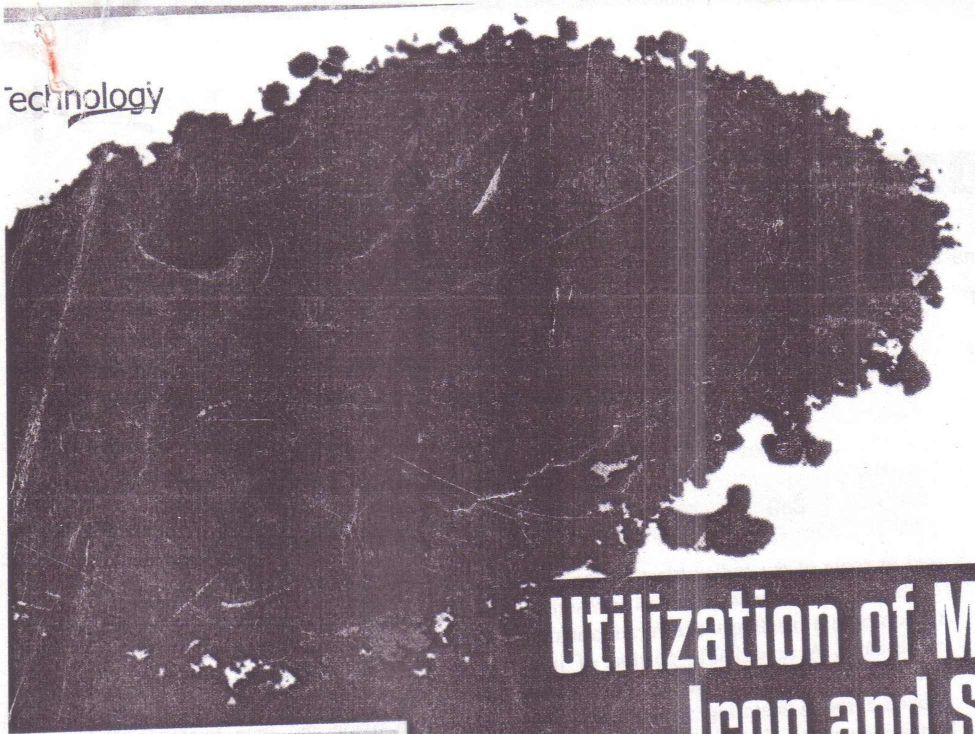


JAGANNATH PAL
Principal Scientist
National Metallurgical Laboratory

Utilization of Microfines in Iron and Steel Making

A huge quantity of iron ore fines (60 % of ore) is generated during production of lump ore. Moreover, iron oxide fines are generated in different units of steel plants such as blast furnace, LD converter, mills etc. Coarser sizes of these are used in sinter plant. However in sintering, there is some restriction of using microfines. It is possible to use in pelletization, but pelletization is a cost intensive process due to its high temperature curing. In present scenario a considerable part of microfines is still unused and termed as solid wastes. Utilization of these fines are very important and becoming mandatory to preserve the natural resources and reducing the disposal cost. Many researchers have tried for improving microfines utilization in different ways. This paper mainly focuses on the recent developmental work at CSIR-NML towards the improvement of micro-fines utilization in iron and steel making such as, development of binder less CO2 treated fluxed pellet, development of micropellets, coke breeze free sintering and development of carbon composite micropellets. Binder less CO2treated fluxed pellet may be used as synthetic flux material for better and faster refining of hot metal. Iron oxide micropellets can be used in sintering. High fluxed sinter produced from waste microfines may be used as flux in refining. Carbon composite micropellet has been developed for improving the utilization of iron oxide and carbon bearing microfines in sinter bed.

Introduction

At present, under sized fines generation rate is around 60% of total iron ore lump production in India. Although a part of it is being used presently, the problem is especially with microfines. There are several areas where micro fines are generated such as (i) in mines area, crushing, screening, washing slurry and blue dust and (ii) in plant area, under sized iron ore (generated in raw materials handling section), LD converter dust, blast furnace flue dust, sludge and slurry. More over concentrates generated from the beneficiation and up-gradation of lean ore are also very fine in size which cannot be used directly in furnaces. All these fines are needed to be used in iron and steel making to preserve the natural resources, for which a suitable technology needs to be developed. This paper discusses the present status, several development work reported and CSIR-NML's contribution on recent development.

