CHAPTER – 3

PHYSICAL AND PHYSICO – CHEMICAL CHARACTERIZATION OF IRON ORE AND AGGLOMERATES

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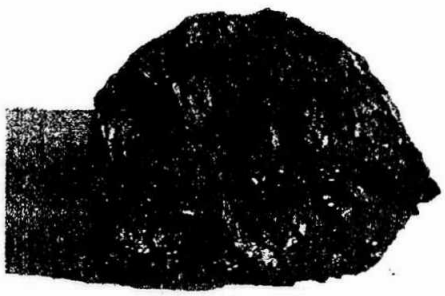
INTRODUCTION

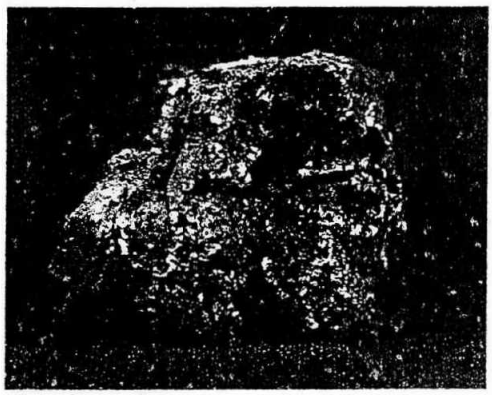
Performance of a blast furnace greatly depends on the quality of input raw materials, specifically the iron ore and its agglomerates, judged mainly through its reduction behaviour and strength property. Parameters like Reducibility Index (RI) and Reduction Degradation Index (RDI) are considered to be the important quality indicators for the selection of iron bearing material as blast furnace burden.

The most commonly used iron ore is Hematite (Fe_2O_3) containing a maximum of 70% Fe. Others of less importance are Magnetite (Fe_3O_4; 72.4 % Fe, max.), Goethite ($Fe_2O_3.H2O$; 60.3%Fe, max.), Limonite ($2Fe_2O_3.3H_2O$; 60% Fe, max.) and Siderite ($FeCO_3$; 48.3% Fe, max.).

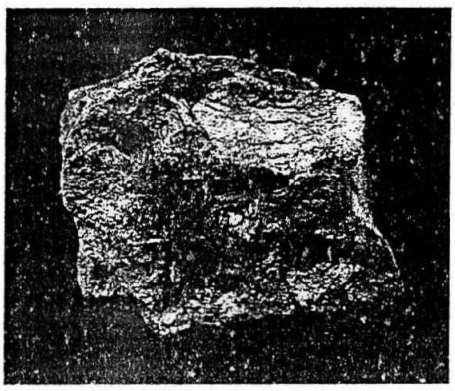


Hematite

Magnetite



Goethite



Limonite

Fig. 3.1 : Raw iron ores (Hematite, Magnetite, Goethite, Limonite).

Amongst the gangue materials present in iron ore, Silica (SiO_2) and Alumina (Al_2O_3) are the most important. In Indian iron ore alumina is more and alumina to silica ratio is more than one.

Quality of iron ore or agglomerate is judged by the assessment of several properties through some laboratory tests that simulate the conditions inside the blast furnace. Based on the results of the tests, suitability of iron ore/ agglomerate as iron burden can be estimated prior to its charging. Characterization of iron burden can be classified as given below:

i) Mineralogical characterization
ii) Chemical characterization
iii) Physical characterization and
iv) Physico-chemical or Metallurgical characterization

Mineralogical characterization helps in identifying mineral phases and associated gangue materials since these materials greatly influence the bulk chemistry of the process and the quality of hot metal. A clear mineralogical analysis of iron ore samples of any particular deposit helps in selecting suitable blast furnace grade ore through the usual practice of blending, beneficiation etc.

Chemical characterization involves the analysis of iron ore and agglomerates, analysis of coke and lime stone. The major constituents of iron burden are Fe_2O_3, FeO, SiO_2, Al_2O_3, and the traces elements like Cu, Ni, Co, Pb, Zn and Mn. Through chemical analysis, the quality of iron burden for the blast furnace can be assessed prior to its charging. The detrimental elements in iron making and subsequent steel making that may be present in quality ore are listed below along with their allowable limits.

