

A comparative characterization of Iron ore Pellet agglomerates prepared from low grade goethite raw ultrafine and beneficiated goethite ultrafine.

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Abstract: In early days, most steel plants using lumps as the major source of iron-bearing raw material. In subsequent years, sinters were used to considerable extent. However, use of pellets was not adopted. Only recently the advantages of pellets are being understood by the steel makers in terms of its efficiency, ease of operation, productivity and overall the conservation of natural resources.

In this paper the influence of structural water present in goethite rich ore ultra fines on pellet properties like porosity, RI, RDI, TI, AI and microstructure were studied. Two different pellets were prepared and characterised by using raw iron ore ultra fines and beneficiated fines.

Key words: *Iron ore pellet, Goethite rich Iron ore, Beneficiation goethite ultra fines, SFCA, Phase and Volume Fraction Analysis as per ASTM E562 and E1245.*

Introduction: During mining of iron ores, lots of fines (<10 mm) are generated which are not suitable for direct use in the blast furnace for iron making. Also scarcity of high-grade iron ores is compelling utilization of low-grade ores. The utilization of such low-grade ores and the generated fines is possible only after beneficiation and enrichment. Low-grade iron ores contain a considerable amount of gangue minerals, e.g. silica, alumina, calcium and magnesium compounds. In the process of concentration, low-grade iron ores are crushed and ground for liberation of the gangue minerals before the implementation of separation techniques. In such processes the fines are generally classified into two categories: one is coarser 'fines' consisting of particles smaller than 10 mm and bigger than 150 microns (100 mesh), and the other is 'ultra-fines' that are below 150 microns. These two classes of fine particles are to be

agglomerated to desired coarser sizes in order to be utilized in the blast furnace or other iron-making processes. Agglomeration technique applied for the coarser fines is generally done in a process known as "sintering" by application of heat where partial fusion of the constituent material occurs. The ultra-fines are agglomerated in a separate process called "pelletization" where balling techniques are used and the balls/pellets are subsequently fired in order to get higher strength.

Only few researchers have left their impressions (eg., Sharma et al, 1990; Sharma et al, 1991; Sharma 1992; Sharma et al, 1992; Sharma et al, 1993; Sharma, 1994; Sharma, 1997; Pandey and Sharma, 2000, Kumar and Patel, 2009).

Background: Scarcity of high-grade iron ores is compelling utilization of low-grade ores. The utilization of such ores warrants crushing and grinding to a very fine particle size (generally below 150 microns) in order to liberate the gangue minerals. These ultra-fine particles are processed to generate higher grade concentrates of iron minerals. However, these ultra-fine particles cannot be charged directly into the blast furnace or the DR-plant without converting it into suitably sized agglomerates. The most commonly employed agglomeration technique for such ultra-fine particles is pelletizing.

In pelletization, a mixture of iron ore ultra-fines, water and any suitable binder is mixed and rolled in a mechanical disc or drum to produce agglomerates that are called *green balls* or *wet pellets*. Green pellets then undergo thermal treatment process, which consists of three stages, namely drying (250-400 °C), preheating (900-1100°C) and firing (1200-1300 °C). Indian iron ores have been extensively studied with respect to their geology, mineralogy, geochemistry and genesis (Sarkar et al., 1969; Banerji, 1977; Chakraborty et al., 1980; Rai et al., 1980; Acharya et al., 1982; Radhakrishna et al., 1986; Chakraborty and Majumder, 1986, Devaraju and

