

CHAPTER-2:
LITERATURE REVIEW

2. LITERATURE REVIEW

Quality of the product pellets broadly depends on green pellet quality, type and amount binders, fluxes & additives used and firing conditions. Quality of green pellets, in turn, depends on input parameters like mineralogy, chemistry and granulometry of ore fines, balling parameters like initial feed size, moisture content and porosity etc. Physical and metallurgical properties of product pellets depend on the amount and type of binder and flux additions, induration parameters like firing temperature and time etc. Ingredients of the green pellets react together, during firing, to form different phases and microstructure.

The type and amount of these phases, their chemistry and distribution plays a vital role in deciding the metallurgical properties of the pellets during reduction in the subsequent iron making process. Green pelletizing and induration studies of magnetite and high grade hematite iron ore fines with low alumina have been carried out in different parts of the world. But the results of these studies cannot be directly interpreted to Indian iron ores due to the difference in chemistry and mineralogy. Indian iron ore fines with comparatively high alumina content exhibit different pelletizing characteristics and were not attempted for such detailed studies.

The main objective of proposed research work is to understand the pelletizing and indurating characteristics of hematite iron ore fines from Tata steel's captive iron ore fines from the Noamundi region of Bonai range in the Orissa-Jharkhand boarder. To convert these ore fines into pellets, the key raw material and process variables that influence the pellet quality needs to be identified and a correlation should be established between them.

The existing knowledge on green pelletizing and the induration in terms of the theoretical aspects and the current status of research have been presented in this chapter. The gaps in the understanding have been identified to serve as the basis for the present study.

2.1 Green pelletizing

2.1.1 Mechanisms of green pellet nucleation and growth

Forces contributing to the formation of green pellets from particulate solids are of two kinds: natural (or physical) and applied (or mechanical) [9]. The natural forces responsible for the formation of agglomerates can result from a number of sources:

- a) Attraction between solid particles due to van der Waals' forces, magnetic forces or electrostatic charges
- b) Interlocking effects between particles, depending on the shape of particles
- c) Adhesional and cohesive forces in bridging bonds, which are not freely moveable
- d) Interfacial and capillary forces due to the presence of a liquid phase.

The strength of green agglomerates results from the physical forces that hold the particles together; and the magnitudes of these physical forces are dependent on the particle size, surface charge: crystal structure, the proximity of the particles, the amount of additives and other physico-chemical properties of the system.

Rumpf [10] gave a detailed account of these forces and developed expressions for estimating their magnitude. His calculations indicate that the major contribution of the physical forces, in the presence of a liquid which completely wets the solid particle surface, is from the capillary attraction between the particles due to the air-liquid interfacial tension. These capillary forces are dependent on the relative distribution of the liquid and air phases in the porous agglomerate.

When the ratio of the liquid to the void volume of the agglomerate is quite low, the liquid is held in discrete lens-like rings at the point of contact between particles; and the air phase forms a continuous phase (**Fig 3(a)**). The entrapped liquid is said to be in a pendular state. The strength of this pendular bond arises from the negative capillary pressure and the surface tension of the liquid. By increasing the liquid content or by reducing the pore volume of the agglomerate, the liquid rings tend to coalesce and form a continuous network, resulting in the air phase becoming trapped. The agglomerate now is said to be in a funicular state (**Fig. 3 (b)**). Finally, the agglomerate is said to be in a capillary state when the void volume of the pellet is completely filled by the liquid (**Fig. 3 (c)**).

Mechanical forces are required to bring into contact with one another the individual wetted particles, within the pelletizing charge so that the natural forces can bring about their growth [11]. This mechanical action of moving the material is imparted by means of rolling, tumbling, agitating, kneading, extruding or compressing in a suitable apparatus. Agglomeration of damp powders makes use of tumbling or agitating the material in balling drums, discs or cones. The tumbling properties of the agglomerate charge are dependent on the physical properties of the powder, size distribution of the growing species, and size, geometry and speed of rotation of the balling device.

In industrial balling systems, the balling devices are continuously operated by making a constant supply of new feed available to previously formed seed pellets. Thus, for a general description of green pelletizing processes, it is convenient to conceptualize that the agglomerating system consists of two classes of species: the well-formed species and the added moist feed fines. The “added moist feed” is considered to consist of species of infinitesimal size and they simply contribute to the formation and/or growth of well-formed species. The “well-formed species” are defined to be those with finite size and those which undergo changes in their number and size by the occurrence of any of the growth mechanisms discussed in the following.

