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Innovative Development on Agglomeration of Iron Ore Fines and Iron Oxide Wastes

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ABSTRACT

In steel industry and in mines, a significant amount of ultra-fines waste iron oxides and iron ore fines is generated. Utilizations of these fines are required to reduce the environmental hazards and conserve the natural resources. Some of these fines are normally used in sintering practice. However, sintering has a limitation of accepting ultra-fines materials. Pelletizing can use ultra-fine iron oxides. However, suitable technology is required for preparation of good quality pellets. Some of the fines, viz. blast furnace (BF) flue dust, Linz Donawitz (LD) converter sludge etc., are not suitable due to their high alkali and Zn content. Some other material like slime is not considered to be suitable in normal pelletizing practice, because of its high alumina and silica content and excessively fine size. On the other hand mill scale and blue dust have poor green bonding property. Therefore, suitable technologies are required to be developed for their utilization/recycling. This paper discusses the various technologies developed such as (i) developing flux for basic oxygen steelmaking process, (ii) improved pelletizing practice for better reducibility, lower reduction degradation and replacing bentonite binder, and (iii) special quality sinters for improving micro-fines utilization. These technologies may have very good application potential.

KEYWORDS

Ultra-fines; waste iron oxide; pelletizing; sintering; flux for steel making; micro pelletizing; replacement of bentonite; pellet-sinter composite agglomerate

1. Introduction

Iron ore is available in nature in form of hematite, magnetite, goethite, limonite etc. Out of which hematite and magnetite are the major source. Hematite can be used directly in iron making furnaces in lump form. Magnetite is generally used after pre processing. In India, the graded hematite lump is widely used in the blast furnaces and in rotary kiln. However, during the lump ore preparation (10-30 mm size) lots of mineral dressing (crushing, grinding, screening etc.) are required wherein a significant amount of fines (~ 60%) are generated. These fines cannot be used directly in any furnaces. For utilization of these fines, agglomeration techniques, such as sintering, pelletizing, or briquetting, are required. Sintering is the oldest, easiest, and energy-efficient process to use these fines. Therefore, in most of the steel plant sintering routes are followed for using these undersize iron ore. However, sintering has a size limitation. Excessive fineness (<0.5 mm) loses its bed permeability. However, a huge quantity of ultra-fines iron oxides is generated both in the mines area and in the steel plant itself.

Main source of generation of ultra-fines in mines area is the ore washing plant. During water washing of iron ore lump, the ultra-fines (majority is below 30μ m) are separated in form of slurry. This is very rich in alumina (3–15%) and silica (3–15%). This slurry is termed as slime. Due to the high gangue content and excessive fineness, the entire slime is still unused.

Due to the weathering of iron ore hills for several thousand years in rainwater, erupted iron ore particles are deposited at the several cavities of hills. They are very clean and rich in iron, because of washing by the rain water. As there is very little gangue, they have hardly any bonding property and they are available in form of fines or dust in blue colors. Therefore, they are termed as 'blue dust'. They are used in pelletizing mix with hematite ore in a low percentage because of their poor green bonding property (Pal et al. 2017a). As they have very low gangue content, the pellets gangue content is proportionally reduced, which may improve the pellet property and increase the performance of the downstream process by reducing slag volume. However, 100% blue dust use is essential to conserve the natural resources.

Apart from these, there are lean grade ores which are not used directly in the blast furnace or DRI making. These ores are generally crushed and ground to powdery size and are upgraded through several beneficiation processes. The beneficiated products are available in form of fines which require agglomeration before using in iron making furnaces.

Magnetite ore is also a good source of iron. Out of 170 billion tonnes (Indian mineral year Book 2012) iron ore deposit worldwide, around 40% is magnetite. Magnetite lump ore has very poor reducibility. It is much denser than hematite and has lower porosity. Furthermore, when hematite ore is reduced to magnetite its structure changes from hexagonal close-packed (HCP) to cubic which causes volume expansion by 23%. Due to this volume expansion, several cracks are generated in the lumps. Therefore, reducing gas can pass easily which enhances the reduction of ore. However, in magnetite ore, this phenomenon does not occur. Therefore, the magnetite ore is generally crushed and ground to fines and after pelletizing and heat hardening these are used in iron

making furnaces. These pellets show much better reducibility due to the presence of pores which allow gas to pass through.

Undersized iron ore fines generated in raw materials handling section are used in sinter plant in regular basis. The micro fines like blue dust and concentrates available from the lean grade ore are used in pelletizing plant. Therefore, in present scenario these undersized fines are not a problem in steel plant. However, a considerable part of other fines generated in deferent sections of plants such as blast furnace flue dust (BFD), LD sludge (LDS), mills scale etc. still remain unused. A brief account of it is given below.

Different types of wastes generated in a typical steel plant with their major constituents, harmful, or beneficial, are listed in Table 1 (Yadav et al. 2002). These oxide wastes are in general recycled as a part of the charge mix during sintering of iron ore fines. It has been reported that several sinter plants in the world recycle (Basu et al. 1997, 2002) up to 180-200 kg of waste oxides per ton of sinter, whereas in India this rate is slightly lower, at 100-170 kg per ton of sinter (Basu et al. 2002). Some iron oxide wastes, like LD and BF sludge, contain zinc and alkalis for which they are not favorable for direct recycling. In India, fortunately, the zinc content of LD sludge is not adverse (Basu et al. 2002). However, these waste materials except slag have excessive fineness below 100 µm size which cannot be used fully in the iron ore sintering due to the permeability problem. These unused iron oxide fines are termed as 'Waste Iron Oxides' (WIO). The typical analysis and generation rate of some of the important WIO are shown in Table 2.

Uses of these waste oxides are imperative to reduce the environmental hazards and conservation of natural resources. It has been mentioned above that undersize iron ore fines available from raw materials handling sections are used in the conventional sintering practice. On the other hand, the microfines of iron oxides (concentrates) available from beneficiation plant are used in pelletizing practice. However, these conventional practices are not sufficient to use all iron oxide microfines generated in steel plant as well as in the mines area. Therefore, a considerable improvement in present

Table	e 1.	Different	waste	materials	s in	steel	plants
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technology is required. Some innovative developments, car-
ried out on their utilization are presented in brief in the
proceeding sections of this paper.

2. Some important development on micro-fines utilization

In order to utilize micro-fines, pelletizing is the conventional practice since several decades. However, innovative approaches are required to improve the use of micro-fines in sintering. In some of the micro-fines, there are limitations related to their chemistry like alkali and high gangue problems for using in BF. However, these can be used in either steel making as coolant or in alternative processes. Our approaches for the development on utilization of micro-fines are described as follows.

2.1. Utilization of steel plant waste and iron ore fines

With the advent of continuous casting, which reduces the supply of home scrap, steelmakers are facing a daunting task of process adjustment to accommodate scrap from open market with widely varying chemical composition. Fluctuations in availability and chemistry of market scrap are also problems of using scrap.

