal/m²·min (total 100·10⁶ J/m²·min)
- Bed height: 400 mm
- Lime in mix: 1 %

The size parameters of coke breeze and ore fines as well as the source of Mg²⁺ was studied.

2.4 Physico-chemical Tests of Sinter

IS 9963: 1981 was followed for the Shatter test and IS 6495: 1984 was followed for the tumbler test. Representative sinter sample after the stabilisation was ground to -200 mesh size for the chemical and X-ray diffraction analyses, while -15+10 mm sized sinter was withdrawn from the representative one for RDI and RI investigations. X-ray diffraction (XRD) analysis of the selected sinter samples ground to -200 mesh were carried out using Co radiation. Porosity of the sinter samples was measured in mercury porosity-meters, Pascal 140 and Pascal 440, supplied by Thermo-Finnigan, Italy. Specification of these equipment are given in **Table 3**. Percent porosity expresses the ratio between the pore volume (volume of internal cavities) and the external volume occupied by the sample.

Response Variables

The response variables are as follows:

- Vertical speed of sintering, VSS (mm/min): the ratio of average bed height (in mm) and the time of sintering (in minute).
- Yield of sinter: % +10 mm of sinter OR% +6.3 mm of sinter after stabilisation of the sinter mass (20 kg) following shatter test.
- Tumbling index: The percentage of +6.3 mm remained after tumbling the 11.4 kg mass of sinter (+10 mm) in a standard tumbler test apparatus (ASTM E279-97) for a total of 200 revolutions. The tumbling index was used as the main criterion for comparing the strength of sinter under various conditions.
- Abrasion index: the percentage of -28 mesh generated after tumbling the 11.4 kg mass of sinter (+10 mm) in a standard tumbler test apparatus (ASTM E279-97) for a total of 200 revolutions.
- Strand productivity:

$$\text{Charge weight} \cdot \text{Yield of sinter } (\% - 10 \text{ mm} / \% + 6.3 \text{ mm})^{\#} (\text{t})$$

$$\text{Cross sectional area of pot (m}^2\text{)} \cdot 100 \cdot \text{Time of sintering (h)}$$

[#]: Depending upon the blast furnace requirement whether +10 mm or +6.3 mm is defined as sinter.

- RDI: Percentage of -3.15 mm size fraction generated after tumbling in a standard tumbler for 900 revolutions following reduction under standard condition (Ref. Annex. 4.3, Monograph on Sinter Making at Tata Steel) is reported as RDI.
- RI: Percentage of loss in weight of the sinter sample after reduction under CO+N₂ atmosphere (30+70%) for 180 min at 900 deg. C to the total weight of available oxygen in the sample. (Ref. Annex. 4.4, IBID) is reported as RI.

3. Results and Discussion

3.1. Porosity vis-à-vis Sinter Reducibility: Effect of Coke Breeze Size

Much work has been reported on the effect of particle size distribution in coke breeze used as heat source for sintering on the sinter-ability of iron ore. The effect of addition of coke breeze of various sizes has been studied by Karabassov *et al.*⁶⁾ and Konilava *et al.*⁷⁾ It has been reported that the optimum coke particle sizes for combustion efficiency and productivity are from 0.25 to 3 mm which are neither so fine nor so coarse.⁸⁾ The sinter quality also

Table 3. Specification of the porosity-meters used.

	PASCAL 140	PASCAL 440
Operating range	0.1-400 k Pa	0.1-400 m Pa
Resolution	0.1 k Pa	0.01 m Pa
Measuring range of pore radius (nm)	1,900-58,000	30-7500

Table 4. Effect of coke breeze size on the porosity and quality parameters of sinter (fuel: 70 kg/T, vacuum: 1300 mm WG, flux size: -3 mm, size of ore fines: -8 mm).

Parameter	Exp.19	Exp. 21
<i>Measurement for Micro-Pores only</i>		
• Avg. pore radius, micron	0.012	0.110
• Total porosity, %	5.23	10.38
<i>Measurement for Micro-Pores & Macro Pores</i>		
• Avg. pore radius, micron	0.22	0.29
• Total porosity, %	10.85	13.41
• Apparent density, g/cc	4.05	4.35
• Bulk density, g/cc	3.61	3.77
Size of coke breeze, - 6.3 mm + 650 micron	80.5%	--
Size of coke breeze, - 3.3 mm + 650 micron	---	71.9%
Size of coke breeze, - 650 micron	19.4%	28.1%
Reducibility, %	57.1	61.1

largely improved with proper sizing.⁹⁾

Table 4 shows total porosity and average pore radius of the sinter samples from the experiments nos. 19 and 21 in relation to the micro-pores and combined macro- and micro-porosity. Micro-porosity in the present case denotes the pore radius of the sinter samples below 10 μm and up to 0.001 μm, whereas the pore radius of the samples in the range 10 to 100 μm corresponds to macro-porosity. Table 4 also shows the reducibility values of these samples. In the Exp. no. 19 normal (-6.3 mm) sized coke breeze (see Table 1 for complete size analysis) was used, whereas in the Exp. no. 21 the coke breeze crushed to -3.1 mm was used. Other parameters were identical in both the experiments.

Table 4 shows that when size of coke breeze in the sinter mix was reduced from -6.3 to -3.3 mm, micro-porosity of the sinter samples increased from 5.2 to 10.4%. Reducibility index (RI) of the sinter sample also increased from 57.1 to 61.1%. It may be mentioned that while micro-porosity of these samples changed quite significantly, the total porosity (consisting of micro- & macro-pores) of the sinter samples remained more or less same, 11% and 13% respectively with -6 mm and -3 mm sized coke breeze in the sinter mix. We may infer that the reducibility of sinter was well correlated with the proportion of micro-pores out of total pores available in the sinter.