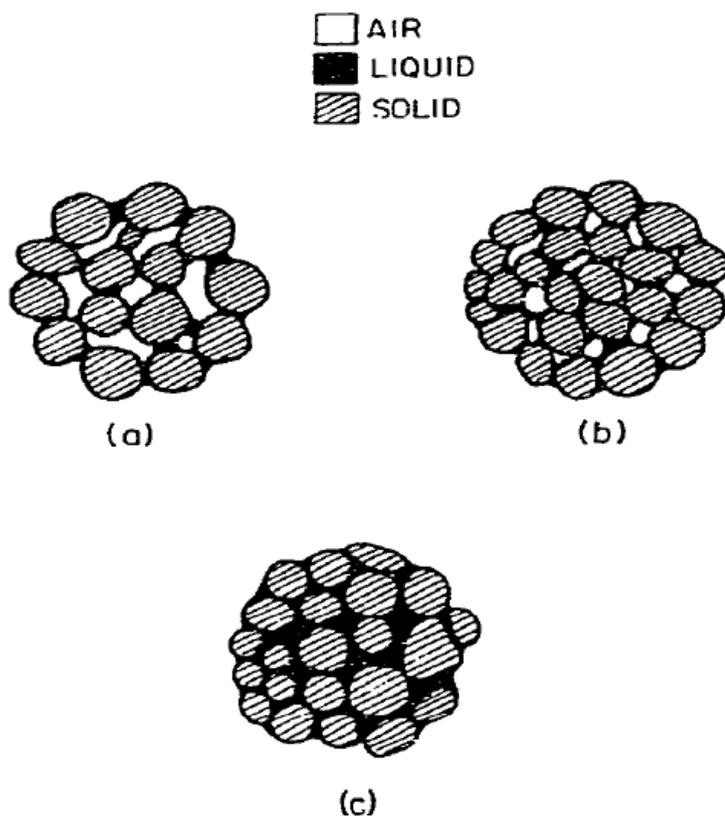


Fig.3 Structure of porous agglomerate with reference to the relative distribution of air-water-solid phases. (a) Pendular (liquid trapped) (b) Funicular (air trapped) (c) Capillary (air expelled-liquid saturated) [9]

Nucleation:

Any formation of new pellets in an agglomeration system from an extra supply of moist feed (i.e. generation of well-formed species), **Fig. 4(d)**, is termed as nucleation. The nucleation of new species results from capillary attraction between collection of individual moist feed particles. In a batch system, the formation of nuclei pellets has been found to occur within the first few drum revolutions [12]. The occurrence of nucleation thus brings changes in both mass and number of well-formed species in the system.

Coalescence:

It refers to the production of large-size species by means of the clumping of two or more colliding nuclei granules. Coalescence events cause discrete changes in agglomerate masses and contribute to an overall drop in the number of pellets, but do not change the total mass of the system. This mechanism is pictorially depicted in **Fig. 4(a)**.

Breakage:

The breakage of the pellets leads to the formation of a collection of daughter fragments, either all of the same size or of different sizes. These broken fragments are considered to belong to the class of well-formed species. **Figure 4(b)** is a schematic representation of this mechanism and for convenience it is shown that all the broken pellets are of unit size. These daughter fragments then redistribute over the surviving pellets, thus causing 'layering'. Clearly, breakage causes discrete changes in agglomerate masses, generates more well-formed species within the total mass.

Abrasion transfer:

Due to interaction and abrasion of the agglomerate species in the pelletizing charge, a certain mass of material is transferred from one species to the other. This is termed "abrasion transfer", as shown in **Fig. 4(c)**. The

abrasion transfer growth mode does not change either the total number or total mass of the pellets in the system and causes only continuous changes in sizes.

Snowballing (layering):

Whenever new moist feed is supplied to a system of pellets, the pellets act as seeds and tend to collect the newly added moist fines. This mechanism is termed as 'snowballing' or layering, as depicted in **Fig. 4(d)**. The pellets change their mass by snowballing in steps, each step occurring in an infinitesimal interval of time and an increase of unit mass by collecting one new feed nucleus. Thus, snowballing causes' continuous change in pellet size resulting in an increase in the total mass of the system and does not change the total number of pellets.

Batch balling of taconite concentrates with 0.5 wt.% bentonite and 10.8 wt.% water shows that green ball growth curve follows a characteristic S- shape indicating varying agglomeration rates. The three stages of agglomeration are; (a) nuclei, (b) transition, and (c) ball growth regions (as shown in **Fig. 5**). From this ball growth curves, it is difficult to identify these three regions precisely. However, by presenting agglomerate growth rates on a differential (as in **Fig. 6**) i.e. by plotting the rate of change of the average diameter as a function of the number of drum revolutions, it is seen that the ball growth occurs in three distinct regions of increasing, maximum and diminishing growth rates.