- $Na_2O + K_2O$: should not exceed 0.8%
- Zinc : maximum allowable limit is 0.02%
- Phosphorous : should not exceed 0.04%
- Cadmium and Sulphur (adversely affect the environment) : should be kept below 0.01%

Physical characterization is carried out through physical tests that are designed for burden material to withstand severe degradation during handling and transportation whereas; the physico-chemical behaviour of iron burden is assessed through metallurgical tests that are designed to correlate with actual operation prevailing in the blast furnace. In the present paper more emphasis will be given to both physical and physico-chemical characterization.

PHYSICAL CHARACTERIZATION

The essential physical properties which are normally characterized are

i) Specific gravity ii) Bulk density iii) Apparent porosity

iv) Friability v) Particle size and size distribution

vi) Strength

Since ores, sinters and pellets possess some inherent mechanical instability; their physical behaviour is ascertained through the tests mentioned above to have prior information on suitability of using as an iron burden.

Specific gravity gives an idea on how dense the material is. It is measured in a flask containing kerosene through the measurement of volume of liquid and the increase in volume that takes place on placing a weighed sample in kerosene. The result is expressed as the ratio of weight of sample in gm to the volume of displaced liquid in ml.

Bulk density is the weight of material in air taken in a unit volume of a container including the voids within and between the particles. It is measured with the help of a metal container having internal diameter of 400 ± 2 mm and internal height of 250 ± 2 mm and is expressed in weight units per unit volume.

While ores and pellets possess mostly open pores, in sinters there are macro- and micro- pores as well as open and closed pores. Apparent porosity measures the open pores through determination of the maximum amount of water that can be absorbed by the sample. The washed ore sample is placed on a support rack in distilled water and boiled for two hours. The sample is then allowed to cool down to room temperature under water and the weight of the sample under water is measured. This weight is designated as (S). The sample is then cleaned with a cloth to remove the surface water and weighed (W). The sample is then dried at 105°C for 2 hours and again weighed (D). Apparent porosity is expressed as given below.

$$\text{App. Porosity} = \frac{W - D}{W - S} \times 100 \text{ vol.\%}$$

Effect of change in apparent porosity on degree of reduction for varying reduction time is shown in Fig. 3.2. It shows that the degree of reduction increases with increase in porosity.

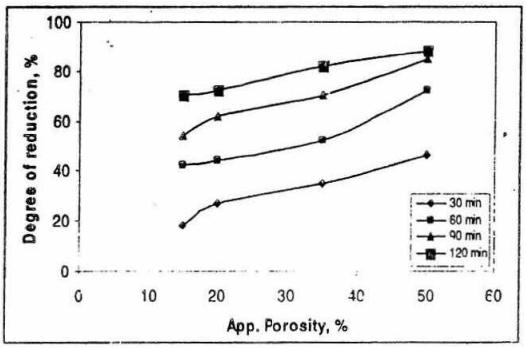


Fig. 3.2 : Effect of apparent porosity on degree of reduction.

Friability is determined by using a cast iron tumbler of 177 mm dia. X 177 mm depth, closed at one end and the other end is fitted with a lid. On the inside wall of the tumbler, there are three lifters of 173 x 37 x 10 mm size. 100 g of sample having size 8 – 16 mm is taken in the tumbler which rotates horizontally at 80 rpm for 4 hours. After tumbling the sieve analysis of the product is carried out and the result is reported in percentage fraction of various sizes. More friable material generates finer fraction.

Particle size is determined with the help of sieve set and the data is reported as the percentage fraction between the two sieves. The correct size as well as the size distribution of the burden is important in the view of the uniform flow of the gas through the charge bed as it influences the reducibility of the particles and the permeability of the bed. Wide size ranges favour in segregation and crest formation. Increased percentages of fine (less than 5 mm size) and larger sizes reduce reduction rate considerably. Normally, the upper size limit is considered to be 2 – 3 times the lower one which ensures a good ratio between the surface and volume of the lumps and an adequate gas-solid contact. By screening out –5 mm fraction, saving in coke, reduction in flue dust loss and increased performance of the furnace are achieved. A narrow size distribution has the advantage of increasing the charge permeability and the gas distribution becomes more uniform. Figure 3.3 shows that the degree of reduction decreases with increase in average size of iron ore.