Present Status of Waste Micro Fines

Oxide wastes generated in ferrous mines and steel plants (blue dust, iron ore fines, mill scale, LD sludge etc) are generally rich in iron oxide. Some of the wastes mainly LD-slag and lime fines contain significant amount of lime. These are partly utilized for in-house consumption, reducing disposal cost as well as pollution problems. Different types of wastes generated in a typical steel plant with their major constituents, harmful or beneficial, are listed in Table 1[1].

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[2,3] 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[1]. 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[1]. However, most of the waste materials except slag occur in form of fines or slurry and excessive fineness (100-0.1 μm) of these oxides affect the permeability of the sinter bed. Accordingly, the sinter plant cannot accept the whole of the waste iron oxide products. The typical analysis and generation rate of some of the important waste oxides microfines are shown in Table 2.

Blue dust is naturally available in mines. It is blue in color, fine and powdery in nature richer in Fe (65-67%) and lower in Al_2O_3 content. However, due to its fineness it is not used directly in the furnaces. Iron ore slime is also a waste in mines area which is generated

TABLE 1 : DIFFERENT WASTE MATERIALS IN STEEL PLANTS[1]

Wastes	Sources	Desirable Constituents	Undesirable Constituents	Harmful Constituents
BF Dust	Dust Catcher of Blast Furnace	Fe Oxides, C	Al_2O_3, SiO_2	Na_2O, K_2O (for Iron Making)
BF Sludge	Gas Cleaning Plant of Blast Furnace	Fe Oxides, C	SiO_2	S, Na_2O, K_2O (For Iron Making)
LD Sludge	Gas Cleaning Plant of LD Converter	CaO, FeO	==	Zn
Mill scale	Rolling mills	Fe Oxides	==	Oil (For Sintering)
Semi-Calcined Lime	Lime Plant	CaO	Loss on Ignition	==

from washing of crushed ores and deposited in slime ponds. Its generation rate is 150-200 kg per ton of ore.

Use of Iron Oxide Fines in Blast Furnace

It is a conventional practice to use iron ore fines (-6 mm) in sintering to make blast furnace quality sinter. However, sinter plants have a restriction to use micro fines, because it reduces the permeability of bed resulting production loss. Some microfines (10-20%) are used in sinter bed by green balling technique presently in some plants. It has been mentioned in preceding section that several sinter plants in the world recycle up to 180-200 kg of waste oxide fines per ton of sinter, whereas in India, this rate is slightly lower, at 100-170 kg per ton of sinter[1]. On the other hand pelletization of micro fines (~2000 cm2/g Blaine fineness) is also an established practice worldwide which can produce blast furnace quality pellet. Iron ore microfines are being used in some of the Indian blast furnaces on regular practice. However, it is cost intensive as it involves with grinding and in duration at high temperature. A remarkable portion of iron oxide fines generated in steel plant can be utilized through sintering and pelletization routes. However, a significant portion of some iron oxide wastes fines are still unutilized due to the above problems, such as zinc and alkali content of LD and BF sludge, availability in form of slurry and excessive fineness (0.1-100 µm).

In view of the above problems, it is a normal practice for the integrated steel plants to dump these huge quantities of unutilized iron oxide and lime fines as land filling materials. One possible option to minimize wastage of these valuables could be agglomeration of the fines into pellets or briquettes. But the inadequate hot strength of regular briquettes precludes their use in the blast furnace. The strength of pellets is also normally very poor; however, a curing treatment at 1250-1350 °C imparts high strength to make the pellets suitable for use in the blast furnace. The curing process being cost-intensive with high energy consumption and low production rate, the waste iron oxide and lime fines cannot be economically recycled to the blast furnace.