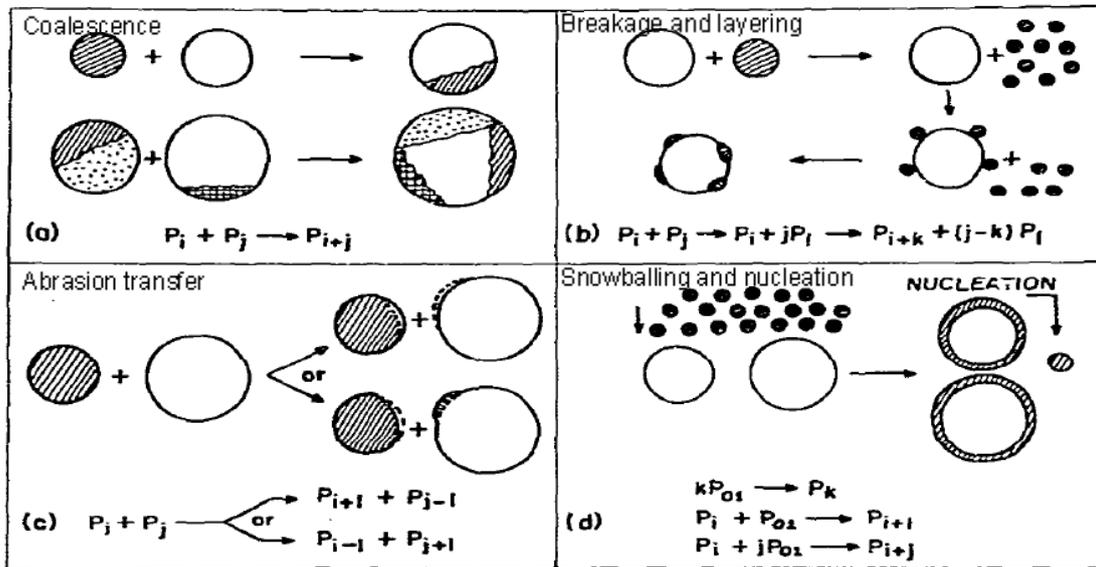


Fig.4 Formal representation of growth mechanisms. The symbol P_i is used to represent a green pellet of mass m_i and P_{01} refers to the freshly-added nuclei of mass h [9]

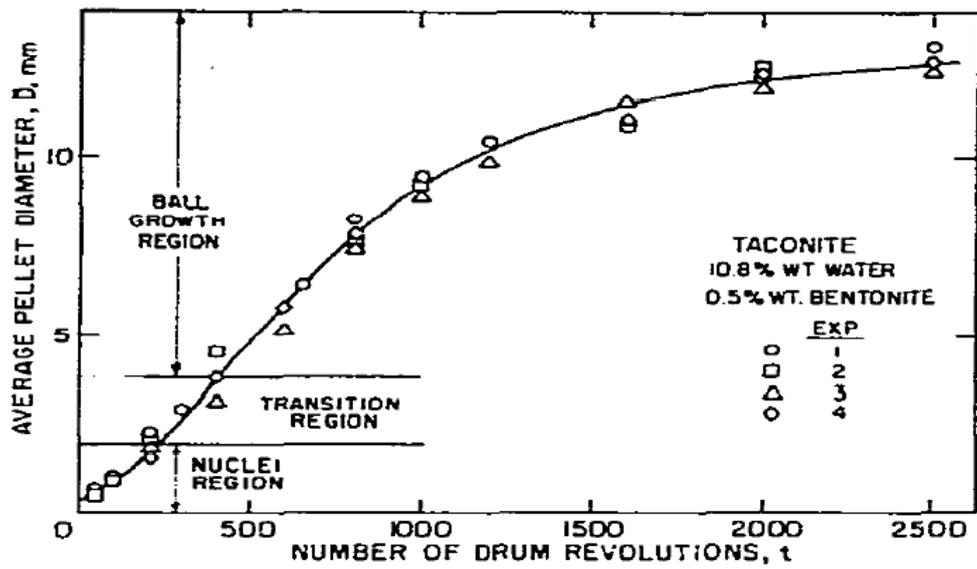


Fig.5 The average green pellet diameter as a function of the number of drum revolutions [9]

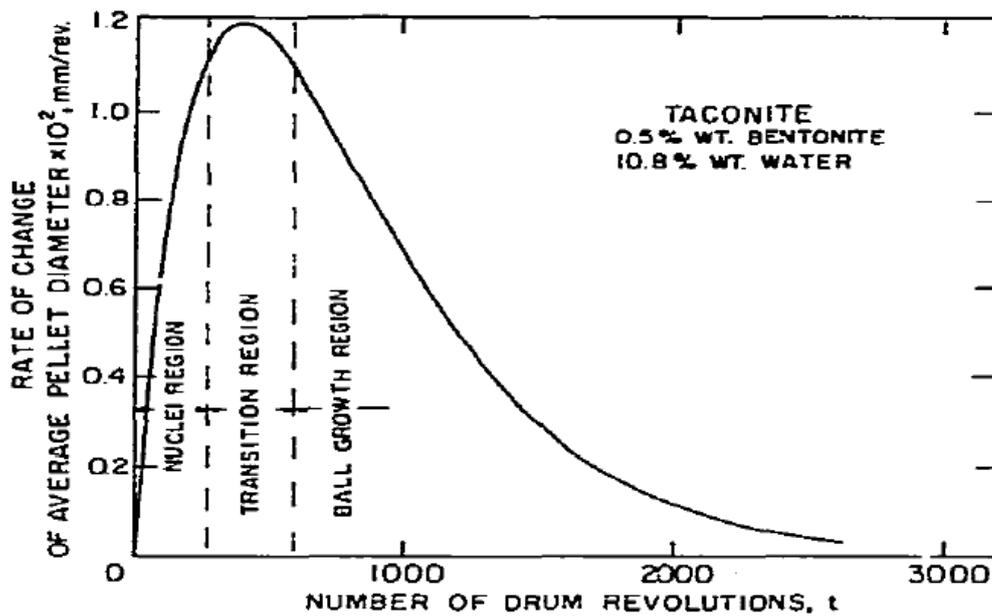


Fig.6 The differential growth rate curve for taconite concentrate [9]

2.1.2 Effect of iron ore quality on green pelletizing behaviour and pellet quality

The pelletizing behaviour of an iron ore as well as the properties of the pellets produced are affected by the various properties of the ore, viz., specific surface area, porosity, mineralogical composition, and particle size distribution of the fine material to be pelletized [13]. The effects of these properties are reflected in the amount of moisture needed for proper pelletizing and the sensitivity of balling kinetics to changes in moisture content and particle size distribution of the feed.