Laajoki, 1986; Mahabaleswar, 1986; Chadwick *et al.*, 1986; Beukes, *et al.*, 2003; Mohapatra *et al.*, 2008). The beneficiation studies are focused mainly towards reducing the alumina content of the ores (De *et al.*, 1995; Rao *et al.*, 2001; Upadhyay and Venkatesh, 2006). However, all the hematitic ore deposits of India, although broadly similar in nature, have their specific problems which may be generic or very specific to that deposit. It is not only the Fe content, but the mineralogy, the type of associated gangue minerals, the physical and metallurgical properties would decide the type of utilization of the ores. If the ores are high-grade (Fe > 64 %) and are able to produce lumps (>10mm), then these can be directly fed into the blast furnace. If the grades are still higher and calibrated lumps of 18-20mm can be generated, then the ores can be used to produce sponge-irons (DRI). However, the ore bodies are unable to produce lumps then the fines (-10mm to 0.15mm) are to be beneficiated and agglomerated (sintered) in order to make them suitable for extraction of metal. The ultra-fines (below 0.15 mm) after suitable beneficiation, can be formed into balls called pellets (~10mm) which can be used in the reduction furnaces after attaining proper physical properties. If the ores are very low-grade ores such as limonite, red ochre or yellow ochre, then these are used as colour pigments. Some have application in powder metallurgy. Besides the above, some ores although contain less gangue material, can produce lumps but still cannot be directly used in the blast furnaces. ***Goethite is one such ore that contains water in its chemical structure which makes the ore unsuitable for direct utilization in the blast furnaces.*** Unlike in Australia (Clout, 2006), in India such ores have not drawn enough attention of the researchers and therefore, have been least studied with respect to their associated problems in iron making and any other possibility of utilization.

Pellets are generally preferred over lump ores and sinters for iron-making because they have some remarkable properties such as:
uniform size distribution within a main range of 9-15 mm diameter

- high and even porosity of 25-30%
- high iron content of more than 63% iron
- practically no loss on ignition or volatiles
- uniform mineralogical composition

- high and uniform mechanical strength, even under thermal stress
- low tendency towards abrasion

Binders play an important role in the success of pelletizing process. Of many binders, bentonite has proven to be the most effective one owing to its high water adsorption capacity and dry film strength. It is generally used at a rate of 0.5 - 1.5%. Bentonite however, is considered as an impurity due to its high SiO₂ and Al₂O₃ contents. These acid oxides are known for their adverse effects on the economy of iron/steel making. For instance, the addition of 1% bentonite decreases the iron content by about 7kg/ton of iron ore. In addition, an increase in the gangue content of the charge leads to an increase in the unit cost of steel production. Therefore, efforts should be made to use the minimum binder without compromising the desired properties of pellets. In view of the adverse affects of bentonite, many researchers attempted to find viable alternative binders. Organic binders have attracted attention as they are known to have good binding properties. The results showed that organic binders produce good quality green and dry pellets. However, they fail to impart enough strength to the pre-heated and fired pellets as a result of reduced slag bonding, which is especially more important in pelletizing of hematite ores due to lack of oxide bonding. As such, organic binders have hitherto failed to be an alternative to bentonite, except in few cases of straight-grate pelletizing, where there is no dynamic pellet bed. In recent years efforts have been focused on improving the pre-heated and fired strength of pellets produced with organic binders. In this context, boron compounds have been considered as an additive in conjunction with organic binders. In any case, whether it is bentonite or any other binder, it will be desirable that the pelletizing process should be optimized with respect to how much binder should be used so that the desired pellet properties can be achieved; and the effort should be towards use of less quantity of binder. There is no thumb rule about how much binder should be used in the pellet-making. It may vary depending on the character of the ore fines, their mineralogy, chemistry, granulometry, particle shape, size etc. Therefore, it is desired that the required properties of pellets are understood at the first hand. A detailed account of iron ore pellets are dealt by Meyer (1980).

Iron ore ultra-fines: Lot of fines are generally generated during crushing of large lumps present in the run-of-mine ores. The ultra-fines were collected from Daitari waste stockpiling. The sample was air dried. Granulometry of the sample was carried out. The

representative sample was prepared by coning-quartering-size reduction method. The final sample is pulverised to –100 mesh (<150 microns top size). The properties of the ultra-fines are given in the Tables 1 and 2.