Use of Iron Oxide Wastes in the Basic Oxygen Steel Making Furnace (BOF)

Owing to these limitations of use as sinters and pellets in the blast furnace, the waste oxide fines, as well as the lime fines, have been considered for utilization in the LD/BOF in some suitable agglomerated form because, zinc or alkali in them is not likely to significantly affect the performance of a LD converter. Many investigators worldwide have employed different types of wastes either in the form of briquettes, pellets or sinters, as discussed below:

Briquettes in LD converter

Landow et al.[6] reported that Inland Steel

TABLE 2 : TYPICAL COMPOSITION OF WASTE IRON OXIDES

Wastes	Generation Rate	Chemical Analysis, wt%									
		Fet	CaO	SiO_2	MgO	Al_2O_3	P	S	C	K_2O	Na_2O
Iron Ore Fines[4]	60% of Total Iron Ore Production	55-65	==	1-4	==	1-3.5	0.01-0.05	0.01-0.05	==		
Blue Dust[4]	==	60-67	==	1-3	==	1-3	0.02-0.05	0.02-0.05	==		
Iron Ore Slime	150-200 kg/Ton Ore	45-60	0.98	2-5	==	4-6	0.011	0.18	==	0.03	0.053
LD Sludge[1]	15-25 kg/tcs	59.1	10.8	1.84	0.81	0.90	0.11	==	==	0.28	0.15
BF Sludge[1]	1 kg/tcs	33.6	3.45	6.40	1.40	3.64	0.31	0.23	21	0.40	0.20
Mill Scale[1]	10-20 kg/tcs	70.2	0.31	0.55	0.16	0.27	0.03	==	==	==	==
Flue Dust[1]	1-2 kg/tcs	39.5	3.66	7.9	1.34	3.0	0.17	0.32	25.2	0.34	0.15

produced oxide briquettes from BOF dust/ sludge, mill scale and other iron oxide fines with the aid of suitable binders and subsequently used them in LD converters as coolant. In Great Lake's steel work[7], briquettes were made from mill scale and ESP dust, mixed in 1:4 ratio. High to medium sloping was observed when used in BOF as coolant. An increase in the hot metal ratio (hot metal/scrap) by 3.38% was achieved when 100% steel scrap was replaced with a 13:5 ratio of scrap to briquettes.

Balajee et al.[8] briquetted BOF waste oxides (35% dewatered sludge and 20% girt) with 45% mill scale, using molasses and lime as binder, and recycled the briquettes to the BOF shops of the Inland Steel. They found that 2.2 ton of waste oxide briquettes (WOB) replace 1.1 ton of scrap, increasing metallic yield and accommodating more hot metal.

The Mc.Lauth Steel[9] in collaboration with the Horse Head Resource Development (HRD) used Iron Rich Materials (IRM) (Zn free electric arc furnace flue dust) both as flux and iron source in the basic oxygen process. IRM was found to be a good substitute for fluorspar, lime and iron ore together with increased steel yield by 0.4% and a decrease in dolomitic lime and oxygen consumption, by 5% and 1.5%, respectively.

In Stelco work[10], the dust and sludges generated in LD converter and blast furnace were briquetted along with carbon with port land cement and lime as binders. The refining trial in LD converter showed better metallic yield without any slopping or increasing iron oxide in slag. Self-reducing, cold-bonded agglomerates with the waste iron oxide fines (BOF and BF sludge, mill scale, BF dust, etc.) and coke dust (12-20%) using cement as binder was prepared by Takano et al.[11]. They investigated the performance of briquettes in laboratory-scale smelting trials and found to increase metallic yield up to about 95 % and the cooling effect was enough to substitute scrap in the BOF.

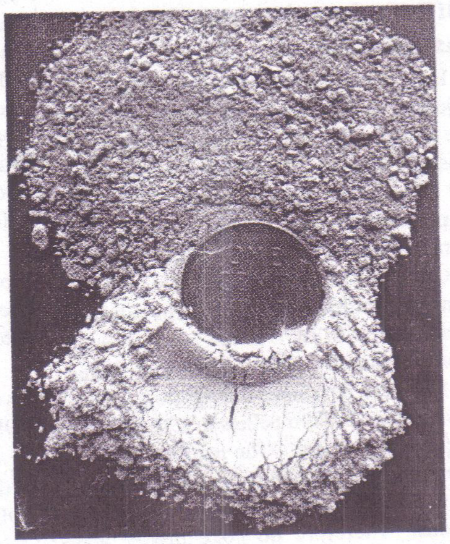
Sinters in LD converter

Irmler et al.[12] produced fluxed sinters using iron oxide wastes and lime, limestone, or dolomite fines for use in the BOF as a low-melting synthetic slag. They evaluated the performance of the sinters, containing varying percentage of FeO, CaO and MgO, in a laboratory scale hot metal refining study. In general, they found that the use of this fluxed pellet promoted better flux dissolution, earlier slag formation, greater removal of both sulfur and phosphorous and increase in metallic yield without any sloping.