Porous ore with substantial amount of goethite and hydrated iron oxide in addition to hematite behave differently as compared to massive ores with specular hematite and magnetite. Under the same grinding conditions, the former type of ores yield more fines with high surface area compared to latter. Porous ores need more water for pelletizing compared to massive ores and the later are more sensitive to moisture content and bentonite addition. Some of the water added to the porous ore penetrates into the pores and attains a state of equilibrium with the water in the interstices and on the particle surface. Excess water may be stored in the pores, rendering the charge less sensitive to moisture content. Hard ore needs more degree of fineness as compared to porous ores for desired pellet growth. This phenomenon may be due to the extreme hardness of the ore and the small amount of fines produced during grinding. As a result, the internal voids in the pellet will be of large diameter, and hence the capillary pressures will be low. Furthermore, the number of points of contact will not be enough to hold the unity or uniformity of the agglomerate.

At given moisture content, porous ores exhibit higher drop numbers and compressive strength as compared to massive ores. This can be explained mainly by the relatively high amount of clay minerals present and wide size distribution in the porous compared to massive ores.

Oxide type iron ores like hematite differ from hydroxide iron ores like goethite in terms of wettability and contact angle. Contact angles of pure hematite and goethite are 53° and $8^\circ (+/- 10^\circ)$, respectively [14] and it increases with increasing hematite content of the ore and decreases with increasing goethite content (**Fig.7**). The wettability of particles, inferred from the contact angle, is one of the critical parameters that determine the amount of water needed during granulation or pelletizing. Increasing contact angle makes particles more difficult to agglomerate because it decreases the strength of the liquid bridges holding particles together. Lower contact angle (better wetting) means that less inter-particle moisture is required to form granules. However, lowering the contact angle will increase the amount of liquid that soaks into the pores of porous particles. This means that less of the added liquid remains at the surface to aid granulation. Therefore, an optimum contact angle of the iron ore needs to be maintained for better pelletizing.

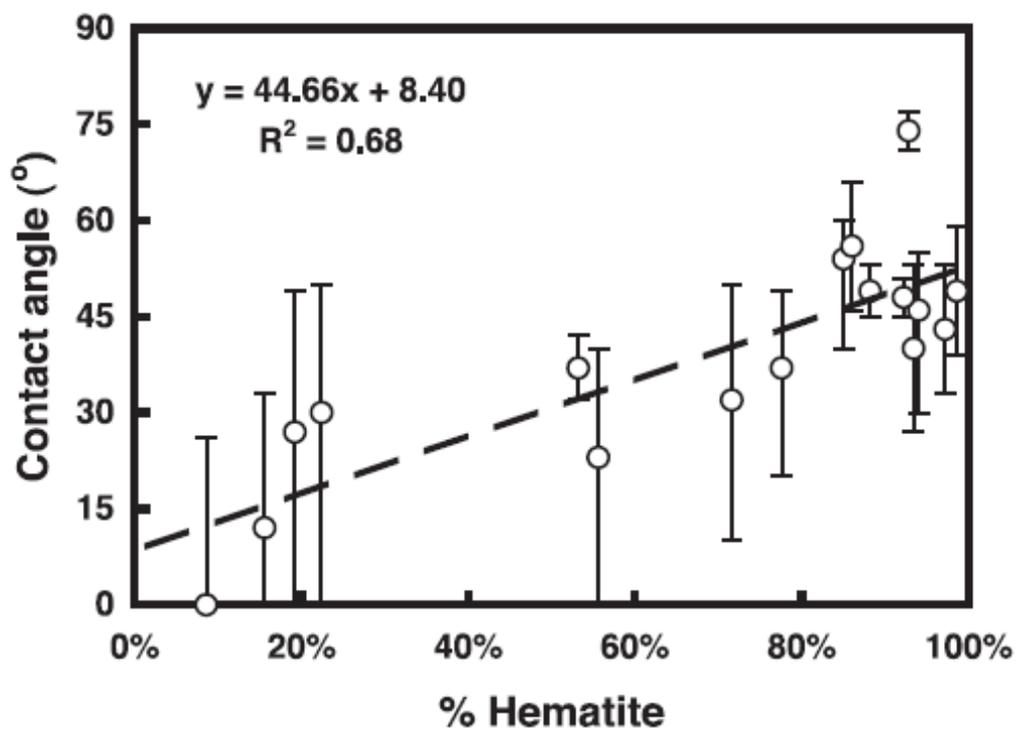


Fig. 7 Contact angle versus ore hematite content [14]

2.1.3 Effect of feed fineness on green pelletizing behaviour and pellet quality

With increasing fineness the drop number of the green pellets increases [15], due to the increased effect of molecular forces such as Van der Waal forces that increase the plastic behaviour. The compression strength of the green pellets decreases with increasing fineness of the pelletizing feed as shown in **Fig. 8**. This could be because of the fact that higher fineness increases the ball growth rate there by reducing the retention time in the balling device resulting in less interlocking & distribution of particles and less effective particle-moisture interaction.

