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Improvement in Quality Parameters of Super-Fluxed Sinter from Indian Iron Ores: NML's Experience

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Abstract

The various studies at NML report that the quality parameters of sinter could be improved by modifying the physical characteristics of the sinter mix and improving the thermal efficiency.

The studies have shown that increasing the solid fuel consumption was not a viable solution to improve TI and RI simultaneously. The mineralogical and morphological compositions of sinter do affect its qualities : A higher amount of calcium ferrites improved the reduction-degradation index and reducibility of sinter. The reducibility was well correlated with the ratio of micro-pores to total pores in sinter. Grain size of the mix did affect the sintering speed and quality parameters. The studies also show that significant improvement in reduction properties could be achieved by narrowing down the flux size and that of coke as well as optimizing the process variables. The RDI also improved with the addition of polymer in the mix, however, sinter productivity decreased.

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1. Introduction

Importance of the proper selection of process and operation variables is generally accepted in order to achieve better quality of sinter and greater productivity simultaneously [1-5]. The strength of sinter during reduction (RDI) and reducibility of sinter (RI) are of greater significance and have drawn considerable attention of the researchers since the furnace performance is largely decided by these indices [6-7]. In case of typical blast furnaces in India a definite relationship between the coke rate and RDI of sinter has been established [8]. Understandably, the fines generated inside the furnace in the stack zone or during reduction affect the permeability of the stack zone, increase the pressure drop and disturb the gas distribution. All these factors result in decrease in driving rate and adversely affect the CO utilization with ultimate consequence of higher coke rate and lower productivity.

The sinter properties, strength and reducibility are influenced by the mineralogical and morphological characteristics of sinter [9] which are influenced greatly from the sinter basicity, CaO/SiO_2 [10]. Satokha et al. [11] observed that influence of sinter basicity on the open porosity. The fact that calcium- rich ferrites with increase in basicity impart beneficial properties of strength and reducibility to fluxed sinter has been accepted [12]. Other factors which do influence the reduction properties of sinter and its strength include lime content in the sinter mix and its grain size, besides particle size of the mix ingredients, flux and coke breeze, particularly [13].

Porosity of sinter is an important parameter which influence its property significantly, in particular its reduction properties. Bristow et al.[14] have studied the effect of porosity on reducibility of sinter. Maeda et al.[15] reported 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. Study of the granulation process has drawn considerable attention of the researchers [16,17] as this parameter is connected with permeability of the sinter bed

Presently, the sinter basicity (CaO/SiO_2) in some of the sintering plants in India is maintained around 2. This figure is possibly not conducive with regards to degradation property of sinter in reducing medium at low temperature [18]. Structure of the sinter could be heterogeneous around this basicity level with a mixture of some basic and some acidic phases in it [10]. This possibly causes short cracks in the sinter which adversely influences the RDI of sinter. Keeping this fact in view, other process parameters, though have marginal effect on the output of sinter and its quality need to be looked into. We have studied the effect of process parameters on the sintering indices at sinter basicity 2 also.

We have also attempted to improve the sinter RDI through the improvement in the mix granulometry by the addition of polymer similar to that reported in the literature which acts as binding agent in pelletisation. Besides, We have studied the effect of basicity ratio, besides its interaction effect with the content of solid fuel in the mix, and MgO content of sinter to get the best possible results while minimizing the coke breeze consumption. In view of the fact that the consumption of solid fuel in the Indian sintering plant is high any saving in coke breeze will improve the profitability of the sintering plant.

2. Experimental Procedure

2.1 Raw Materials

Blended iron ore fines (Fe = 67.81%, SiO_2=2.27%, Al_2O_3 = 1.04%) and other sinter mix ingredients from a typical sinter plant was used in the preset study. Hematite was the major iron bearing mineral phase in the ore samples. The minerals, goethite, hydrated iron oxide, gibbisite, kaolinite and quartz. ch were present in in minor to trace quantity. Calcite was the major mineral phase present in limestone while dolomite and quartz were present in minor amount.

2.2 Sintering

Sintering tests were carried out in a batch square shaped sintering unit of 30*30 sq. cm cross sectional area with 400/ 550 mm high sinter box having removable grate bar at the bottom. The sinter mix prepared in a disc pelletizer was put into the pot up to the top layer level and ignited for 2 minutes. 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^oC. The sinter cake was then dislodged and subjected to stabilisation / shatter test. Heat input for ignition was 24 thousand Kcal /m^2* min. (100*10^6 J/m^2 *min)

2.3 Phyisco-Chemical Tests of Sinter

IS 9963:1981 and IS 6495:1984, respectively were followed for the shatter and tumbler tests. 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 analysis of the sinter sample was done using Cu/Co k-alpha radiation. Porosity of the sinter samples was measured in mercury porosity-meters, Pascal 140 (operating range 0.1-400 kilo Pa), and Pascal 440 (operating range 0.1-400 mega Pascal).