Hosotani *et al.*¹⁰⁾ have also observed that number of fine pores increased in the sinter when smaller sized fraction of limestone or/and coke breeze was used in the mix. Fine pores could be prevented from coalescing into coarser pores if expansion of the heat pattern is suppressed. Similar results were obtained by Matsuo *et al.*¹¹⁾ in their experiments on reduction of pellets. They synthesised pellets A with micro-pores alone and pellets B with both macro-pores and micro-pores from hematite mineral. From the reduction tests with the pellets A and B they observed that while the overall porosity was equal, pellets B with smaller amount of 15 μm and finer pores than the pellets A are reduced at lower rates than pellets A.

Our results, similar to others, suggest that if the coalescence of fine pores was suppressed and the number of small pores was increased in the sintering process, the surface area of sinter could be increased to achieve a substantial improvement in its reducibility.

Table 5. Effect of ore size on the porosity and quality parameters of sinter (fuel: 70 kg/T, vacuum: 1 300 mm WG, flux size: -3 mm, size of coke: -6 mm).

Parameter	Exp. 19	Exp. 20
Measurement for Micro-Pores only		
• Avg. pore radius, micron	0.012	0.205
• Total porosity, %	5.23	08.04
Measurement for Micro-Pores & Macro Pores		
• Avg. pore radius, micron	0.22	0.81
• Total porosity, %	10.85	12.76
• Apparent density, g/cc	4.05	4.23
• Bulk density, g/cc	3.61	3.69
Size of ore fines	-8 mm	-6.3 mm
Reducibility, %	57.1	59.7

3.2. Porosity *vis-à-vis* Sinter Reducibility: Effect of Ore Size

Table 5 shows the total porosity and average pore radius of the sinter samples from the experiments nos. 19 and 20 in relation to the micro-pores and combined macro- and micro-porosity. Table 5 also shows the reducibility values of these samples. In the Exp. no. 19 normal sized ore fines (see Table 1 for complete size analysis) was used, whereas in the Exp. no. 20 the ore fines crushed to -6.3 mm was used. Other parameters were identical in both the experiments.

From the Table it is apparent that when the ore fines of reduced size was used in the mix micro-porosity of the sinter sample increased, besides the average pore radius and density of the sinter sample also increased. Micro-porosity of the samples denotes the pore radius below 10 μm and up to 0.001 μm .

Similar results have been obtained by Sato *et al.*¹²⁾ who report that reducing the particle size of iron ore reduces the size of pores in sinter and unifies the pore distribution of sinter (or improves the sinter reducibility). Jeulin *et al.*¹³⁾ have observed that reducibility of the sinter samples increased with their pore specific area and decreased with the range of pore co-variance.

3.3. Porosity *vis-à-vis* Sinter Reducibility: Effect of Pyroxenite/Dolomite

Table 6 shows the total porosity and average pore radius of the sinter samples from the experiments nos. 14 and 19 in relation to the micro-pores and combined macro- and micro-porosity. Table 6 also shows the reducibility values of these samples. In the Exp. no. 19 pyroxenite was the MgO bearing flux material, whereas in the Exp. No. 14 dolomite was used. Other parameters were identical in both the experiments.

From the Table it is apparent that when pyroxenite was replaced by dolomite, the micro-porosity increased marginally whereas the total porosity decreased and density increased. Total porosity of the samples corresponds to the combined micro-porosity and macro-porosity. It is apparent from the Table that reducibility of the sinter also increased marginally when pyroxenite was replaced by dolomite. The reducibility (or the mineralogy) of sinter is crucially decided by the process of diffusion of Mg^{2+} into magnetite lattice to form mixed spinels during the sintering.⁵⁾

4. Conclusions

- The reducibility of sinter is well correlated with the proportion of micro-pores (pore radius in the 0.001–10 μm range) out of total pores consisting of micro-pores and macro-pores (pore radius - 100+10 μm) available in the sinter. With the change in process parameter(s), the micro-porosity of the sinter samples is significantly af-

Table 6. Effect of source of MgO on the porosity and quality parameters of sinter (fuel: 70 kg/T, vacuum: 1 300 mm WG, flux size: -3 mm, size of coke: -6 mm, size of ore fines: -8 mm).

Parameter	Exp. 19	Exp. 14
Measurement for Micro-Pores only		
• Avg. pore radius, micron	0.012	0.202
• Total porosity, %	5.23	5.80
Measurement for Micro-Pores & Macro Pores		
• Avg. pore radius, micron	0.22	0.36
• Total porosity, %	10.85	7.35
• Apparent density, g/cc	4.05	4.54
• Bulk density, g/cc	3.61	4.21
Source of MgO	pyroxenite	dolomite
Reducibility, %	57.1	58.7

ected while total porosity of the sample may remain more or less same or marginally affected

- The micro-porosity of sinter samples (pore radius in the 0.001–10 μm range) and consequently the sinter reducibility increase with decrease in the size range of coke breeze. That is, when coke breeze below 6.3 mm size is screened at 3.3 mm and +3.3 mm size fraction is crushed and mixed to the -3.3 mm size fraction (100%, -3.3 mm sized coke breeze).
- Sintering of ore fines with reduced size increases micro-porosity of the sinter sample. Besides, the average pore radius and density of the sinter sample and consequently the sinter reducibility increase with narrowing down the ore size from -8 to -6.3 mm.
- The micro-porosity and reducibility of the sinter samples increases marginally with the replacement of pyroxenite by dolomite.

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