Increasing the fineness of the feed increases the mean size (d_{50}) of the pellet at given moisture content [16]. **Fig. 9** shows the effect of top size of the feed on the size distribution of manganese concentrate and **Fig. 10** shows the effect of top size of feed on mean pellet diameter. This could be due increased cohesion of particles due to increased fineness at the given moisture content.

Increasing moisture content of the feed increases the mean size of the pellet [17]. **Figure 11** shows the effect of moisture content on the size distribution and mean pellet diameter of manganese concentrate. This could be due to the fact that increased moisture replaces the air in the air-solid-water system, and provides more contact points between solid-solid and solid-liquid phases.

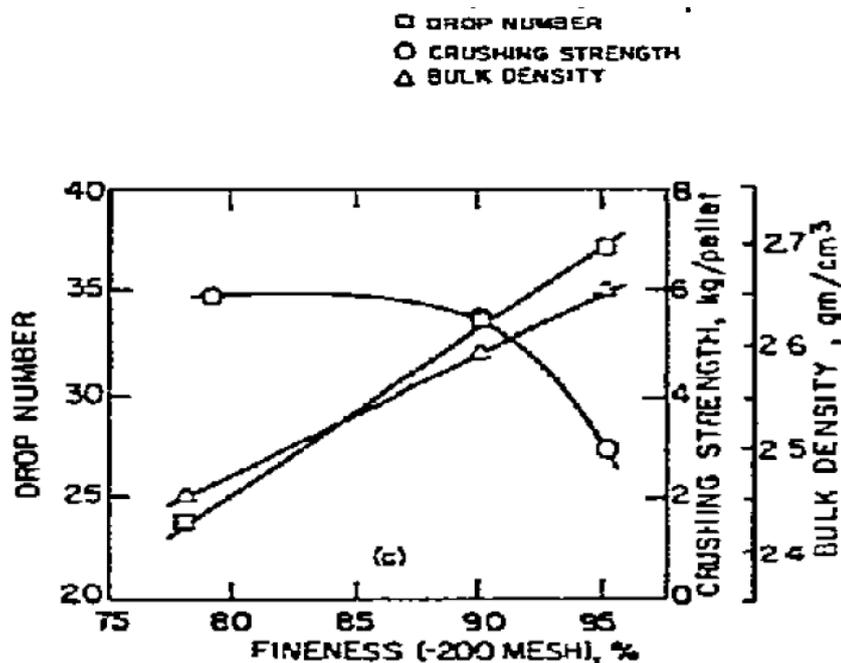


Fig. 8 Effect of pelletizing feed fineness on the drop number and compression strength [15]

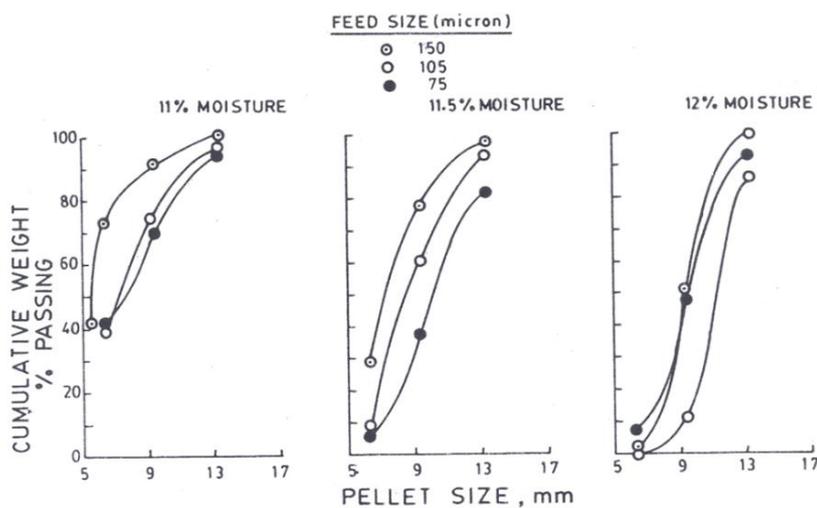


Fig. 9 Effect of feed fineness on the size distribution of manganese concentrate [16]

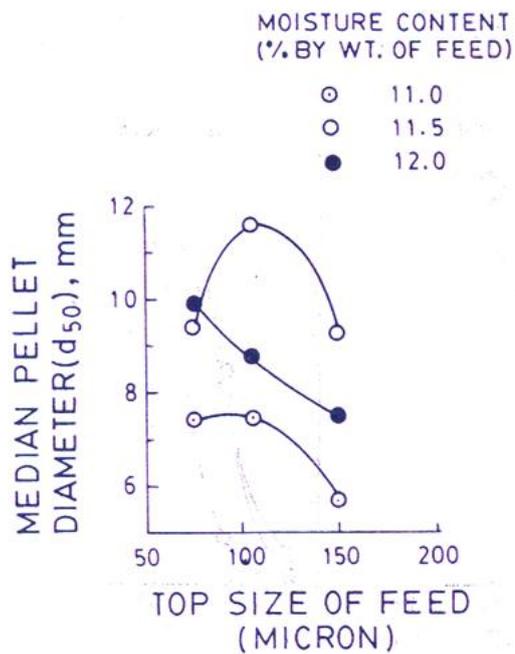


Fig. 10 Effect of feed fineness on the mean pellet diameter of manganese concentrate [16]