Iron ore lump is usually charged into the basic oxygen furnace (BOF) as a coolant (as well as a stirring agent); also, it is often used as a scrap substitute. These contain lower amount of residual elements such as copper, zinc, nickel, and molybdenum. In recent times, methods have been developed to use waste oxides as well as sponge iron in the BOF in place of ore.

In the basic oxygen steelmaking, burnt lime consumption is in the range of 18–45 kg per ton of steel produced. Use of lump lime of specific sizes causes rejection of all undersized lime, adding to the cost of production. Moreover, lime, being a lighter material, does not quickly go into the solution during the bath turbulence caused by the oxygen blowing and, being a refractory oxide, increases the blow time of refining. A

Wastes	Sources	Desirable constituents	Undesirable constituents	Harmful constituents
BF slag	Blast furnace	CaO	Al ₂ O ₃ , SiO ₂	S, Na ₂ O, K ₂ O (for iron making)
BF dust	Dust catcher of blast furnace	Fe oxides, C	Al_2O_3 , SiO_2	Na ₂ O, K ₂ O (for iron making)
BF sludge	Gas cleaning plant of blast furnace	Fe oxides, C	SiO ₂	S, Na ₂ O, K ₂ O (for iron making)
External Desulphurization slag		CaO	S, SiO ₂	S, Na ₂ O, K ₂ O (for iron making)
LD slag	LD converter	CaO, FeO	Al_2O_3 , SiO_2	P (for steel making)
LD sludge	Gas cleaning plant of LD converter	CaO, FeO	-	Zn
Secondary steel making slag	Secondary steel making	CaO	Al ₂ O ₃	Al ₂ O ₃ , SiO ₂ (for iron making)
Mill scale	Rolling mills	Fe Oxides	-	Oil (for sintering)
Semi-calcined lime	Lime plant	CaO	Loss on ignition	

Table 2. Typical composition of waste from oxides (Ambesn 2007; Fadav et al. 2002; Basu et al. 2002)
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						Chemic	al analysis, wt%	6			
Wastes	Generation rate	Fet	CaO	SiO ₂	MgO	AI_2O_3	Р	S	С	K ₂ O	Na_2O
Iron ore fines	60% of total iron ore production	55–65	-	1–4	-	1-3.5	0.01-0.05	0.01-0.05	-		
Blue dust	-	60–67	-	1–3	-	1–3	0.02-0.05	0.02-0.05	-		
LD sludge	15–25 kg/tcs	59.1	10.8	1.84	0.81	0.90	0.11	-	-	0.28	0.15
BF sludge	1 kg/tcs	33.6	3.45	6.40	1.40	3.64	0.31	0.23	21	0.40	0.20
Mill scale	10–20 kg/tcs	70.2	0.31	0.55	0.16	0.27	0.03	-	-	-	-
Flue dust	1–2 kg/tcs	39.5	3.66	7.9	1.34	3.0	0.17	0.32	25.2	0.34	0.15

certain percentage of lime usually gets carried by the exit gas from the converter, increasing the load in the dust catching system.

The aforesaid problems associated with the use of scrap and lime necessitate identifying a suitable alternative feed material which will be free from such limitations. Lime iron oxide combination can yield a CaO-Fe_xO eutectic slag, which has melting point to be around 1230°C as shown in Figure 1 (Verein Deutscher Eisenhulttenleute 1981). Fluxing iron ore fines with lime powders and agglomerating it into a suitable agglomerate and using this agglomerate as flux may be one solution to get a low melting basic and oxidizing slag. Several investigators have agglomerated iron oxide fines in form of briquettes (Balajee et al. 1995; Dukelow et al. 1995; Lherbier and Green 1995; Landow et al. 1998; Catherine and Freuhan 2000), sinters (Irmler et al. 2003), or pellets (Imazumi 1991; Choi and Kim 2002) and used in BOF. But, there are certain difficulties about preparations of sinters and briquettes. For example, in sintering, the restriction of very fine materials and a high temperature requirement limit the scope of utilization of ultra fine iron ore. Similarly, in briquetting, organic binders are very costly and inorganic binders contain very high silica and alumina which increases slag volume in the downstream process. Therefore, a low-cost feed material in the form of fluxed iron oxide pellets or super fluxed sinter from waste iron oxides has been produced in our study. Such agglomerates in contact with the liquid iron bath may impart the following two benefits: (i) early formation of primary slag, facilitating the onset of refining reaction and hence a reduction in tap-to-tap time and (ii) better utilization of raw materials/wastes.

2.1.1. Binderless cold bonded super fluxed pellet

In order to produce the low melting oxidizing flux, the waste oxides of steel plant and iron ore fines have been agglomerated in presence of high percentage of burnt or hydrated lime. Pelletizing route has been followed. Since, the pellet needs to be charged in to BOF its minimum handling strength is required. Induration at high temperature can increase the pellet strength, however, it is a very cost intensive process. In this purpose many investigators have used costly binders. But, binders contain high alumina and silica which may increase the slag volume in the downstream process. Therefore, a new technique has been developed to bind the fluxed pellet by treating it with industrial waste gas, which contains a significant amount of carbon dioxide [16]. This process neither requires any high temperature curing nor any binder. Pellet thus prepared is termed as 'Fluxed Lime Iron oxide Pellet' (FLIP)

Initially, during pellet making calcined or slacked lime in presence of sufficient moisture provides green bonding. After drying also a poor bonding is observed in pellet. Further, upon treatment with industrial waste gas/CO_2 at room temperature the hydrated lime reacted with CO_2 gas to impart the cold strength. The mechanism for this room temperature strengthening is as follows (Pal et al. 2009a, 2009b)

When the lime (CaO), present in the base mixture, comes in contact with added water before pelletizing, it reacts to form calcium hydroxide:

$$CaO(s) + H_2O(l) = Ca(OH)_2(s); \Delta H = -65.3kJ$$
 (1)

On pelletizing, this calcium hydroxide provides primary bonding amongst the particles and imparts strength to the green pellets. During subsequent treatment of the partially air-dried green pellets by a stream of CO_2 , the $Ca(OH)_2$ transforms to $CaCO_3$ according to the following reaction:

$$Ca(OH)_2(s)+CO_2(g) = CaCO_3(s)+H_2O(g); \Delta H = -69.41kJ$$
(2)

 CO_2 enters through the pores of the partially dry pellets and forms carbonate. The XRD pattern of lime fluxed pellet before and after CO_2 treatment is shown in Figure 2 (Pal et al. 2009a). After CO_2 treatment, the figure mainly shows $CaCO_3$ peaks



Figure 1. Binary Phase diagram of Fe₂O₃-CaO.