Pellets in LD Converter

In an important study[13], lime pellets were coated with iron oxides (a mixture of mill scale, yellow soil and silica) and used in BOF to enhance slag formation. A plant trial with this quoted pellets at Pohang Works in a 100-ton converter showed improvement in lime consumption, enhancement of metallic yield, increase in slag basicity and improvement in dephosphorization compared to the conventional process. However, the difficulties encountered in coating of lime pellets restrict its commercialization.

In the Nippon Steel, Imazumi et al.[14] developed cold-bonded pellets, made of 44-66% LD sludge and other iron oxide fines, and



6% cement to replace iron ore in an LD converter. They found that a crushing strength of 39 kg/pellet was suitable for cold handling of pellets.

Waste iron oxide pellets with cement as binder was developed by Takano et.al[11] for use in BOF and a good dry strength (30.6 kg/pellet) was achieved. However, pellets took 28 days for curing, which is too long for industrial application. Further, 10-20% of port land cement in the pellets contributed significant amount of alumina to affect the refining efficiency of the slag.

The under sized and over sized iron oxide pellets not conforming to COREX and blast furnace specification were used as feed in LD converter in JSW Steel[15] to explore the possibility of their use in LD converter for the formation of earlier oxidizing slag and faster refining.

CSIR-NML has developed some techniques to utilize micro fines in steelmaking or iron making which are discussed in proceeding sections.

Recent Development at CSIR-NML

CO_2 Treated Fluxed Pellets for LD Converter

There is a shortage of steel scrap for use as coolant in the basic oxygen steel making furnace (BOF) due to the advent of continuous casting. Iron ore, lime stone, and the directly reduced iron (DRI), with or without lump, burnt lime, have been tried as different alternatives. Presently, lump lime is being widely used as coolant as well as flux. However, due to its high melting point, poor dissolution property, fines generation tendency, and hygroscopic nature, problems are often encountered in operation. In order to control environmental pollution along with recover metallic values, waste iron oxides are being utilized as coolant in the BOF in the form of waste oxide briquettes, sinters, or pellets as discussed in Section 4. However, existing process of sintering, briquetting and pellet making of oxide fines suffer from the drawbacks of non acceptance of excessive fines, presence of harmful and expensive binder and energy intensive high temperature curing process, respectively. As a solution to this problem, it was noted that, although pure, lump lime is a refractory material and dissolves very slowly in the BOF bath, the compound formed by a mixture of 22% CaO and 78% Fe_2O_3 exhibits a peritectic melting point of about 1200°C only. Thus, lime in combination with iron oxide is expected to dissolve faster in the bath and accelerate the refining process due to early formation of an oxidizing slag. In view of all these, a novel method[16] was developed to make fluxed lime-iron oxide pellet (FLIP) as a low-cost feed material using waste iron oxides and lime and without resorting to high temperature curing and addition of costly binders. Iron ore fines was selected as the representative of different types of waste iron oxides such as blue dust, mill scale, LD sludge, BF dust, and iron ore fines itself for this particular study.

The partially dry pellets demonstrated cold compressive strength (CCS) of 1-3 kg/pellet. They were subsequently treated with carbon dioxide in a reaction chamber at room temperature to transform the calcium hydroxide ($Ca(OH)_2$) into hard calcium carbonate ($CaCO_3$).[17] The associated volume expansion resulted in a significant improvement in the strength of the pellets.