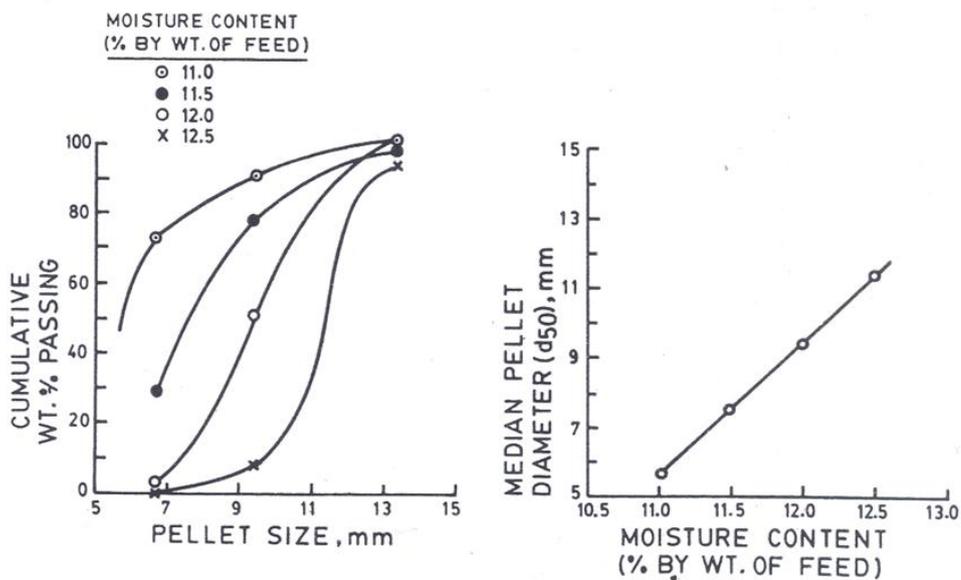


Fig. 11 Effect of moisture content on the size distribution and mean pellet diameter of manganese concentrate [17]

2.1.4 Effect of binders on green pellet quality

Green pellet growth and their properties are primarily controlled by their plasticity and viscosity of the liquid phase between the particles. The former is controlled by moisture content whereas the latter is controlled by the binder addition [18]. The plasticity of green pellets need to exceed a minimum level to enable their growth. The viscosity in the liquid phase, which is binder controlled, will help in coalescing the free pellet feed with the superficial water in the growing pellet.

The binder is supposed to fulfil two functions in the green pelletizing [19];

- I. It is supposed to impart plasticity to the moist ore to enable nucleation and growth
- II. It is supposed to hold the particles during drying in the absence of moisture till the pellets are hardened

Bentonite is most widely used binder in pelletizing. With increasing bentonite content, the drop number and green compression strength of the pellets increase as shown in **Fig. 12 & 13** [18]. Bentonite also influences the growth of pellets by way of increasing the growth rate of pellets due to increase in the viscosity of the liquid phase within in the pellet, as shown in **Fig. 14**[19].

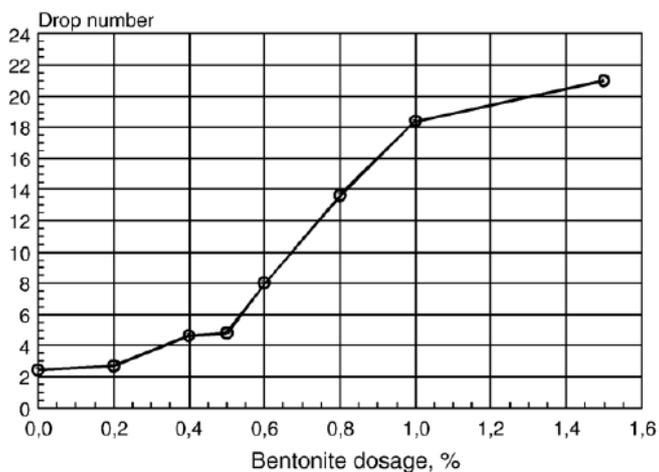


Fig. 12 Effect of bentonite dosage on the drop number [18]

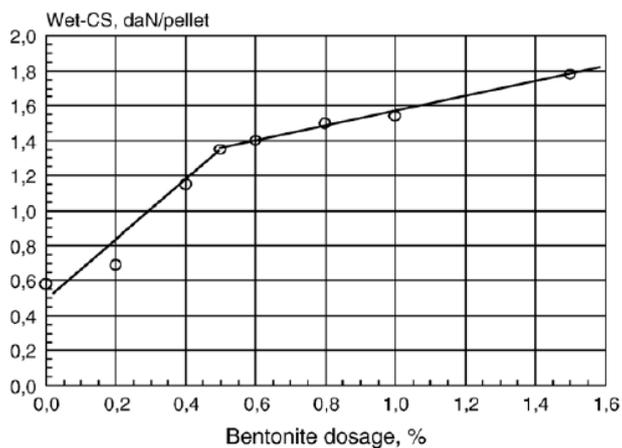


Fig. 13 Effect of bentonite dosage on the compression strength [18]