Table 1: Granulometry (sieve size analysis) of the iron ore ultra-fines

Sl. No	Parameters	Wt.%
1	+ 100 mesh	7.82
2	+ 150 mesh	36.7
3	+ 200 mesh	36.1
4	+ 300 mesh	12.02
5	- 300 mesh	7.36

Table 2: Chemical composition of the raw- and beneficiated iron ore ultra-fines

Sl. No	Parameters (in wt.%)	Raw ultra- fines	Washed ultra-fines	Slime Rejects
1	Total Fe	54.79	62.30	50.51
2	SiO ₂	4.16	1.71	5.91
3	Al ₂ O ₃	7.45	3.05	9.28
4	TiO ₂	0.231	0.145	0.887
5	Mn	0.396	0.522	0.29
6	Na ₂ O	0.100	0.098	0.102
7	K ₂ O	0.210	0.009	0.340
8	S	0.019	0.014	0.030
9	P	0.120	0.068	0.150
10	LOI (at 900°C)	9.04	5.34	10.84
11	Al ₂ O ₃ /Fe	0.136	0.05	0.18
12	Al ₂ O ₃ /SiO ₂	1.79	1.78	1.57
13	Al ₂ O ₃ + SiO ₂	11.61	4.76	15.19

Beneficiation of the iron ore ultra-fines: The ultra-fines were of low-grade having a total Fe content about 55 wt. %. Therefore, these were to be upgraded to increase the iron content and reduce the gangue content. Process adopted to upgrade the ultra-fines was simple washing and scrubbing on a 200 mesh screen till clean water is found at the outlet. In the process the clayey matter was removed and the ultra-fines were enriched with iron-particles and there by the grade was improved which is

evidenced from the following table. Beneficiated ultra-fines are further ground to – 200 mesh by a laboratory pulveriser to reduce the size.

Bentonite: Bentonite, Loba-make laboratory grade bentonite was procured from market for the pelletization experiments. It is a mixture of clay minerals, consisting of montmorillonite as the major component and small quantities of quartz and other minerals such as mica, feldspar and kaoline.

Table 3: Chemical composition of the bentonite

Bentonite	Fe	SiO ₂	Al ₂ O ₃	CaO	MgO	TiO ₂
Wt.%	7.0	54.3	18.3	8.4	3.2	1.25

Limestone: Limestone was collected from NINL raw material yards and were dried and ground to – 200 mesh

by the laboratory pulveriser. The chemical composition of the limestone used in the pellets is given in Table 4.

Table 4: Chemical composition of limestone

Parameters	%
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CaO	51.28
MgO	1.41
SiO ₂	3.06
Al ₂ O ₃	0.35
Na ₂ O	0.022
K ₂ O	0.224
Fe	0.34
LOI (1000°C)	40.60

In view of the great economic importance, limestone is generally added to the mix, chiefly in conjunction with the production of self-fluxing pellets (Tayama et al, 1978). The main reason for the addition of limestone or dolomite is the production of pellets with a rising portion of basic constituents and thus with increasing basicity.

Coal: Coal was collected from the NINL coal yard. The collected coal was dried and further ground to -200

mesh by the laboratory pulveriser. Coal is added to the base mix to bring down the fuel consumption during heat hardening. The proximate analysis and inorganic components in the coal ash are presented in the following table 5.

Table 5: Proximate analysis and ash composition of coal

Proximate Analysis				Ash Composition (w r t total)					
MC	VM	Ash	FC	S	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe
2.12	25.8	27.5	46.7	0.64	16.72	8.91	0.66	0.33	2.20

Preparation of iron ore pellets

Two different types of pellets were prepared to study the chemical, mineralogical and metallurgical characteristics. The blend parameters of these pellets are given in the Table 7.6. Only the iron ore ultra-fines were varied keeping the limestone, coal and bentonite at fixed proportions.