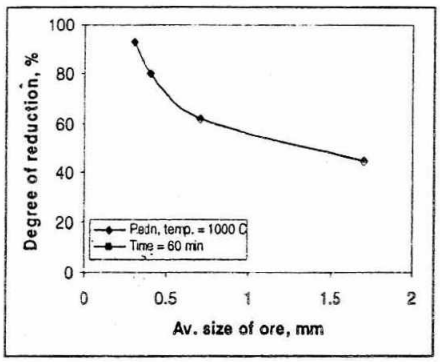


Fig. 3.3 : Effect of size of ore on degree of reduction.

Iron ore and agglomerates as charge material should be resistant to abrasion. If they break into finer fractions due to impact, abrasion, compression and volume change within the furnace, the smaller particles result in choking of voids thereby affecting reduction and productivity. **Strength** is the physical property of the material by virtue of which it withstands degradation during handling and transportation. The extent to which material breaks down during handling has an important bearing on the quality of charge material. It is imperative to evaluate the strength aspect of material by suitable tests such as Tumbler and Shatter, which are mainly devised to determine the generation of fines. Tumbler test means the susceptibility of ferrous material to break due to abrasion during transportation, handling and charging into the blast furnace. Around 15 kg of sample is rotated at 25 rpm for 8 minutes. Resulting +6 3 mm size fraction gives the measure of tumbler index and the -0.5 mm size fraction indicates the abrasion index. For good pellets the tumbler and abrasion indices are 85-95%, and 3-7% respectively, for sinters[4] these are 65-80% and 5-10% whereas for ores these vary over a wide range such as 60-95% and 2-25%. Shatter test measures the susceptibility to break down due to impact during loading, unloading and charging into the furnace. In this test around 20 kg of material is allowed to fall three times on a steel plate from a height of 2 metres. The percentage of +10 mm size fraction over 80 is the indication of a good sinter. Salient features of tumbler and shatter tests are given in Table 3.1.

Table 3.1: Salient features of tumbler and shatter tests

Tumbler Test (IS: 6495-1984):	Shatter Test (IS: 9963-1981):
Total weight of sample: 15 ± 0.15 Kg. Size: 10 – 40 mm. Total revolution: 200 at 25 rpm. Result: TI: %(+ 6.3 mm.) Abrasion: % (- 500 µm.)	Total weight of sample: 20 ± 0.2 Kg. Size: 5 – 40 mm. for sinters and ores 9 – 16 mm. for pellets. Dropping Height: 2 m. No. of Drops: 3 Result: % (10 mm.) and % (-5mm.)

Fig. 3.4 shows the increase in blast furnace productivity with increase in tumbler indices of sinter samples when blast temperature changes between 900 and 1000^{0}C.

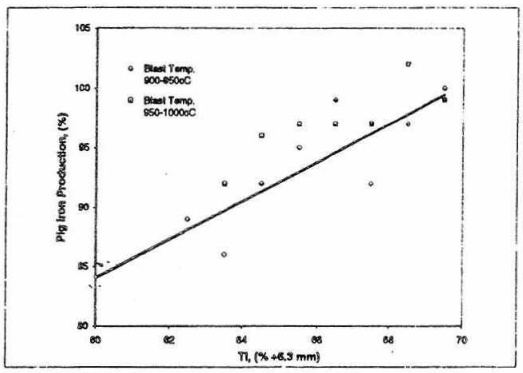


Fig. 3.4 : Effect of tumbler index of sinter on blast furnace productivity

PHYSICO-CHEMICAL CHARACTERIZATION

Quality of iron ore can also be judged through the assessment of several physico-chemical properties of ores. Characterization of iron ore helps in assessing these properties through some laboratory tests that simulate the conditions inside the blast furnace. Based on the results of the tests, the suitability of the iron ore as iron burden can be estimated prior to its charging.

Decrepitation

Decrepitation is a phenomenon of generation of deleterious fines from the iron bearing materials either having low tumbler/shatter index or being suddenly exposed to the exhaust gas temperature. It may also happen due to internal pressure developed from evaporation of inherent moisture or thermal shock. Iron bearing materials undergoing degradation due to abrasion, thermal shock and chemical reaction after being charged into the furnace may be pre-evaluated by Thermal Degradation Index and Reduction degradation index.