2.4 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).
- Tumbling index (TI) : 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.
- Strand productivity (P_{+10}):

  $$\frac{\text{Charge weight *Yield of sinter (\%+10 mm) \# (t)}}{\text{Cross sectional area of pot (sq.m) *100 * Time of sintering (d)}}$$

- RDI : Percentage of –3.15 mm size fraction generated after tumbling in a standard tumbler for 900 revolutions following reduction under standard condition [19]
- RI: Percentage of loss in weight of the sinter sample after reduction under (30%+70%) $CO+N_2$ atmosphere for 3 h at 900 deg.C to the total weight of available oxygen in the sample [19]

3. Results and Discussions

3.1 Mineralogical Compositions of Sinters

The X- ray diffraction analysis of the sinter samples shows the presence of hematite, magnetite, calcium di-ferrite, calcium ferrite, di -calcium ferrite and silicates of Ca and Fe. Interestingly, highest (100%) peak was observed at d-space 2.53 which is characteristics of magnetite and calcium ferrite for the sinter samples from the experiments carried out at 550 mm bed height; whereas highest (100%) peak was observed at d- space 2.70 which is characteristics of hematite for the sinter samples at 400 mm bed height . The content of magnetite phase increased with the increase in bed height from 400 to 550 mm.

3.2 Effect of Basicity Ratio and Content of Coke Breeze

Table 1 shows the results of the experiments where we have attempted *low temperature sintering* by reducing the consumption of coke breeze. At 8% coke breeze in the mix, sinter with TI around 70%, could be produced (Exp. 5 & 20). The sinter mass, as expected was over-fused. A very high FeO (27.8%) in the sinter sample pertaining Exp. 5 reflects that the sintering was under highly reducing condition. With the modification in the sinter basicity and MgO content from 1.9, 3.0% (Exp. 5), respectively to 2.5, 1.5% (Exp. 20) the productivity increased significantly solely due to decrease in the sintering time. Besides, cooling time also decreased. In either of the cases the yield of sinter was low generating more return fines than the input. At fixed higher coke breeze (8%) and 3% MgO, with increase in basicity the yield and TI decreased while times of sintering and cooling also decreased (Exp.5 & 16). Basicity remaining the same, when MgO content decreased from 3% to 2%, similar results were observed (Exp. 5 & 19).

Table 1 : Effect of sinter basicity and coke breeze in mix on the sintering indices at different MgO content showing the inter-influence of these parameters (Bed Height 400 mm)

Exp.	*Input parameter*			*Output parameter*				
	Sinter Basicity	MgO in Sinter,%	C/B in mix , %	*Yield % +10*	*Sinter Time, min*	*Cooling Time, min.*	*Prod T/m2/h*	*Tumb Index*
04	1.9	3.0	6	42.69	17.5	10.5	1.28	58.4
05	1.9	3.0	8	44.28	20.5	14.5	1.14	68.8
16	2.2	3.0	8	27.60	13.5	7.5	0.94	60.0
17	2.2	3.0	6	28.40	11.5	6.5	1.10	63.5
19	2.0	2.0	8	35.02	13.5	8.5	1.21	63.6
20	2.5	1.5	8	39.71	11.5	10.5	1.54	70.1
22	2.5	1.5	6	39.57	11.5	8.0	1.66	70.9
24	2.5	1.5	4	46.34	12.5	7.5	1.87	73.9
26	2.5	2.5	4	44.65	13.0	7.0	1.64	72.2
27	2.5	3.0	4	42.85	11.5	8.5	1.74	69.88
30	2.5	2.5	4	45.14	13.5	6.5	1.61	72.3

The inter-influence of basicity ratio and coke breeze has been reflected from the results of Exp. 4, 5, 16 and 17. At 2.2 basicity with increase in coke breeze TI decreased marginally, while at 1.9 basicity with increase in coke breeze TI increased significantly. Similar inferences could be drawn when the results from Exp. 20, 22 and 24 are compared. TI increased with decrease in C/B whereas productivity and yield increased, the cooling time also decreased. Exp. 24 possibly gives the best results amongst those investigated. At 4% coke breeze and 2.5 basicity , similar to the results from Exp. 5 and 19 the TI and yield increased with decrease in MgO content of sinter whereas the productivity and yield increased marginally. At 4% coke breeze Return fines was not balanced. So in order to balance the return fines 33% return fines was added. Thus the return fines was balanced, however there was compromise in strand productivity (Exp. 26, 30).

3.3 Porosity vis-à-vis Sinter Reducibility : Effect of Size Parameters

The effect size parameters of coke breeze has been studied by Karabasov et al. [20] and Konilava et al [21]. Tthe optimum coke particle sizes for better combustion efficiency and productivity are from 0.25 mm to 3 mm [22]. The sinter quality also largely improved with proper sizing [23].

Table 2 shows porosity and average pore radius of the sinter samples from the experiments nos. 39, 40 and 41 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 in between 10 and 0.001 micron, whereas the pore radius of the samples in the range 10 micron to 100 micron corresponds to macro-porosity.