Figure 2. XRD pattern of pellet (FLIP) before and after CO₂ treatment.

along with hematite. It indicates that almost the entire lime has converted to carbonate. The optical microstructure in Figure 3 (Pal et al. 2009a) shows the distribution of the hematite particles, CaCO₃, and pores. The calcium carbonate formation imparts good strength to the pellet. The molar volumes (Perry and Chilton 1973) of CaCO₃ and Ca(OH)₂ are 34.10 cm³/mole and 33.59 cm³/mole, respectively. In Reaction (2), one mole of CaCO₃ is produced from one mole of Ca(OH)₂. Thus, this transformation yields 1.52% volume expansion for lime. This volume expansion helps pellet to decrease the porosity and increase in the compactness. Thus, the transformation of Ca (OH)₂ to CaCO₃ plays a predominant role for strength development of the pellets (Pal et al. 2009a, 2010).

Cold crushing strength (CCS) of FLIP after CO_2 treatment for varying lime content and duration of treatment is shown in Figure 4 (Pal et al. 2009a). It is obvious from the figure that 25% lime with 15 min of treatment time shows maximum CCS and beyond 25% lime, the CCS again deteriorates, because excessive CaCO₃ formation can develop internal stress and micro-cracks. XRD pattern (Figure 2) shows calcium hydroxide and hematite before treatment and mainly calcium carbonate and hematite with minor quantity of calcium hydroxide after treatment. This reveals that after CO_2 gas treatment for 22 min some Ca(OH)₂ is retained. The quantity of retained Ca(OH)₂ is measured by weight loss analysis at different temperature and presented in Figure 5



1- Iron ore particle, 2- Lime(CaCO₃/Ca(OH)₂, 3- Pore

Figure 3. Optical microstructure of untreated and CO₂ treated (15 min) pellet (FLIP) samples (a) Untreated, (b) CO₂ treated.



Figure 4. Effect of CO₂ treatment time on CCS of pellet.



Figure 5. Amount of transformed CaCO₃ and residual Ca(OH)₂ in pellet versus treatment time.

(Pal et al. 2009a), which may be around 5 wt% after 15 min treatment. Thus, CO_2 treated cold bonded fluxed lime pellet has been prepared which has a finely mixed structure of iron oxide and carbonate. It has very good strength properties.

It has been reported (Pal et al. 2009a) that very high free moisture in green pellet provides hindrance to the passage of CO_2 gas entering in the pellet and makes the reaction very slow. On the other hand, a very dry pellet is not prone to react with CO_2 gas. The maximum reaction has been found when free moisture in the pellet is between 1.5 and 2 wt%. Dry slaked lime (Ca(OH)₂) does not absorb carbon dioxide unless a trace of moisture is present (Parkes 1961). Thus, the presence of a small amount of moisture appears to catalyze the CO_2 absorption process. Possibly, the free moisture present in the pellet first reacts with CO_2 gas to form carbonic acid that subsequently reacts with $Ca(OH)_2$ to form $CaCO_3$ as per the reactions in Equations (3) and (4).

$$Ca(OH)_2 + H_2CO_3 = CaCO_3 + 2H_2O$$

(4)

Further, the above reaction (Equation 2) generates a lot of exothermic heat which helps in the removal of uncombined moisture produced from the reactions in Equations (2) or (4). Thus, the pellets become dry. Here, instead of pure CO_2 , waste gases from steel plant containing CO_2 (viz. blast furnace off gas) may also be used, which is obvious from Figure 6 (Pal et al. 2009a).

It can be mentioned that CO_2 has also been used by many other investigators for the strength improvement in many other purposes. For example, investigators (Franklin et al. 1965) have found that alkaline earth metal oxides, in the presence of borax or non-metallic chloride, convert into carbonates by reacting with CO_2 gas at room temperature and improve the strength of the iron ore pellets by cold bonding. In another study, any in-situ carbon in pellet can enhance the reduction of cold bonded pellet in direct reduced iron (DRI) production (Pal et al. 2015a). Accordingly, carbon was used in the pellet for making intimate contact with iron oxides and

$$H_2O + CO_2 = H_2CO_3 \tag{3}$$



Figure 6. Effect of gas composition on the CCS of pellet at varying treatment times.

the cold bonding technology was developed to prepare coal composite pellet. Some investigators (Aota et al. 2006) used Alumina cement as a binder to obtain a high mechanical strength even at elevated temperatures. For the same purpose, carbon composite pellets with cement binding were produced by CO_2 curing of the green pellets at room temperature (Yanaka and Ohno 1991; Pal and Venugopalan 2015) and also at 100–300°C (Liu 2003) and good strength was observed. The pellets developed from these processes have been used in DRI making. Fluxed pellets containing carbon were also prepared and cured using CO_2 earlier (George 1968). However, only up to 5% coal could be used in these pellets.

Let us see what the other properties of the pellet are. On heating, the FLIP slowly disintegrates because of dissociation of calcium carbonate to CaO and CO₂. However, it takes sufficient time and before that the melting of the FLIP starts. Melting point of the FLIP has been experimentally found out to be 1180°C (Pal et al. 2009b). It dissolves very fast in the hot metal bath. Dissolution time at varying temperature is shown in Figure 7 (Pal et al. 2011), which is around 30 min at 1400°C hot metal temperature. After melting/dissolution, its slag has been analyzed by XRD and, as shown in Figure 8 (Pal et al. 2011), contains mainly Ca-iron oxide low melting slag. This may be favorable for the refining.

The performance study of FLIP in 8 kg scale refining bath has been carried out and the results are shown in Figures 9 and 10 (Pal et al. 2010). Both, decarburization and dephosphorization are much faster than the normal blowing practice with lump lime. This is because of basic and oxidizing slag generation at the early stage of blow. Si and Mn removal was found to be normal, slag foaming was within the control, blow time and oxygen consumption could be reduced by 15–20%. Thus, FLIP has a very good application potential for faster refining of BOF bath.

2.1.2. Coke breeze free sintering of steel plant waste

The above process of FLIP preparation is an agglomeration process for mixture of flux materials by cold bonding



Figure 7. Effect of bath temperature on dissolution time of FLIP.



Figure 8. XRD pattern of FLIP after melting at 1245 °C.



Figure 9. Performance of FLIP in decarburization of hot metal bath during oxygen blowing.

without using any costly binder. Since, there is no heating, low melting slag formation is happened when these are charged in the steel making bath. A prefused low melting flux may be more advantageous from melting and dissolution point of view which will enhance the formation of basic and oxidizing slag at the early stage of blowing. In order to develop a partially prefused synthetic flux (PSF), sintering process was adopted wherein the combination of iron oxide and lime fines and blast furnace flue dust (BFD) have been used (Pal et al. 2013a, 2013b; Pal and Venugopalan 2015). Main objective was to utilize ultrafine iron oxides wastes, such as Linz-Donawitz converter Sludge (LDS) and BFD in form of micro-pellets for developing a prefused sinter. Good binding property of calcined lime offered green bonding in the micro-pellets (Pal et al. 2013a). Thus, no external binders were used. The heat of oxidation of metallic iron, wüstite, and magnetite in LDS and C in BFD was used to get sufficient temperature during sintering (Pal et al. 2013b) as per Equations (5)-(10) and thus avoiding the use of coke breeze in the sinter mix. The



Figure 10. Performance of FLIP in dephosphorization of hot metal bath during oxygen blowing.

sinter would be a combination of Fe-oxide and CaO and free from combined moisture as shown in Figure 11 (Pal et al. 2013b) and termed as PSF.