Thermal Degradation Index

The generation of fines from iron ore due to internal pressure developed from evaporation of inherent moisture or thermal shock has deleterious effect on the furnace performance and productivity. Such behaviour of iron bearing materials is pre-evaluated by Thermal Degradation Index (TDI). The reacting vessel containing 500 g of sample is placed inside the heating chamber and N_2 gas is allowed to pass through the reacting vessel at 5 ltr./min. The temperature is raised to

550^{0}C and the sample is heated at that temperature for 30 minutes. The vessel is then cooled to room temperature under the flow of N_2 gas @ 5 lit./min. The cold sample is taken out and rotated in a drum (200 mm length and 130 mm ID, having 2 lifters) for 30 minutes at 30 rpm. It is then screened through 3.15 mm size screen and the TDI value is calculated as follows:

$$TDI = \frac{\text{Wt. of (-3.15 mm) fraction}}{\text{Wt. of sample taken for experiment}} \times 100$$

There are little differences in the Indian standard procedure with Japanese standard in terms of temperature, duration of reduction and representation of results. Salient features of thermal degradation test for both the Indian and Japanese standards are given in Table 3.2.

Table 3.2 : Salient features of thermal degradation test for both the Indian and Japanese standards

Thermal Degradation in Normal Atmosphere		
Reference Standard ⟶	(IS 10823 : 1994; Reaffirmed Jan.2001)	**(JIS : M 8720 [2001])**
Weight of sample:	500 gms.	500 gms.
Size:	10-12. 5 mm.	10-15 mm.
Temperature:	600^{0}C.	550^{0}C.
Soaking Time:	60 min.	30 min.
Rotation speed:	30 rpm	30 rpm
Rotation time:	30 mins	30 mins
Result:	% (+ 5 mm)	% (+ 3.15 mm)

Reduction Degradation Index

The generation of fines from iron ore after charging in the blast furnace by decrepitation at lower temperature by abrasion and chemical reaction has deleterious effect on the furnace performance and productivity. Such behaviour of undergoing disintegration of iron bearing materials after being charged into the furnaces may be pre-evaluated by Reduction Degradation Index (RDI).

Based on the requirements of the industries the test is normally carried out as per Japanese standard. The reacting vessel containing 500 g of sample is placed inside the heating chamber and N_2 gas is allowed to pass through the reacting vessel at 5 ltr./min. The temperature is raised to 550^{0}C and is stabilized at that temperature for 10 minutes. N_2 gas flow is stopped and a mixture of 70% N_2 and 30% CO gas is passed for 30 minutes after drying the gas by passing it through KOH solution, pyrogallol solution and silica jel. The vessel is then cooled to room temperature under the flow of N_2 gas @ 5 lit./min. The cold sample is taken out and rotated in a drum (200 mm length and 130 mm ID, having 2 lifters) for 30 minutes at 30 rpm. It is then screened through 3.15 mm size screen and the RDI value is calculated as given below:

$$RDI = \frac{\text{Wt. of (-3.15 mm) fraction}}{\text{Wt. of sample taken for experiment}} \times 100$$

Here also exist little differences in the Indian standard procedure with Japanese standard in terms of temperature, duration of reduction and representation of results. Salient features of reduction degradation test for both the Indian and Japanese standards are given in Table 3.3.

Figure 3.5 shows the variation of RDI with FeO content in sinter for two sets of samples. It indicates a lower RDI value in the range of 6 to 8% FeO content in sinter samples.

Table 3.3: Salient features of reduction degradation test for both the Indian and Japanese standards

Reduction Degradation Index		
Reference Standard ⟶	(IS 10823 : 1994; Reaffirmed Jan.2001)	(JIS : M 8720 [2001])
Weight of sample	500 gms	500 gms
Sample Size	10-12. 5 mm.	10-15 mm
Drying of the sample	at 105^{0}C for 2 hrs	at 105^{0}C for 2 hrs
Temperature	600^{0}C	550^{0}C
Soaking Time	60 min	30 min
Rotation speed	30 rpm for 30 mins	30 rpm for 30 mins
Result	% (- 5 mm.)	% (- 3.15 mm.)