When the lime (CaO), present in the base mixture, comes in contact with water, added before pelletization, they react to form calcium hydroxide :

$$CaO\ (s) + H_2O\ (l) = Ca(OH)_2 \quad [1]$$

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

$$Ca(OH)_2\ (s) + CO_2\ (g) = CaCO_3\ (s) + H_2O\ (l/g) \quad [2]$$

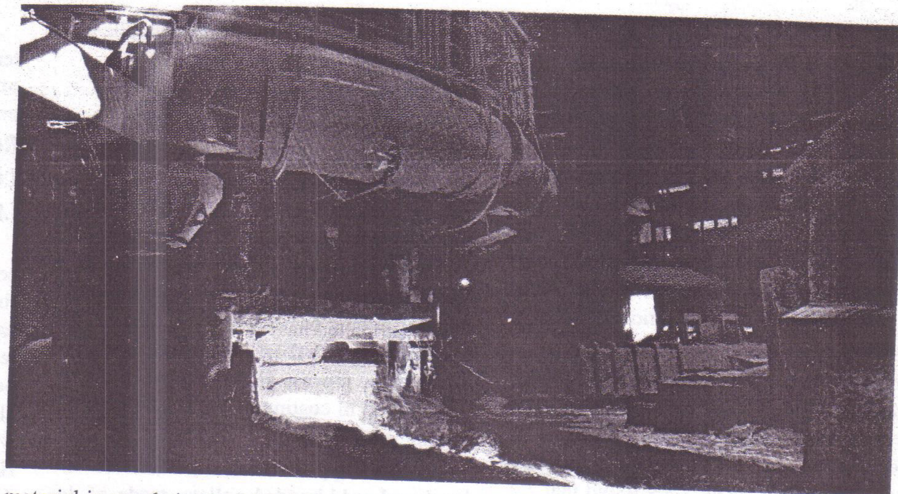
Due to the above reaction, a hard CaCO3 phase is formed in the pellet.

The formation of $Ca(OH)_2$ into $CaCO_3$ is primarily responsible for imparting good strength to the pellet because of volume expansion during the transformation. The molar volumes[17, 18] of $CaCO_3$ and $Ca(OH)_2$ are 34.10 cc/mole and 33.59 cc/mole respectively. Therefore, the transformation as per Reaction [2], results in 1.52% volume expansion of lime. This volume expansion is likely to be accommodated by the internal pores of the pellet, otherwise, it will create internal stress. The reduction in porosity increases the compactness of the pellet and accordingly, strength increases.

The study on FLIP in detailed has been reported else where[19-21]. The developed FLIP showed up to 28 kg/pellet compressive strength very low softening point(1180°C)[19], 30-40 sec of dissolution time[20] and makes the refining process faster (15-20% lowering of refining time) and improved P removal[21].

Development of Iron Oxide Micropellets

In order to alleviate the problems of using microfines directly in sinter bed, this study has developed a process for preparing micro-pellets (2-6 mm size) of waste iron oxide fines without using any binder.[22] The strength of micro-pellet has been increased by CO_2 treatment process at room temperature as described in Section 5.1. Developed micro-pellets exhibits very suitable drop strength (125 Nos), tumbler properties and CCS (~ 9 kg/pellet) to withstand cold handling. High lime containing micro-pellets may be exploited for making super fluxed sinter that for use as synthetic flux in BOF process towards formation of low melting oxidizing slag at the early stage of blow, while, low lime containing micro-pellets can suitably be used as a mixed



material in usual sinter making. Both of these are discussed below.

Self Propagating Sintering of Waste Microfines

High lime containing micropellets are subjected to sintering. The pellet with 35% lime shows highest CCS, drop strength and abrasion resistance. Since, lime percentage is very high, during sintering, it may form fused compound with iron oxide. Binary phase diagram of CaO-Fe_2O_3 shows eutectic melting point at 1230°C with 20% CaO. This offers a distinct possibility of using the micro-pellets of current interest in BOF in the form of sinter. Therefore partially prefused sintered fluxed (PSF) has been developed through coke breeze free sintering of micro pellets in a 10 kg scale capacity sintering pot[23]. The required heat for the sintering was available from the exothermic oxidation of FeO/Fe_2O_3 in LD sludge or C in BF flue dust. Therefore no coke breeze was required to add.

Since, burnt lime has high melting point (~2700°C), it dissolves very slowly and causes delay in refining process. On the contrary, the sintered micro-pellets, containing pre-fused lime-iron oxide compounds (possibly, CaO.FeO_X type) is likely to dissolve into the bath quickly and form a low melting, oxidizing slag at the early stage of the blow. Early formation of slag is expected to facilitate the refining process. Production of sinter with these micro-pellets and assessment of its actual performance towards refining of hot metal under simulated condition has been carried out and reported elsewhere.