Fe +
$$1/2O_2$$
 = FeO; ΔH^0 = -266.9 kJ mole⁻¹ (5)

$$3\text{FeO} + 1/2\text{O}_2 = \text{Fe}_3\text{O}_4; \Delta \text{H}^0 = -319.7 \,\text{kJ}\,\text{mole}^{-1}$$
 (6)

$$2/3Fe_{3}O_{4}+1/6O_{2} = Fe_{2}O_{3}; \Delta H^{0} = -76.4 \text{ kJ mole}^{-1}$$
 (7)

$$C + 1/2O_2 = CO(g); \Delta H^0 = -110.5 \text{ kJ mole}^{-1}$$
 (8)

$$C+O_2 = CO_2; \Delta H^0 = -393.5 \text{ kJ mole}^{-1}$$
 (9)

$$CO + 1/2O_2 = CO_2; \Delta H^0 = -283.5 \text{ kJ mole}^{-1}$$
 (10)

The chemical composition of the produced sinter was found to be Fe_{total} : 40%, CaO: 37% SiO₂: 1.5%, Al₂O₃: 1.4% and Na₂O and K₂O are 0.34% each and rest is oxygen combined with iron. Most of the above phases found in Figure 11 are low melting and have high FeO content and high basicity. From the TG-DTA study it has been found that the softening



Figure 11. XRD pattern of PSF prepared.

point of sinter was 1180°C and melting completes at around 1280°C.

Other physical properties like Shatter index, tumbler index, and abrasion index were found to be 90%, 65–70%, and 8–9%, respectively for 35–37% lime containing PSF (Pal et al. 2013b). With further increase in lime these properties deteriorate. Furthermore, weathering property of PSF increases due to the presence of free lime in sinter beyond 37% lime. Therefore, the lime percentage was optimized at the range of 30–37 wt%.

This sinter dissolves very fast in the hot metal bath as shown in Table 3 (Pal et al. 2015b). While pure lump lime not at all dissolves in the liquid bath, PSF dissolution rate is 30 sec/g. This is much less than pure lime in FeO rich bath. This reveals that this flux can produce basic oxidizing slag at the early stage of blow and improve the refining process.

Refining study in 8 kg bottom blowing facility has been carried out to assess the performance of PSF. In Figures 12 and 13 (Pal et al. 2015b), the refining results are compared with only lime fluxed heat and lime plus iron ore fluxed heat.

Performance of PSF in refining of hot metal shows faster removal of C and P because of formation of low melting basic and oxidizing slag at the initial stage of blow. The blow time and oxygen consumption was reduced to around 40% and slag foaming was decreased. The refining process

Table 3. Dissolution time of different PSF and pure lump lime in hot metal bath at 1400 $^{\circ}$ C.

Material	Weight of lump, g	Dissolution time, sec	Specific dissolution time (Sec/g)
Pure lump lime in hot metal	0.5034	Does not dissolve/melt	-
Pure lump lime in FeO rich slag	0.5132	75	146
PSF (contained 35% lime)	1.467	44	30

is much faster than FLIP charging also. Thus, the developed PSF can be used as a flux material in BOF with full replacement of iron ore and partial replacement of lump lime.

2.2. Development of pelletizing practice to improve pellet quality

Pelletizing of iron ore is a very well known and technocommercially established agglomeration process. In many steel plants, pellets are used in blast furnace to replace lump ore and sinters partially. It is also used in direct reduced iron (DRI) making in rotary kiln and vertical shaft. Maintaining the quality of pellets and subsequent improvement is required to increase productivity, decrease energy consumption, and using lean ores and micro-fines.

2.2.1. Replacement of bentonite in iron ore pellet

Bentonite is universally used as binder for green pellet making. However, due to its high alumina and silica content, it proportionally increases Al₂O₃ and SiO₂ content of pellet. Finally, it increases the slag volume in downstream process of blast furnace iron making and increases the energy consumption. Moreover, the bentonite is a costly binder. Therefore, its replacement is required with a cheaper binder which has lower alumina and silica content. This may be either organic binder or inorganic binder. Eisele and Kawatra (2003) have reviewed on the several binders used so far. They have reported that apart from bentonite, the use of a numerous types of alternative binders such as starch, dextrin, Peridur, lignin, molasses, sodium silicate, fly ash, quick lime, cement etc. have been tried out worldwide. However, bentonite is considered to be the most suitable binder for iron ore pelletizing. The binding mechanism of bentonite in iron ore pellets has been studied by Kawatra and Ripke (2003a). Its effectiveness of



Figure 12. Performance of PSF in decarburization of hot metal bath during oxygen blowing.



Figure 13. Performance of PSF in dephophorization of hot metal bath during oxygen blowing.

bonding has also been studied by measuring plate water absorption (Kawatra and Ripke 2003b).

Many investigators have used organic binders. Bitumen, a by-product of mineral oil processing, was found to improve green and dry compressive strength of pellet (Meyer 1980; Ansari et al., 1984). Sastry et al. (1985) reported cellulose derived organic binder, 'Peridur' as effective binder for pelletizing of iron ore. Srivastava et al. (Srivastava et al. 2013) also found good properties of iron ore pellets using 0.1% peridur. Shivaramakrishna et al. (1990) reported that starch-based binder could be used without any treatment to make cold bonded ore-coal pellet for using in DRI production but did not mention for blast furnace quality pellet making. Polyacrylamide wetted by water molecules formed long molecular chains and provided strength in pellet. However, when the pellets were heated to 105°C, organic binder burnt out or evaporated resulting a highly porous pellet (Chizhikova and Vainshtein 2003). Organic binders viz. starch, dextrin, and alginate found to provide good green drop number and dry compressive strength but they failed to improve the strength in the region of high temperature because, these additives were burnt off before commencing recrystallization due to which widespread application in production of fired pellet have not been found (Ball et al. 1973).

The organic binders, hemicellulose, sodium lignosulphonate, and lactose monohydrate were also able to provide good green as well as strong indurated pellets. Only 0.5% lignosulphonate has been found to be sufficient in developing required strength (Haas et al. 1989). Srivastava et al. (2013) also used sodium lignosulphonate (NLS), an extract from paper mill waste and compared with a series of organic binders in magnetite concentrate pellet. Use of lignosulphonate salt had also been examined under the scheme of novel binder development (US patent 4659374) and an encouraging result had been observed (Alanko and Atwell 1987).