Table 2: Effect of coke/ ore fines size on the porosity and quality parameters of sinter (Flux size: -3 mm, Bed height: 400 mm)

Parameter	***Exp.39***	***Exp.41***	***Exp. 40***
Measurement for Micro-Pores only			
• *Avg. pore radius, micron*	*0.012*	*0.110*	*0.205*
• *Total porosity, %*	*5.23*	*10.38*	*08.04*
Measurement for Micro-Pores & Macro Pores			
• *Avg. pore radius, micron*	*0.22*	*0.29*	*0.81*
• *Total porosity, %*	*10.85*	*13.41*	*12.76*
• *Apparent density, g/cc*	*4.05*	*4.35*	*4.23*
• *Bulk density, g/cc*	*3.61*	*3.77*	*3.69*
Size of coke breeze, - *6.3 mm + 650 micron*	*80.5%*	--	*80.5%*
Size of coke breeze, - *3.3 mm + 650 micron*	---	*71.9%*	---
Size of coke breeze, - *650 micron*	*19.4%*	*28.1%*	*19.4%*
Size of ore fines	-10 mm	-10 mm	-8 mm
Reducibility , %	57.1	61.1	59.7

Table 2 shows that with the increase in micro-porosity of the sinter samples from 5.2% to 10.4% through 8% the reducibility index (RI) increased from 57.1% to 61.1% through 59.7%. Table 2 also shows that when size of coke breeze in the sinter mix was reduced from –6.3 mm (Exp. 39) to –3.3 mm (Exp. 41) micro-porosity of the sinter samples increased significantly with corresponding increase in reducibility index (RI). It may be noted that while micro-porosity of these samples changed quite significantly with the change in the process variables, the total porosity (consisting of micro- & macro-pores) of the sinter samples remained more or less same, 10.85% and 13.41% 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. [24] 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. The present result is similar to Hosotani et al. [24] Matsuo et al. [25] who suggest that fine pores could be prevented from coalescing into coarser pores if the number of small pores increased in the sintering process and consequently to achieve a substantial improvement in its reducibility.

Table 2 also shows that when the ore fines of reduced size was used in the mix micro-porosity of the sinter sample increased (Exp. 39 vs. Exp.40), besides the average pore radius and density of the sinter sample also increased. Similar results have been obtained by Sato et. al.[26] who report that reducing the particle size of iron ore reduces the size of pores in sinter and improves the sinter reducibility.

3.4 Effect of Flux Size

Table 3 shows that the elimination of –0.5 mm from the flux improved the RDI value while the RI value was marginally affected. The Table also shows that the VSS increased when –0.5 mm size fraction in limestone was eliminated compared to the base. Hosotani et al. [24] have also observed that the sintering time was shortened by using limestone from which -1mm size fraction was removed. Shigaki et al. [27] report that increase in calcium ferrite(s) and increase in magnetite are some of the crucial factors which affect the RDI value of sinter positively. This, amongst the several means, could be achieved by using coarser sized limestone particles in the sinter mix. Bhagat et al. [28,29] report that when limestone contains excess fines (-0.5 mm) in the sinter mix the calcination of limestone and its assimilation into hematite and other mineral phases gets affected.

Table 3: Effect of flux size on the sintering indices
(Fuel size: -6 mm, Size of ore fines: -10 mm, Bed height 550 mm)

Indices	***Values***					
Size of flux, mm	-3 mm			-3+0.5 mm		
VSS, mm/min	23.6	23.6	23.8	25.1	25.1	25.0
TI, %+6.3 mm	67.6	67.8	68.2	69.3	69.0	69.1
RDI , % -3.1 mm	27.3	28.2	26.8	26.1	26.4	25.6
RI , %	ND	74.2	75.4	81.1	79.9	82.3

3.4 Effect of Polymeric Additives

Typically a polymeric additive similar to that reported in the literature [30-33] was added in the proportion of 1 kg/ T of sinter mix to assess improvement in the sintering indices. While significant improvement in the tumbler index and RDI was observed when the polymer was added into the sinter mix, the strand productivity decreased marginally compared to the base figure. This was due to the improvement in mix granulometry. The medium sized mix fraction increased by 15% due to the addition of the polymer compared to base one when only water was added.

4. Conclusions

- The amount of coke in the sinter mix is inter-influenced by the basicity and MgO content of sinter. This could be exploited to reduce the coke consumption through `low temperature sintering process'.
- The sinter reducibility is well correlated with the proportion of micro-pores (pore radius,0.001-10 micron) out of total pores consisting of micro-pores and macro-pores (pore radius -100+10 micron) available in the sinter. With the change in process parameter(s), the micro-porosity of the sinter samples is significantly affected while total porosity of the sample may remain more or less same or marginally affected.
- The micro-porosity of sinter samples and consequently the sinter reducibility increase with decrease in the size range of coke breeze from 28 % 3.3mm to 100 % -3.3 mm.
- 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.
- When the size of flux was narrowed down to –3+0.5 mm from –3 mm, RDI value decreases to 25.6% (from a level of 26.8%) with marginal decrease in RI of sinter. The speed of sintering also increased with narrowing down the flux size.
- Addition of polymer in the sinter mix improves the RDI of sinter , but decreases the productivity marginally

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