It has been mentioned earlier that cold bonded iron oxide briquette disintegrates and shows chances of explosion at high temperature of BOF converter during charging.

Both the mentioned problems are ruled out for sinter prepared with fluxed micro-pellets. Further the alkali impurities present in LDS and BFD are not likely to pose any adverse effect in BOF operation. In view of the above, the sinter prepared with fluxed micro-pellets appears to have excellent potential to at least partially replace addition of lump lime in BOF and hastened refining process, which has the following advantageous features.

(1) Excellent shatter (85-95%) and tumbler properties (60-80%) of developed PSF have been observed which are suitable for smooth cold handling.

(2) Excellent thermal shock resistance of developed PSF indicates its smooth charging in BOF without generating fines.

(3) Low softening point of the PSF would facilitate the formation of low melting slag in BOF.

(4) PSF is not hygroscopic unlike lime, which makes it favorable for storage.

(5) Very fast dissolution (27-80 sec for 1-3 g lumps), enhanced removal of C and P (11-12 min), controlled slag foaming and reduced oxygen consumption has been found for using PSF.

Micropelletization and Sintering of Iron Ore Concentrate

Micropelletization of iron oxide concentrate through CO_2 treatment has also been done.[25] The developed iron oxide micro-pellets with low lime content (10%) has CCS of around 5 kg/pellet, good drop strength and abrasion resistance which may be suitable for cold handling. This micro-pellet has been used in making of sinter for use in blast furnace. Micro fines use is increased by 30 % in sintering. Since, blast furnace operation is sensitive to alkali and Zn content of the feed material, the micro-pellets prepared from LDS and BFD may be used in a very limited proportion in BF grade sinter preparation. This use can improve the permeability of sinter bed and supply a supplementary heat to reduce coke breeze consumption.

Development of Coal Composite Micro-pellets

Microfines of non coking coal and other carbon bearing materials viz. BF flue dust and coke fines are not used extensively in metallurgical industries due to operation difficulties and handling problems. In order to utilize these microfines, the coal composite iron oxide micropellets (2-6 mm size) has been made in an innovative technique, wherein, lime and molasses has been used as binding materials for micro-pellets. The micro-pellets have been subsequently treated with CO_2 or industrial waste gas for chemical bond formation. At the very high carbon level of 22% (coal: 38%), cold crushing strength has been found to be 2.5-3 kg/cm^2. Abrasion index 5-9% which appears suitable for cold handling. The good strength development has been possible when combination of molasses and lime followed by CO_2 treatment is done. Here molasses provides its natural bonding property to the pellets. Further, on the treatment with CO_2 at room temperature in which hydrated lime is reacted with CO_2 gas to develop the cold strength. The combined effect of carbonate formation during CO_2 treatment and binding property of molasses produced good strength to the micropellets. Here instead of using pure CO_2, steel plants waste gases containing CO_2 (viz. blast furnace off gas) may also be used.

These micropellets have a potential to use in smelting reduction for iron making and in sintering as heat source to reduce coke breeze. The developed micropellets with blast furnace flue dust or coke fines has been used (8-12%) in sintering for the feasibility test in 12 kg scale pot and found good sinter at par with conventional blast furnace quality sinter and 30-40 % reduction in coke breeze.

Conclusions

(1) A considerable part of microfines are still unused which are mandatory to recycle or use in iron making and steel making process. Earlier investigators have reported to use a part of it in BOF in form of briquettes (WOB). The recent study at CSIR-NML has developed several techniques such as binder less CO2 treated pellets, micro pellets, coke breezeless sintering and carbon composite micropellets which improve microfines utilization in iron and steel making and show other advantages.

(2) Waste iron oxide fluxed pellets has been prepared without using external binder has very good strength for handling which can be used for faster refining of hot metal.

(3) Micropellets have been developed without using any external binder. These are suitable for cold handling to use in sinter bed for improving microfines utilization.

(4) Sintering of waste iron oxide miceripellets has been conducted without using any coke breeze and the developed sinter (super fluxed) has been used as flux materials in refining.

(5) C composite micropellet of good strength has also been developed to improve iron oxide and carbon bearing microfines utilization in sinter bed by 30%.

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