From the above it is evident that organic binders may have a potential to use in iron ore pellet making. Organic binder does not contain any significant alumina and silica. However, during drying and induration in strand, the temperature of green pellets gradually increases. Organic binders gradually evaporate and completely disappear at certain temperature (600-700°C). Accordingly, organic binder loses its strength properties and pellets become less compact/weak. Coppersmelting slag (Cu-SS) has been used for this purpose as it contains a considerable amount of iron oxides (mainly FeO). FeO and Fe₂O₃ present in Cu-SS oxidize in induration atmosphere and provide diffusion bond above 500°C that maintains the strength of the pellet during drying in spite of the evaporation of NLS. Therefore, NLS provide green and dry strength and Cu-SS provide dry strength above 500°C (Ammasi and Pal 2016).

In conventional practice, limestone (CaCO₃ mineral) is used as CaO input in pelletizing. However, lime stone fines have so poor green bonding property that it is inferior to iron ore fines too. Thus, it calls for using bentonite as binder. Burnt lime contains >90% CaO, 1–3% SiO₂, and Al₂O₃ each with other minor impurities. When it comes in contact with water, it forms Ca(OH)₂ and disintegrates into very fine form. Due to this fineness it shows excellent green binding properties. Therefore, researchers have used this for replacing bentonite either partially or fully.

De Sauja (De Souza 1976) has used hydrated lime in pelletizing and reported to achieve good cold crushing strength (CCS: 367 kg), swelling index (18.5%) and reducibility index (69%) of indurated pellets. Eisele and Kawatra (2003) have also found very high green compressive strength (4 kg/pellet), drop numbers (10.4), and dry compressive strength using hydroxide lime. However, some investigators (Sarkar et al. 2013) have observed severe cracking in green and dry pellets for using hydroxide lime due to the loss of plasticity on the use of high amount of hydrated lime. Holley (1985) has also found disintegration of green pellets due to the hydration of lime resulting in expansion. Therefore, the complete hydration of lime is required before making green pellet, because, hydration of calcined lime after making the pellet may form cracks or crumbling the pellets into fines. Other investigators (Anon 2013) have also observed the similar phenomena. Furthermore, when the calcium hydroxide is mixed with bentonite, it may decrease the efficiency of bentonite as a binder. This is because it replaces the more efficient sodium ion (Na+) with calcium ion (Ca^{2+}) in the interlayer of bentonite and converts it to the more calcic and less efficient one, resulting in the deterioration of the pellet properties (Ahmed and Mohamed 2005; Fan et al. 2010; Pal et al. 2014a).

It is obvious from the above reported literature that calcined lime or hydrated lime has enough potential to provide good bonding in green pellets. However, due to the crack formation tendency and some other disadvantages, this is not widely used in the plant practice, presently. These problems are may be due to the improper operating parameters (making technique, induration temperature *etc.*) causing incomplete hydration before pelletizing as well as unfavorable basicity or other undesired composition of the pellets. Furthermore, high alumina hematite pellets shows very high RDI (Pal et al. 2015c) and a suitable quantity of MgO addition may also solve these problems. Thus, the pellet chemistry and making parameters have to be optimized to prepare good quality calcined lime pellet without bentonite. Moreover, some investigators as mentioned above have used bentonite also with the calcined lime, but it deteriorates the quality of bentonite as discussed in the previous section. Since calcined lime has very good bonding property, it is imperative to develop a suitable technology, which can eliminate the above problems. It will help in reducing silica and alumina load in the pellets and in the downstream process of blast furnace iron making.

In the recent study (Pal et al. 2014a) first, several parameters (MgO content, basicity, fineness *etc*) have been optimized using olivine as MgO source and limestone as CaO source and bentonite as binder. Subsequently, the pellets were prepared with calcined lime or hydrated lime as per optimized conditions of basicity and wt% of MgO replacing the bentonite fully. Some of the important results are presented as follows (Pal et al. 2014a).

The green pellet properties of calcined lime pellet without bentonite and lime stone plus bentonite added pellets are shown in Table 4 (Pal et al. 2014a). The GCS and drop numbers of calcined lime added pellets are much higher than bentonite added pellet because of the good green bonding property of calcined lime. Dry compressive strength is relatively lower than bentonite added pellet but, it is well above the acceptable limit. Now on heating during drying the moisture combined with hydrated lime starts to evaporate at and above 400°C. Therefore, there is a chance of decreasing the strength of calcined lime pellet. To assess its strength and stability during drying, the pellets were heated at 800°C in a chamber furnace and CCS was measured which were found to be 6.5 kg/pellet and 3 kg/pellet for bentonite added pellet and calcined lime pellets, respectively. It loses the strength at drying temperature. However, the load test at hot condition was done in a chamber furnace at 900°C (Figure 14) (Pal et al. 2014a), which confirms its stability during drying.

Other metallurgical properties of calcined lime pellets are comparable with the limestone plus bentonite added pellets as shown in Table 5 (Pal et al. 2014a). Silica and alumina content of calcined lime added pellet (Table 6) (Pal et al. 2014a) has been found to be lower than the limestone plus bentonite added pellet, which will be beneficial in blast furnace iron making. In brief, the calcined lime can provide better green pellets properties as well as desired strength at high temperature without any bentonite addition. It also provides required basicity to the pellet. Thus, both limestone and bentonite can be replaced in pellet and hence alumina and silica load will be

 Table 4. Green and dry pellets properties of calcined lime and limestone plus bentonite added pellets.

Lime flux added	Basicity	Moisture %	MgO %	Bentonite %	GCS, kg/ pellet	Green drop No	DCS kg/ pellet
Limestone: 0.95%	0.25	8.5	1.0	0.3	1.3	9	5.5
Calcined lime: 0.45%	0.25	8.8	1.0	Nil	1.5	12	3.5



Heating under load

Figure 14. Photograph of calcined lime fluxed pellets during heating under load.

reduced. Thus, it is advisable to use calcined lime in pellet making that is available from the lime calcinations plant in almost all integrated steel plant.

2.2.2. Improving reducibility of hematite ore pellet

Reducibility of pellet is an important property. Pellet with good reducibility can improve the indirect reduction in blast furnace and reduces the energy consumption. Though, pellet generally has better reducibility than lump ore and sinter due to its micro-porosity, it depends upon several parameters viz, chemistry, physical structure, induration temperature, shapes etc. Many researchers have tried to improve the reducibility of pellets.