Raw mix preparation: The raw mix (approximately 10 kg in each batch) for each pellet was mixed thoroughly in dried condition in a laboratory mixing drum. The final mixture was taken from the mixing drum. Manually 12 % water was added to the raw-mix in step by step to

yield wet raw-mix. First 5% water was added to the raw mix in a bucket and then mixed thoroughly; subsequently 7% water was added and mixed thoroughly.

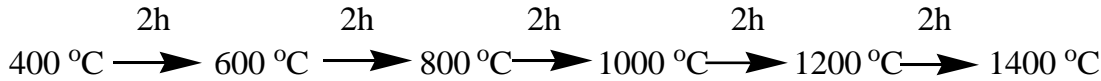
Green ball preparation: The pellets were prepared manually by hand rolling the wet raw-mix. Care was taken so that the balls are round in shape and are close in size ranges. Green balls can be prepared by using a disc or drum. However, the final properties of the balls are not much dependant on the machine or method of preparation (Löfgren et al, 1977).

Table 6: Blending compositions of the prepared pellets

Raw materials	Pellet 1	Pellet 2
Iron ore ultra-fines	96.9 % (-200 mesh lean grade 100 %)	96.9 % (-200 mesh beneficiated grade 100 %)
Limestone	1.4 % (-200 mesh)	1.4 % (-200 mesh)
Coal	1.2 %	1.2 %

Bentonite	0.5 %	0.5 %
Drying: The green balls were allowed to dry on their own for three hours by keeping them in open atmosphere. Subsequently these were dried in an oven at		150 °C for 2 hours. Over drying was avoided because sometimes it may lead to breakdown of the green ball (Vityugin et al., 1971)

Induration: For heat-hardening, the pellets were heated in a muffle furnace in the following sequences at different temperature programmes:



Therefore, the peak temperature may be considered to be around 1350°C. The theoretically possible acceleration of crystal growth by higher induration temperatures cannot be realized (Yefimenko et al, 1977). At

temperatures above 1350°C hematite starts to dissociate into magnetite and oxygen, resulting in weakening of pellet strength.

EVALUATION OF PELLET PROPERTIES

The prepared pellets were spherical in shape and were in the size range of 10 to 15 mm (Fig. 7.1). After induration, it was observed that pellet-1, that was prepared from the raw iron ore ultra-fines was more blackish in colour. While pellet 2 showed very fine, irregular micro-cracks on the surface. However, these cracks were not universal.



Fig. 1: Prepared pellets from Daitari iron ore ultra-fines.

The chemical compositions of pellets are given in Table 7.



Chemical analysis of pellets

All the pellet samples were analysed by wet-chemical gravimetric methods. The chemical analysis results of pellets produced from beneficiated iron-rich ultra-fines were found to be almost identical. Only in two three components, there was slight variation in the second decimal point. Therefore, for all practical purposes we consider that the final composition is the same. However, pellet produced from the lean-grade ultra-fines was obviously found to be quite different.

Mineralogy and internal structure of the pellets

Polished mounts of all the four pellets were prepared and examined under reflected plane polarized light in an optical petrological microscope with a total magnification of 200 using dry objective. It was found that magnetite is the dominating iron-bearing phase that has been developed in these fired pellets with subordinate quantity of hematite (Fig. 2).

Table 7: Chemical composition of the prepared pellets

Parameters	Pellet 1	Pellet 2
Fe (T)	58.99	64.72
FeO	0.35	0.28
SiO ₂	5.04	2.33
Al ₂ O ₃	8.24	3.38
CaO	0.81	0.82
MgO	0.03	0.04
TiO ₂	0.26	0.16
P	0.13	0.07
Mn	0.43	0.54
S	0.022	0.015
Al ₂ O ₃ /SiO ₂	1.63	1.45
Al ₂ O ₃ +SiO ₂	13.28	5.71
Basicity	0.16	0.35
Al ₂ O ₃ /Fe	0.14	0.05