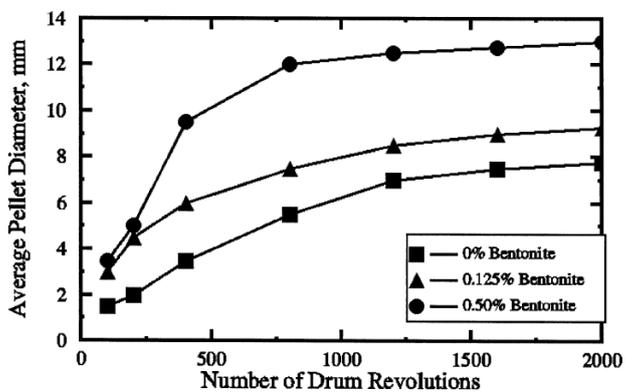


Fig.14 Effect of bentonite on growth of green pellets during batch balling [19]

2.1.5 Modelling of green pelletizing

Green pelletizing modelling involves predicting pellet size distribution for given level of variables. During green pelletizing, size distributions obtained under different operating conditions exhibit similar features, termed as “self-preserving behaviour” [20], a typical curve is shown in **Fig. 15**.

Pellet size distribution is predicted by quantifying the self-preserving curve and correlating D_{50} (mean pellet diameter) with the variables. Several models were derived for self-preserving curve by different workers, viz., Capes and Danckwerts [21], Kapur and Fuerstenau [22], Sastry and Fuerstenau [23], Ramabhadran [24] and Venugopal [25].

Venugopal developed a non-linear regression equation to relate d_{50} of pellets with different operating variables [26].

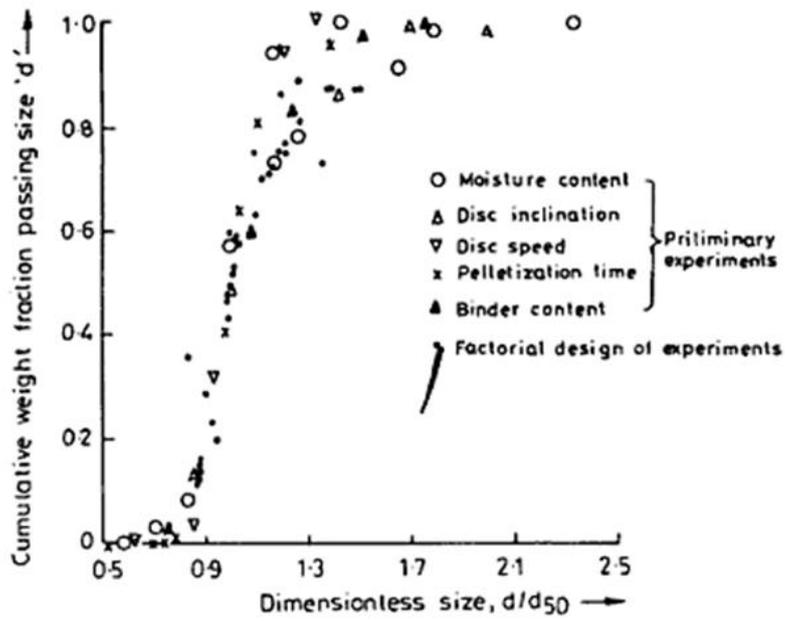


Fig. 15 Self preserving behaviour of manganese concentrate during pelletizing [25]

2.2 Effect of fluxing agents on the pellet quality

To meet the blast furnace slag chemistry, different fluxes, like limestone, dolomite, magnesite or pyroxenite need to be added to the burden. But it is uneconomical to add fluxes directly to the blast furnace, as their dissociation demands more energy leading to higher coke rate. They are usually added in the agglomeration process so as to increase the content of either CaO or MgO in the agglomerates. Effect of these basic oxides on the quality of sinter is well known, but their effect on pellet quality is scanty due to limited research work carried out.

2.2.1 Effect of CaO in the form of limestone on the pellet quality

During induration, green pellets are subjected to high temperature to attain strength that also results in the physical and chemical changes. High temperature results in thermally activated process like solid state diffusion, compound formation, melting, dissociation & precipitation and grain growth etc.

When limestone is added as flux, after its calcination it forms calcium ferrite ($\text{CaO}\cdot\text{Fe}_2\text{O}_3$) at contact points between lime and hematite for pellets with CaO/SiO₂ ratio above 0.5 [27]. At around 1150-1200°C, calcium ferrite reacts with hematite to form calcium diferrite ($\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$). $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ ferrite melts at 1216°C whereas $\text{CaO}\cdot 2\text{Fe}_2\text{O}_3$ melts at 1185°C, as shown in **Fig.16**. With further increase in temperature, liquid ferrite reacts with silica particles to form complex iron calcium silicates that form as bonding phase.

Calcium diferrite (CF_2) is thermodynamically unstable and it decomposes to calcium ferrite and hematite below 1155°C [28]. CF_2 formation is undesirable as it precipitates secondary hematite in the slag phase and its reduction generates stress that breaks the bonding in the pellets.