A dolomite (Bin et al. 2013) and other MgO-bearing materials such as olivine, magnesite (Pal et al. 2015d; Md. et al. 2016) and serpentine were effectively used as basic fluxing materials to improve both reducibility and reduction degradation index. During induration of MgO containing iron oxides, MgO diffuses in the Fe₂O₃ lattice forming magnesio-ferrite (MgO Fe₂O₃) spinel (melting point 1713° C). The magnesioferrite in the fired pellets improves their strength during reduction and increases the softening temperature. Porosity, pore volume and pore diameter in pellet also increases in presence of MgO in pellet (Bin et al. 2013). Nasr et al. (1995) studied on the reduction of NiO doped hematite compacts wherein, the reduction rate was gradually increased with the increase in reduction temperature and NiO content due to the formation of more porous compound, NiFe2O4 that is more reducible than iron oxide. Botelho et al. (2014) developed a process of improving reducibility of iron ore by adding metallic Ni containing materials because the metallic Ni provides the catalytic effect for the reduction. Presence of Cr³⁺

 Table 6. Chemical analysis of limestone added and calcined lime added indurated pellets.

Pellets	Bentonite added, %	Fe _{total} , %	CaO, %	SiO ₂ , %	Al ₂ O ₃ , %	MgO, %	Basicity
Limestone plus bentonite added	0.3	65.1	0.64	2.59	2.57	1.04	0.247
Calcined lime added	0	65.5	0.61	2.41	2.51	1.02	0.253

also increases the reducibility of iron oxide by CO due to catalytic effect of partially filled d-band and unpaired election (Sarangi and Sarangi 2011).

Investigators have tried to improve the reducibility by changing different parameters mainly through the change in chemistry and phase formation by different additives and fluxes. However, in our study reducibility index (RI) of hematite ore pellet has been increased with respect to the current level at the plant (Tata Steel, India) (Pal et al. 2017b). However, other properties were maintained in the acceptable limit. This has been done by optimizing the physical parameters of pelletizing such as induration temperature, size distribution of fines, and improving apparent porosity without changing any chemistry of green pellets or additives (Pal et al. 2017b). The effect of induration temperature on reducibility of iron ore pellet is shown in Figure 15 (Pal et al. 2017b) that it decreases with increasing induration temperature. However, too much decrease in induration temperature may hamper the strength and other properties of pellet. Therefore, an optimization study has been carried out. Optimum values of parameters have been found as induration temperature: 1275°C, lime stone size: below 350 mesh, coal size: below 350 mesh, for the iron ore Blaine fineness of 2855 cm^2/g . The properties of pellets with these optimized values are shown in Table 7 (Pal et al. 2017b). It is obvious from the table that reducibility index (RI) could be improved by 7-8% point and other properties viz. CCS, reduction degradation index (RDI) and swelling index has also been improved. Tata Steel now uses around 1275°C induration temperature and $2700-2900 \text{ cm}^2/\text{g}$ Blaine fineness.

2.2.3. Lowering reduction degradation index of hematite pellet

Degradation of pellets during low temperature reduction is happened due to lattice distortion and internal stress generation due to hematite to magnetite transformation. This is an undesirable property of iron ore pellet. Maximum reduction degradation index (RDI) of around 20% is considered to be tolerable in blast furnace. However, most of the Indian ores and many other hematite ores contain high alumina has high RDI in their pellet. A suitable flux addition has been done by several investigators. Serpentine has been used (Wang and

 Table 5. Comparison of properties of pellets with limestone plus bentonite and calcined lime.

Pellets	Bentonite added, %	Induration temperature, °C	CCS, kg/ pellet	RI, %	RDI, % of -3.15 mm	Swelling Index, %	Apparent porosity, %
Limestone plus bentonite added	0.30	1280	310	75.5	11.8	14.7	22.6
Calcined lime added	0	1280	312	74.7	12.1	14.9	23.54



Figure 15. Effect of induration temperature on RI of pellet.

Table 7. Properties of pellets with optimized values.

	1						
	Blaine			RI,	RDI,	SI,	AP,
Pellet	No	Basicity	CCS	%	%	%	%
Reference pellet	2855	0.32	249	69.5	20	14.1	9.9
At Optimized condition	2855	0.32	374	77.9	12.4	11.3	9.5

Wu 2014) to reduce RDI which help in forming high melting point magnesium wustite. Olivine has also been used (Forsmoa and Hagglund 2003) in iron ore pellets to decrease DRI. However, Semberg et al. (2011) found the appearance of cracks in olivine added magnetite ore along the boundary between secondary magnetite and magnesioferrite during reduction at 600-700°C. The similar crack formation in olivine added magnetite pellet has been found by Lingtan et al. (1983) though it improved the high temperature reducibility of pellets. The basicity of pellet has an important role in reducing the RDI of pellet. Umadevi et al. (2011) found better RDI of pellet in the range of 0.33-0.78 than 1.5 basicity pellets. Since, high basicity pellet shows high RDI, Shigaki et al. (1990) prepared two layered pellet with relatively low basicity at the shell and high basicity with high MgO content at the core. As shell had lower RDI, the cracks did not propagate and overall RDI of the pellet was found to be decreased. CaO and MgO bearing mineral can reduce RDI to a great extent (Gao et al. 2014; Md. et al. 2016). However, the scope of flux addition is not always available. Moreover, added flux can effect on many other properties such as reducibility, porosity etc. of pellet. Apart from the flux addition, if carbon is added in pellets, some hematite in pellet reduces to magnetite during induration (Pal and Venugopalan 2015). This magnetite formation helps to reduce RDI. However, Umadevi et al. (2008) and Umadevi et al. (2013)) reported that the reduction of RDI with addition of coke breeze is limited up to a certain carbon level after that RDI again increases with increase in carbon.

RDI of iron ore sinter has been reduced by salt solution treatment (Taguchi et al. 1990; Larrea et al. 1998; Xu et al. 2010). This technique of treatment has been used on reduction of RDI in iron ore pellet as iron ore pellets also have micro-pores. The study has been carried out to identify the effect of varying concentration of several salt solutions such as, CaO, MgO, MgCl₂, CaCl₂ and NaCl of under vacuum (45 mm Hg) to reduce RDI and their optimum levels has been investigated (Ranjan and Pal 2016).

Treatment of hematite pellets with CaO and MgO solution does not show any reduction in RDI of pellet as these oxides have very low solubility in water. Among all these salts NaCl showed best performance on reduction in RDI. It is envisaged from the Figure 16 (Ranjan and Pal 2016) that with increase in concentration of NaCl solution, RDI decreases drastically from very high level (86%) to very low level (2.4%) only at 6% solution concentration. The apparent porosity also decreases with increase in salt concentration. The main reason of decreasing RDI would be the blockage of micro-pores and hindrance of reducing gas for the reduction at low temperature. Furthermore, conforming to Xu et al. (2010) Cl⁻ ions and Fe₂O₃ in the sinter have surface reaction, which enhances the binding energy of Fe-O band in hematite. Due to this, during low temperature reduction at 500-600°C it is more difficult for CO to despoil of O²⁻, which causes decrease in reduction rate (Xu et al. 2010; Ranjan and Pal 2016). Thus, inhibition of Fe₂O₃ to Fe₃O₄ reduction at low temperature prevents generation of stress induced cracks due to crystal transformation, which help reducing RDI (Ranjan and Pal 2016).