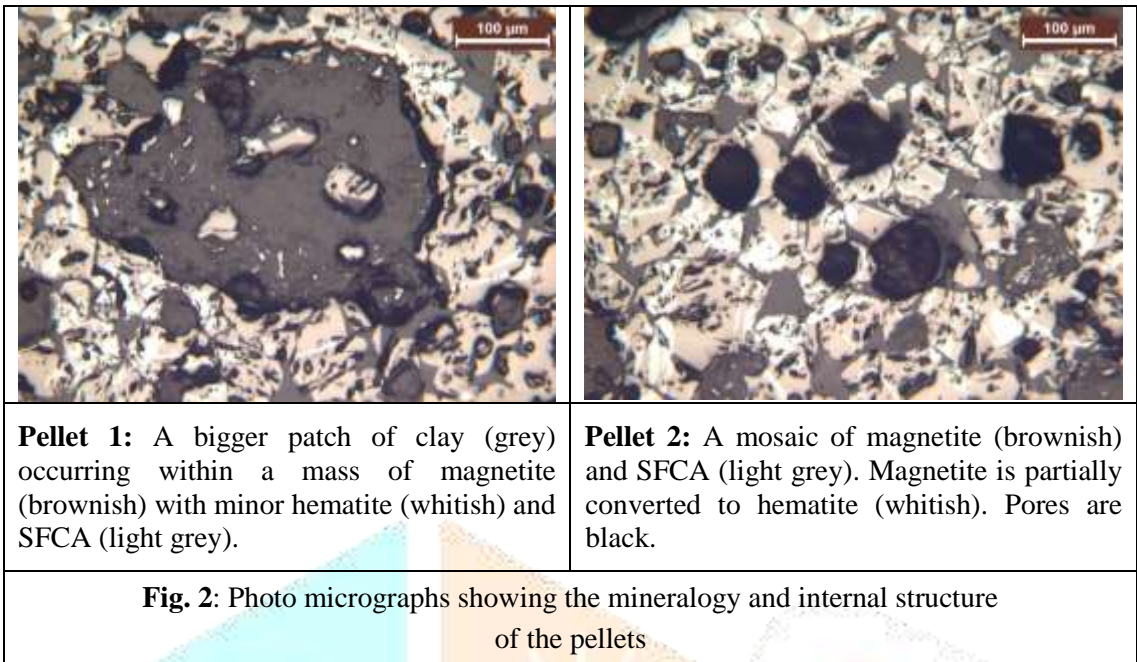
Hematite does not appear as separate grains rather forms due to oxidation and alteration of magnetite. The gangue phases are mostly silicoferrites of calcium and aluminium (SFCA). In rare instances residual clay phases are also visible. The grain sizes remain around or below 100 microns. Pores have formed almost in the

Metallurgical properties of pellets

To evaluate the metallurgical properties of the pellets, measurements were taken on the apparent porosity, bulk density, apparent specific gravity,

similar size ranges. It was also seen that pellet-1 has the least porosity and the gangue content is high. Unconverted clays occur in bigger patches. Optical photomicrographs displaying the general characters of the pellets are presented in Fig. 2.

swelling index, tumbler index, abrasion index, reducibility index and reduction degradation index which are summarized in the Table 8.



From Table - 7.8 and Fig. 7.2, it appears that pellet 1 does not satisfy most of the pellet properties. Although, pellets 2, 3, and 4 are usable, lots of differences exist between them. Pellet 3 has highest

reducibility which may be due to the high porosity in it. However, its bulk density, RDI, and AI are not the best. On the contrary, pellet 2 appears to be the best amongst all.