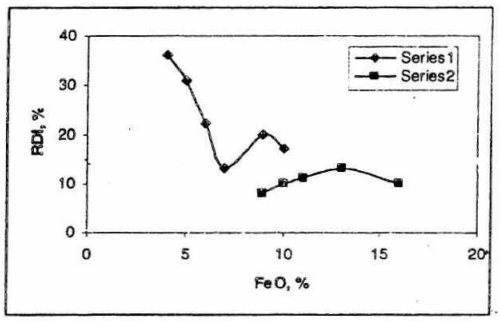


Fig. 3.5 : Variation of RDI with FeO content in sinter

Reducibility Index

It is one of the most important criteria to assess any iron bearing material along with other characteristics. It is the ease with which the combined oxygen with iron can be removed indirectly.

The reacting vessel containing 500 g of sample is placed inside the heating chamber and N_2 gas is started to pass through the reacting vessel at 5 ltr./min. The temperature is raised to 900^{0}C and is stabilized at that temperature for 10 minutes. N_2 gas flow is stopped and a mixture of 70% N_2 and

30% CO gas is passed for 180 minutes after drying the gas by passing it through KOH solution, pyrogallol solution and silica jel. The vessel is then cooled to room temperature under the flow of N_2 gas @ 5 lit./min. The cold sample is then taken out and weight is taken using a digital electronic balance. The Reducibility Index (RI) value is calculated as mentioned below.

$$RI = \frac{\text{Loss in weight of the sample}}{\text{Wt. of available oxygen in the sample}} \times 100$$

Salient features of reducibility test for both the Indian and Japanese standards are given in Table 3.4. The two standards agree in all respect but the size of sample.

Table 3.4 : Salient features of reducibility test for both the Indian and Japanese standards

Reducibility test		
Reference Standard →	(IS 11292 : 1985; Reaffirmed Dec.1991)	(JIS : M 8713 : [2000])
Weight of sample:	500 gms.	500 gms.
Size:	10- 12.5 mm.	10-15 mm.
Reductant	30% CO + 70% N_2	30% CO + 70% N_2
Temperature:	900 ± 10^{0}C .	900 ± 10^{0}C .
Soaking Time:	180 min.	180 min.
Gas flow rate:	15 lit. /min.	15 lit. /min.
Result:	%RI (% Oxygen removed)	% RI (% Oxygen removed)

Fig. 3.6 shows the photograph of the reducibility furnace used for carrying out reducibility test at NML. It also shows the capsule containing the sample in a hanging condition within the furnace.

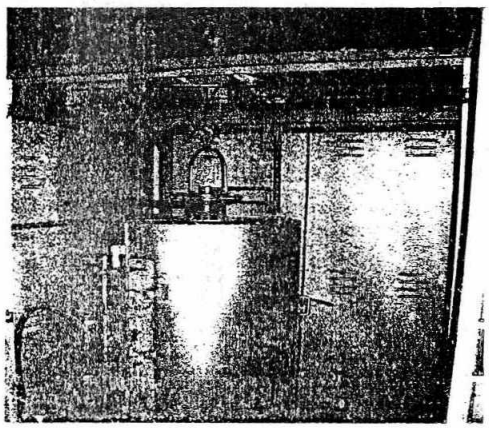


Fig. 3.6 : Photograph of reducibility furnace

Variation of degree of reduction with reduction time for pellets having two different porosities is shown in Fig. 3.7. It also shows that with increase in porosity the degree of reduction increases. Further, reducibility has the dependence on RDI value. More the RDI value of sinter indicates

that the sinter is more prone to disintegrate, however, improves reducibility. There should be an optimum between RI and RDI.

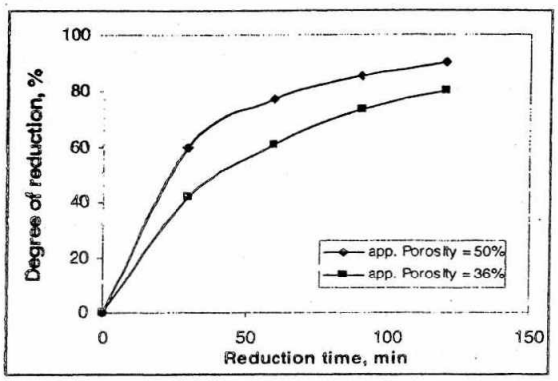


Fig. 3.7 : variation of degree of reduction with reduction time for pellets having different porosity