RDI has been found to be reduced by 2.5% in acidic pellet, when 6% NaCl solution was used for the treatment. However, it shows high chloride input in pellet and poor degradation resistance at relatively high (>800°C) temperature and breakage. In contrary, the fluxed pellet (Basicity: 0.25), treated with only 2% NaCl solution under vacuum, showed very low RDI (6%). This pellet does not show any breakage during reduction at relatively high (>800°C) temperature. Thus, the fluxed pellets with only 0.25 basicity treated with only 1–2% NaCl solution at room temperature under vacuum have very low RDI (6–10%) with good CCS (330 kg/pellet), reducibility (75%) and swelling index (13%)(Ranjan and Pal 2016). Such pellets are likely to be useful for blast furnace iron making.

2.3. Innovation in sintering for increasing use of microfines



Figure 16. Effect of NaCl solution on reduction of RDI in acidic pellet.

Conventional sintering process for iron ore has limitation of accepting micro-fines, because it affects on the permeability of the sinter bed and decrease productivity and deteriorates the quality. Therefore, a suitable technology needs to be developed to increase the fine acceptability of sinter bed.

2.3.1. Micropelletizing and sintering of iron ore micro-fines Micro-fines (below 100 mesh) has been micro pelletized by several investigators and mixed the micro-pellets with normal sinter mix. Several investigators (Anon 1997; Nakano et al. 2000; Chaudhary et al. 2001) prepared micro-pellets of these fines and produced BF grade sinter. However, sufficient cold handling strength of these micro-pellets is required to minimize fines generation during their transportation, handling in granulation drum and charging in sinter strand. Further, the strength is also necessary to withstand the load of sinter bed during sintering. Several investigators (Rankin and Rolloer 1985) have explored microfines utilization in the sintering bed by pre-balling the green mix in presence of water in the secondary drum before charging in the bed and found a good result. The performance of pre-balling was further improved by addition of hydrated lime in sinter mix. However, they achieved only up to 30% microfines utilization. Microfines of iron ore with fluxes were pelletized into 2-6 mm pellets and named as 'micro-pellets' (Panigraphy et al. 1989) and used in the sinter mix. Much better utilization has been observed.

Coal composite iron oxide micro-pellets (2–6 mm size) were produced through an innovative technique, wherein lime and molasses were used as binding materials for micro-pellets (Pal et al. 2015a). The micro-pellets were subsequently treated with CO₂ or industrial waste gas for chemical bond formation. At very high carbon level of 22 wt% (38 wt% of coal), cold crushing strength of the micro-pellets was 2.5–3 kg/cm² and abrasion index was 5–9 wt%, which appear suitable for cold handling. These micro-pellets have a great potential for use as heat source in smelting reduction in iron making and sintering to reduce coke breeze etc. The properties of micro-pellets prepared from iron ore micro-fines with three different C sources viz. coal, blast furnace flue dust (BFD) and coke fines are shown in Table 8 (Pal et al. 2015a).

Since the micro-pellets prepared in this study contain carbon and have very good handling strength, they can be used in sinter bed to reduce the coke breeze consumption in sintering as well as to improve fines utilization. The feasibility test on this was carried out in a 12 kg scale sintering pot (Pal et al. 2015a). Here, the green sinter mix containing iron ore fines, coke breeze and fluxes were mixed with the BFD-added or coke-added micro-pellets and sintered in a 12 kg capacity down draft sinter pot (150 mm internal dia. and 470 mm long). The temperature of the sinter bed was found to be raised up to 1350°C (Pal et al. 2015a). The properties of produced sinter viz. sinter yield, shatter indices, and abrasion indices are found to be very good and acceptable (65%, 91% and 5%, respectively). It may be noted that coke breeze consumption in sintering with developed BFDadded and coke-added micropellets are 4 and 3.4 wt%, respectively. However, in usual sintering it is 6.5 wt%. Thus, it reduces the coke breeze consumption by 30-40 wt% without affecting the sinter quality.

Table	8.	Properties	of	micro-pellets	prepared.
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Molasses (wt%)	Lime (wt%)	C-bearing material (wt%)	lron ore conc.	CCS, kg/ pellet	Drop Nos	Abrasion index, % (15 kg sample)
4	10	Coal: 38	Rest	4.0	100	9.97
4	10	BFD: 38.7	Rest	4.7	130	8
4	10	Coke fines: 18	Rest	4.3	130	8.5

2.3.2. Development of pellet-sinter composite agglomerate (P-SCA)

The burden combination with acidic pellet and super fluxed sinter can improve the utilization of fines in iron making. For the micro-fines utilization, pelletizing is a suitable route. However, it shows very high energy consumption in its induration and hardening. To avoid costly induration, hybrid pelletizing (Sakamoto et al. 1989; Pal et al. 2014b) was done for utilizing micro-fines, wherein the green pellets were coated with carbon powder and then sintered in a sinter bed to make a composite mass, called hybrid pelletized sinter (HPS). HPS may disintegrate in to individual pellets during treatment and transportation due to their inadequate contact area between fired pellets (Jiang et al. 2010). However, conforming to Niwa et al. (1993), this process has been implemented in Japan and showed improved blast furnace productivity.

The investigators (Jiang et al. 2010) have developed the composite agglomeration process (CAP), which has produced a composite mass of pellets and sinter wherein, acidic pellets were embedded in to the basic sinter mass. They found very good properties such as shatter index, tumbler index, reducibility index and reduction degradation index for magnetite pellets. They suggested using carbon in hematite pellets for heat generation in pellet and improve its strength, but the obtained strength was not reported.

National Metallurgical Laboratory (NML) has also developed composite agglomerate utilizing hematite ore wherein, in-situ heat generation in pellet was tried out with different materials viz. carbon, LD Sludge (LDS) and mill scale (Pal et al. 2014b). First, the green pellets were made from the micro-fines of -100 mesh as shown in Figure 17 (Pal et al. 2014b). Then it was mixed with sinter mix and the sintering was done in a pot of 10-12 kg capacity.

The good quality composite agglomerate was produced when LDS or mill scale were used as in-situ heat source in pellet. The formation of in-situ heat in pellet was happened by oxidation of metallic iron and its lower oxides (Fe, FeO, and Fe₃O₄ present in LDS) during sintering as per reactions in Equations (11)–(14).

 $Fe + 1/2O_2 = FeO; \Delta H^0 = -266.9 \text{ kJ mole}^{-1}$ (11)

$$3\text{FeO} + 1/2\text{O}_2 = \text{Fe}_3\text{O}_{4;}\Delta\text{H}^0 = -319.7 \,\text{kJ}\,\text{mole}^{-1}$$
 (12)

$$2/3Fe_{3}O_{4}+1/6O_{2}=Fe_{2}O_{3}\Delta H^{0}=-76.4 \text{ kJ mole}^{-1}$$
(13)

$$2Fe + 3/2O_2 = Fe_2O_{3;}\Delta H^0 = -823.4 \text{ kJ mole}^{-1}$$
(14)



Figure 17. Preparation of Pellet-sinter composite agglomerate.