Table 8: Metallurgical Properties of the prepared pellets

Sample	AP (%)	BD (gm/cc)	A.Sp.gr	Swelling Index	TI	AI	RI	RDI
Pellet1	4.80	3.40	3.57	5.375	86.4	6.8	64.7	14.2
Pellet2	19.95	3.89	4.86	4.855	94.2	3.6	74.2	8.2

AP: Apparent Porosity; BD: Bulk Density; A.Sp.gr.: Apparent Specific gravity; TI: Tumbler Index; AI: Abrasion Index; RI: Reducibility Index; RDI: Reduction Degradation Index

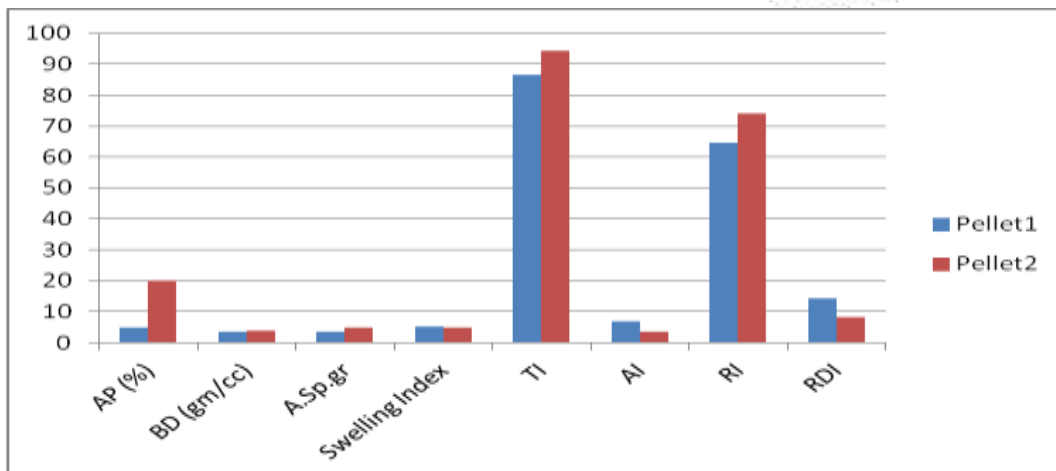
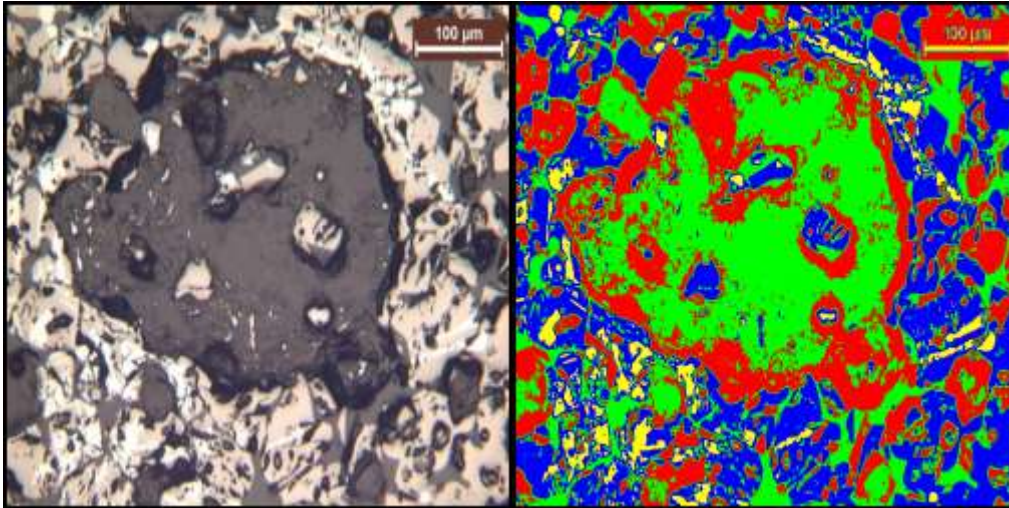