Softening and Melting

The solid to liquid transformation takes place in the cohesive zone through softening and melting[7] of materials over a temperature range. The complexity of blast furnace iron making is accentuated by the presence of softening melting zone that plays a vital role in the overall behaviour and performance of the furnace. Softening refers to the stage prior to the actual melt down of the iron bearing burden material. During the softening stage, the permeability of the iron bearing layers decreases markedly and thus strongly affects the distribution of gases. In the melt down stage, materials become semi fluid and drips to the hearth of the furnace. Softening or pre-mature fusion of raw ore and agglomerates is totally undesirable for better furnace performance. The charge becomes sticky and bed permeability decreases resulting in a considerable pressure drop in this zone.

Softening Temperature is basically the temperature at which the softening of the iron bearing material starts (Ts). Again, the temperature at which the melt of the sample drips is called the melting Temperature (Tm).

The condition under which the test is conducted is as follows:

Maximum temperature	1650°C
Sample bed diameter	48 mm
Sample bed height	100 mm
Particle size range	8 to 10 mm
Sample weight	Variable (~ 250 to 300 gms)
Reducing gas	30% CO + 70% N_2
Gas flow	6 liters/min at NTP
Heating rate	programmed as per requirement
Applied load*	1.0 to 2.0 kg/cm2 at 900°C up to end of the test

The sample holder consists of a graphite tube having the test sample of approximately 250 to 300g within it taken in between two perforated graphite blocks, one placed at the bottom and the other placed above the surface of the test material taken in between the graphite blocks. The bed

diameter is 48 mm and the height of the bed is approximately 100mm. A layer of coke of size 8 to 10 mm is placed on the top of the test sample and then top perforated graphite block is placed over it. The graphite crucible holding the sample is placed centrally inside the reaction chamber.

The top load ram is lowered down to the sample top surface and the depth to which the ram is lowered is measured. The melt collection chamber is placed at the appropriate position below the reaction chamber. All the thermocouples for measuring the sample temperature, furnace temperature and refractory wall temperature are placed at their appropriate positions. The high temperature softening-melting apparatus is shown in Fig.3.8.

The test is allowed to run under the programme indicated earlier. Sharp increase in gas pressure drop indicates the temperature for start of softening (Ts) as shown in Fig. 3.9. Melt collection chamber is rotated automatically to collect the dripped material. On completion of the heating schedule, the furnace is allowed to cool down to room temperature under neutral gas flow.