At the initial stage, the pellets may absorb heat from the sintering gas to reach at the elevated temperature, then the oxidation reactions (Eqs. (11-14)) become faster and a significant quantity of heat (0.236 kJ/g of pellet) is generated inside the pellet. The in-situ heat in pellet exhibits the bond formation in pellet (Pal et al. 2014b). As above reactions do not produce any gas, the bonding seemingly becomes stronger to provide good CCS in pellet. However, if C is used as heat source CO or CO_2 gas formation may be happened and affect the bond formation which may weaken the pellet strength.

The properties of such P-SCA produced are shown in Table 9 (Pal et al. 2014b) and compared with usual sinter made from the same iron ore. It is obvious from the table that P-SCA has much better physical and metallurgical properties for the same (5.1%) coke rate. For achieving the comparable property, much higher amount of coke rate is required for usual sintering. This energy consumption was reduced by ~ 20%, while around 60% micro-fines utilization was possible. Due to the lowering energy consumption and coke rate reduction CO_2 emission was also

reduced. Thus, the process can be considered as energy friendly.

It may be mentioned that conventional pellet charging in blast furnace may create inhomogeneous distribution when it charges with other materials in blast furnace due to its low angle of repose. However, in P-SCA no such problem is expected because, the pellets are sticked with sinter mass which have less rolling tendency than normal pellet. Another advantage is that the pellet in P-SCA may be acidic of less basic than the sinter mass surrounding of it. Acid pellet has much better reducibility. Thus, P-SCA has a very good application potential.

2.4. Prospects of the techniques

It has been mentioned above that iron ore has been used as a conventional coolant and lump lime as flux as well as coolant in the BOF steel making. However, the use of iron ore resulted severe foaming of steel bath and use of lump lime takes time for dissolution. Therefore, several

Table 9. Comparison among composite sinter and usual sinter.

SI	Sinter	Pellet Used,	Sinter	MgO	Overall coke	(%)		Shatter index (%	Tumbler Index%	RI	RDI
No	Group	%	Basicity	content,%	rate, %	+ 5 mm	+ 10 mm	+ 5 mm)	(+ 6.35 mm)	%	%
1	P-SCA	30	2.1	1.7	5.1	68.2	55	91	74.2	70	27
2	Usual	0	2.1	1.7	5.1	57	43	-	83.2	-	34
	Sinter										
3	Usual	0	2.1	1.7	6.5	66.3	57	90	83.1	66	25
	Sintor										

investigators have used waste oxides of steel plant in form of cold bonded briquettes or pellets as coolant as well as refining agent. Although it shows improvement in refining process, there are several problems such as;

- (i) It uses a considerable amount of organic or inorganic binders. While organic binder is very costly, inorganic binder contains high alumina and silica.
- (ii) It requires a long (several days) curing time.
- (iii) It contains considerable moisture, due to which the crumbling of briquettes may happen at high temperature of BOF.

Therefore, the binder-less process for the preparation of FLIP is developed. This process uses CO_2 or CO_2 containing industrial waste gas for the strengthening of the pellets, which make it environment friendly. The all raw materials are waste oxides. The whole process is operative at ambient temperature. Thus, the energy consumption in this process is also very low. Therefore, this technique is expected to be of low cost. Although, the techno economic could not be calculated from the laboratory scale experiments.

Like wise prefused synthetic flux (PSF) has been developed without using any coke breeze utilizing plant's waste material. The oxidation of metallic Fe in LD sludge and C in BF flue dust provides required heat for sintering. Therefore, this process is also not cost intensive and the CO_2 emission is lower than conventional sintering.

The improvement in reducibility of iron ore pellet has been found to improve up to 7–8% by optimizing the process parameters viz. lowering induration temperature to 1275° C, grain size of iron ore, flux and coke particles. No chemical change is there. The reduction in temperature indicates less CO₂ emission. This can be implemented in plant only by modification of existing practice without any extra investment. On the other hand, RDI improvement by salt solution treatment is a room temperature process after preparation and induration of pellet. No emission is there. It can be implemented in any plant without any major investment. However, techno-economics can be assessed after its large-scale trial.

In a conventional sintering, there is a restriction of undersize fines. The green balling technique can utilize 20–30% microfines in normal iron ore sintering practice. Both micro-pelletizing technique and P-SCA preparation can improve fines utilization up to 60%. Micro-pelletizing improves permeability of sinter bed. On the other hand, P-SCA sintering reduces coke breeze consumption and improves the bed permeability. Thus, energy consumption is reduced. However, the feasibility of P-SCA preparation in large scale needs to be developed.

All the above techniques are developed in laboratory in 10–12 kg scale. For their scaling up, a support from the steel industries is required. The above processes use waste materials and are not so cost intensive. However, only on the basis of result from plant trial, a technoeconomic evaluation is possible.

3. Conclusions

In sintering practice there is limitation of using micro-fines of iron oxides which are generated in steel plant as well as in mines area. In pelletizing, the micro fines are used however; due to the adverse chemistry and size restriction, some micro-fines are not used. Several techniques are developed for their utilization. Flux with lime iron oxide combination can provide low melting oxidizing slag in BOF. These low meting flux has been developed either by CO_2 treated binderless pellet or by coke breeze free sintering of micro-pellets made from LD sludge and BF flue dust. Earlier one is infused flux and later one is partially fused flux. Both have shown very good performance in faster refining of steel bath. However, later one has shown much better performance. In these techniques, alkali has no adverse effect.

For enhancing micro-fines recycling, use of pellet and better quality pellet preparation is required. In order to improve the pellet quality, RI of pellet has been improved by 7–8% point than the normal pellet by optimizing the process parameter viz. fineness, inducation temperature, apparent porosity etc. without changing pellet chemistry. Reduction degradation of pellet has been improved by treating it with several salt solutions. Treatment in 1–2% NaCl solution has shown a significant improvement in RDI. The conventional binder, bentonite, which increases silica and alumina in pellet has been replaced by use of calcined lime keeping the basicity constant.

Use of micro fines in sintering has been improved by adopting micro-pelletizing technology. Coal fines or BF flue dust has also been used in micro-pellets which reduces the requirement of coke breeze in sintering. P-SCA has better shatter tumbler and other metallurgical properties than normal sinter. It consumes less energy than conventional sinter and also improves microfines utilization by 30%. Thus, these technologies may be the solution for the better utilization of micro-fine waste iron oxides. Steel industries have to come forward with us for their upscaling which will help assessing the technoeconomic feasibility.

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