Fig 3: Metallurgical Properties of the prepared pellets

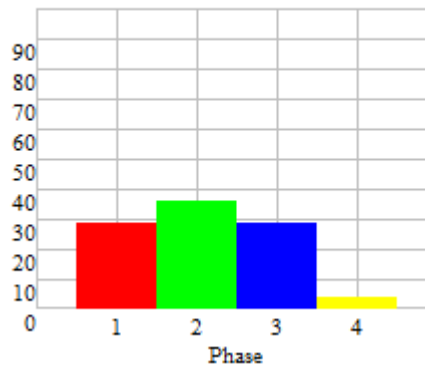
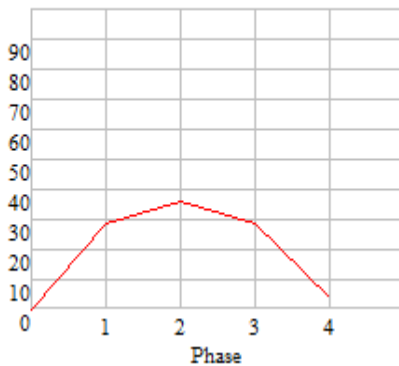
Phase and Volume Fraction Analysis as per ASTM E562 and E1245:

From the study it is found that pellet prepared from raw ore ultra fines covered substantially with fused clay (36.93 %). The porous portions of the pellet are quite negligible in comparison to beneficiated fines (21.02%). The SFCA which determine the strength of the pellet is found higher in pellet 2 that pellet1. The pellets are reduced from goethite / hematite to magnetite since both the pellet have substantial quantity of magnetite. The same results are inferred from chemical composition of pellets where the percentage of FeO is very less.