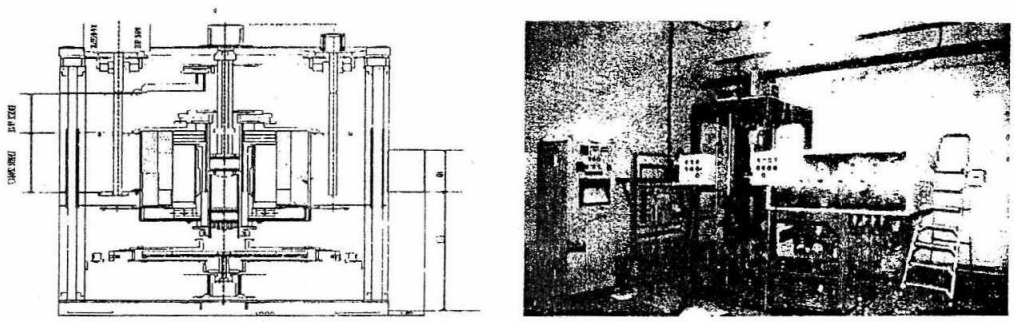


Fig. 3.8 : High temperature softening – melting apparatus

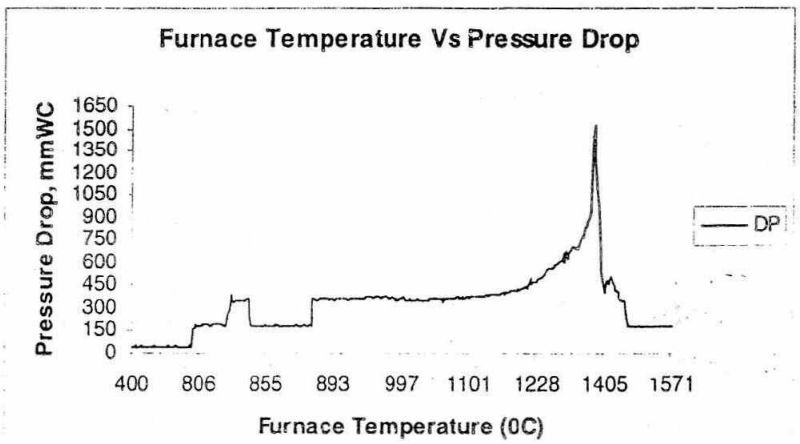


Fig. 3.9: Drop in pressure with furnace temperature during softening– melting experiment

Reduction under load test

This test simulates the reduction of iron bearing materials inside the blast furnace when the material is under load due to the material present over it.

Test conditions:

1) Composition of reducing gas

   $CO = (40 \pm 0.5)\%$ and $N_2 = (60 \pm 0.5)\%$

2) Purity of reducing gas

   Maximum impurity $H_2 = 0.5\%$, $CO_2 = 0.2\%$, $O_2 = 0.1\%$ and $H_2O = 0.2\%$.

3) Reducing gas is to be pre-heated by passing through the space between internal and external tube, at a flow rate of 5 m^3/hr S.T.P.

4) Temperature of reduction $1050^0C \pm 10^0C$.

5) Sample of ore, pellet, sinter in the size range of 10 to 12.5 mm [8 to 10 mm and 12.5 to 16 mm may also be considered for further tests].
   Charge weight = 1200 g.

6) Sample should be dried at $105^0C \pm 5^0C$ prior to test.

7) Load of 0.5 daN/cm^2 is to be applied.

Swelling

Some iron bearing materials particularly the pellets, exhibit a volume change[8] of unusual proportion with increase in degree of reduction. Swelling or volume increase occurs generally in hematite pellets when reduced at high temperature by indirect reduction. Various factors such as composition, nature and quality of impurities, time, temperature and degree of reduction, reducing gas composition, etc. can be attributed to the occurrence of swelling in pellets. Swelling index is the measurement of percentage increase in volume after reduction with respect to the original volume and is measured by the following relation.

$$S.I. = \frac{Vt - Vo}{Vo} \times 100$$

Where, Vo = Original volume before reduction
Vt = Volume after reduction

Maximum volume change for hematite pellets normally occurs at 900-1000°C and at a degree of reduction of 45-50%.

CONCLUDING REMARKS

The iron bearing feed material to iron making units bears the responsibility of smooth running as well as increase in productivity of the unit and needs to be characterized mainly for its physical and physico-chemical properties. Quality of iron ore or agglomerate is normally judged by the assessment of above properties through some laboratory tests that simulate the conditions inside the blast furnace. Based on the results of the tests, suitability of iron ore/ agglomerate as iron burden can be estimated prior to its charging. The pre-requisites for a good quality ore or agglomerate can be listed as in the following :

- Accurate size grading
- Good resistance to mechanical abrasion
- Good reducibility
- Low RDI
- Beginning of softening at high temperature
- Short interval between softening and melting temperature
- No unusual swelling
-

The better the quality of iron bearing feed material better is the furnace performance.

REFERENCES

1. Biswas, A.K. – Principles of Blast furnace iron making, SBA publication, (1999), 189.

2. Kortmann , A. - Agglomeration, 1, (1977), 219.

3. Goswami, M.C., Mahapatra , A.K.S. and Gupta , K.N. - NML Technical Journal, 29, (Feb.-Nov., 1987), 33-38.

4. Goswami, M.C., Pal, J. and Singh, D.P. – IIM Metal News, 10, No.-1, (Feb. 2007), 27-31.

5. Mahapatra, A.K.S., Goswami, M.C. and Gupta, K.N. – Tool & Alloy steels, (sept. 1993), 290-296.

6. Bhagat, R.P., Sil, S.K., Chattoraj, U.S., Goswami, M.C., Singh, D.P. and Das B.K. - Tata Search, 1, (2006), 127-134.

7. www.nmlindia.org/download/BF/HTSM.htm

8. Gupta, R.C. – Proc. of the seminar on "Experimental approaches in pyro-metallurgical research", (April 20-21, 2000), RRL Bhubaneswar, 11-19.