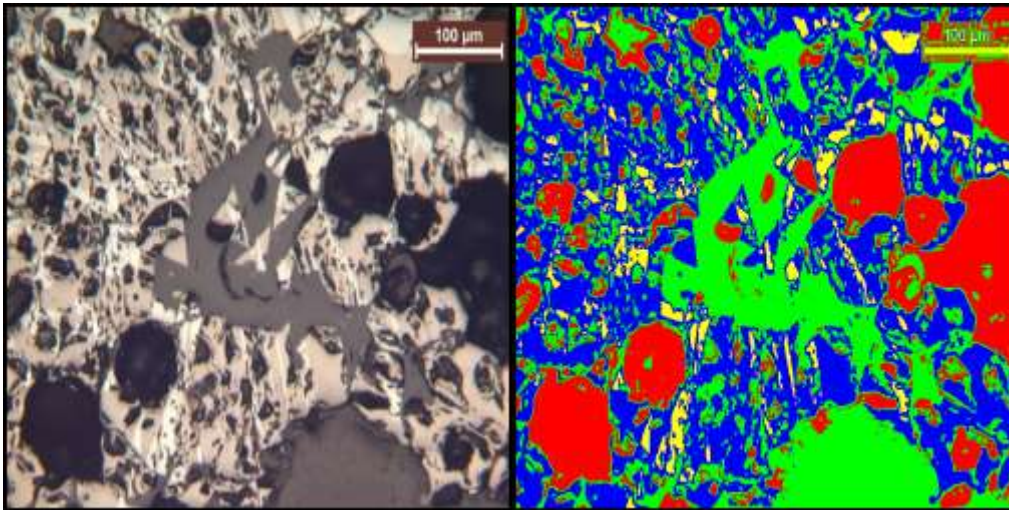
Pellet 1



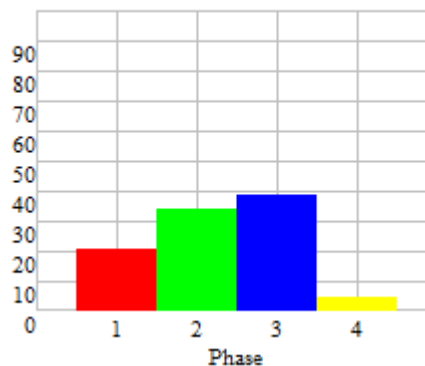
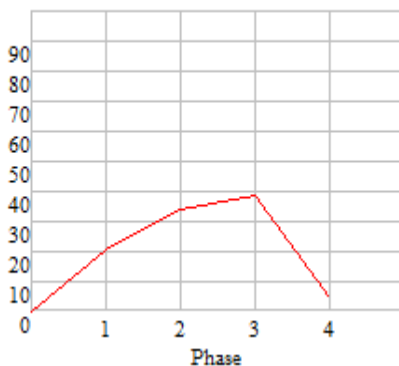
SNo	NAME	AREA	AREA_PER
1	Magnetite	738137.119 Micron Sqr	29.003
2	Clay	939882.271 Micron Sqr	36.93
3	SFCA	748192.521 Micron Sqr	29.398
4	Hematite	118801.939 Micron Sqr	4.668



Pellet 2



SNo	NAME	AREA	AREA_PER
1	Pores	518137.119 Micron Sqr	21.02
2	Magnetite	845131.579 Micron Sqr	34.285
3	SFCA	971544.321 Micron Sqr	39.413
4	Hematite	130214.681 Micron Sqr	5.282



DISCUSSION

Pellets differ from lump ore and, to a certain extent, also from sinter by several properties which are predetermined and definable. Despite the great variety of raw materials used, the pellets produced must have similar properties which are judged in accordance with internationally acceptable norms. Porosity, tumbler index (TI), abrasion index (AI), reducibility index (RI) and reduction degradation index (RDI) are generally considered as very important parameters for fired pellets that determine the efficiency of the furnace which produces the hot metal. While the physical properties

such as TI and AI determines the stability of the pellets before they rich the furnace, porosity allows the reducing gases the passage through the raw material within the furnace. RI and RDI are important parameters within the furnace during the reduction stages of pellets. If RDI is high, then lots of fines will be generated and the furnace will choke. If RI is low, then it will take lots of time to produce hot metal and it may consume more reducing gas. Therefore, pellets should be engineered in such a fashion that a balance should be maintained between all these properties. Of course beforehand the chemistry of the pellets should be fixed keeping the basicity and alumina/silica ratio in their desirable limit.

Successful pellet production calls for an optimum efficiency and harmony between all the three process steps: (i) raw material preparation, (ii) green ball formation, and (iii) induration of green balls. An error made in the preceding stage largely affects the next stages; for example no good pellet can be produced from a defective green ball. In addition to these, various forces act which gives proper binding and strength to the initial ball formation that are described in Rumpf (1962).

Pellet-1 with the unbeneficiated raw iron ore ultra-fines which was not matching the desired chemistry. The intention was to know whether pellets can be prepared and what will be their physical and physico-chemical properties. From table 8 it is clear that this pellet is very inferior in terms of porosity, TI, AI, RI and RDI. Therefore, such pellets should not be tried with. Normally $TI > 92$, $AI < 5.0$, porosity $\sim 20\%$, $RI > 70$ and RDI around 10 % are preferred. Pellet 2 is the best for the metallurgical industry which is due to the combination of optimum porosity, tumbler index and lower reduction degradation index. The bulk density and specific gravity of pellet 2 is higher which indicates the effective utilisation of working volume of the reactor. The reduction degradation index of pellet 2 indicates this pellet will have improved process permeability due to less fines generation inside the reactor, so it will have highest productivity. Therefore, -200 mesh or ~ 75 microns particle is good for pellet making.

CONCLUSION:

Hence from the above studies it is concluded that good metallurgical-grade pellets can be prepared from goethitic Daitari iron ore ultra-fines. Granulometry of the ultra-fines must be kept around and below 75 microns for better quality pellet preparation. Raw ultra-fines should not be used in pellets. Ultra-fines should be beneficiated and then agglomerated.

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