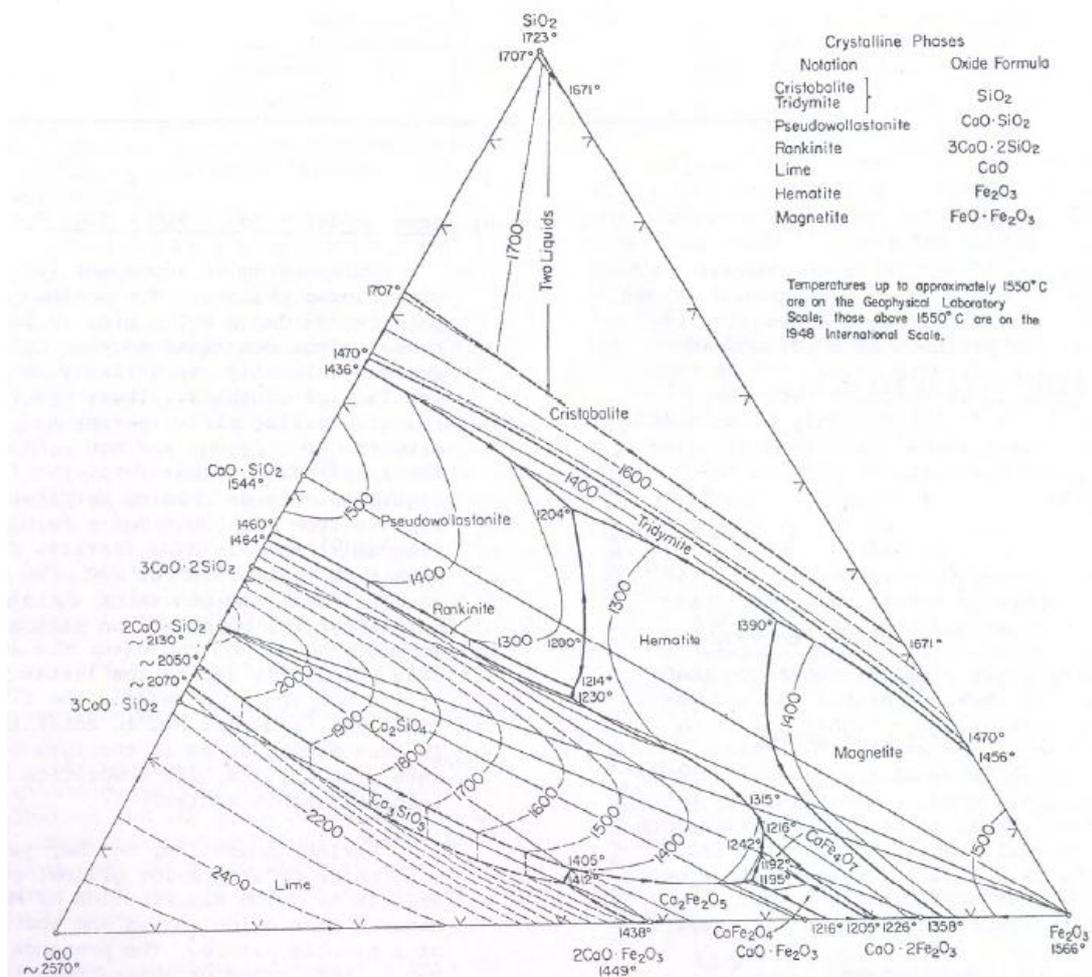


Fig. 16 CaO-Fe₂O₃-SiO₂ system in air [27]

Addition of limestone to the pellets decreases their strength after preheating, as shown in the **Fig.17 (a)**, as they hinder the micro-crystallization of hematite grains [29]. Strength of fired pellets with limestone addition increases up to 0.4 to 0.6 basicity (B_2) and decreases thereafter, (**Fig.17 (b)**). At lower basicity, small amount of liquid phases formed helps in recrystallization of hematite grains increasing the strength, whereas at high basicity, increased amount of liquid phase destroys the structure of pellets.

In the limestone fluxed pellets, maximum swelling occurs in the range of 0.2- 0.8 basicity, as shown in the **Fig.18**, due to the formation of low melting point olivines with 80% Fe_2SiO_4 and 20% Ca_2SiO_4 with melting point as low as $1115^\circ C$ [30]. Work of Akira et. al., on self-fluxed pellets also confirmed that highest swelling occurs in the CaO fluxed pellets in the basicity range of 0.5 to 0.7 due to the solid solution of slag components in iron oxide [31].

CaO in the pellet, during reduction, forms solid solution with wustite to form calcio-wustite. During metallization, calcia (CaO) promotes nucleation and growth of iron whiskers, especially at high CaO sites [32]. CaO also diffuses into the wustite phase in solid state and lowers its melting point [33]. In the CaO fluxed pellets, decomposition of ferrite and formation of CaO-FeO- SiO_2 ternary liquid slag increases the swelling tendency [28].

Among the pellets with varying basicity ranging from 0 to 1.6, excellent reducibility was obtained at 1.3 basicity [34], as shown in **Fig.19**. This could be due to the fact that CaO forms a solid solution with wustite, forming porous iron morphologies as final product as compared to dense iron layer formed from pure wustite at lower basicity levels.

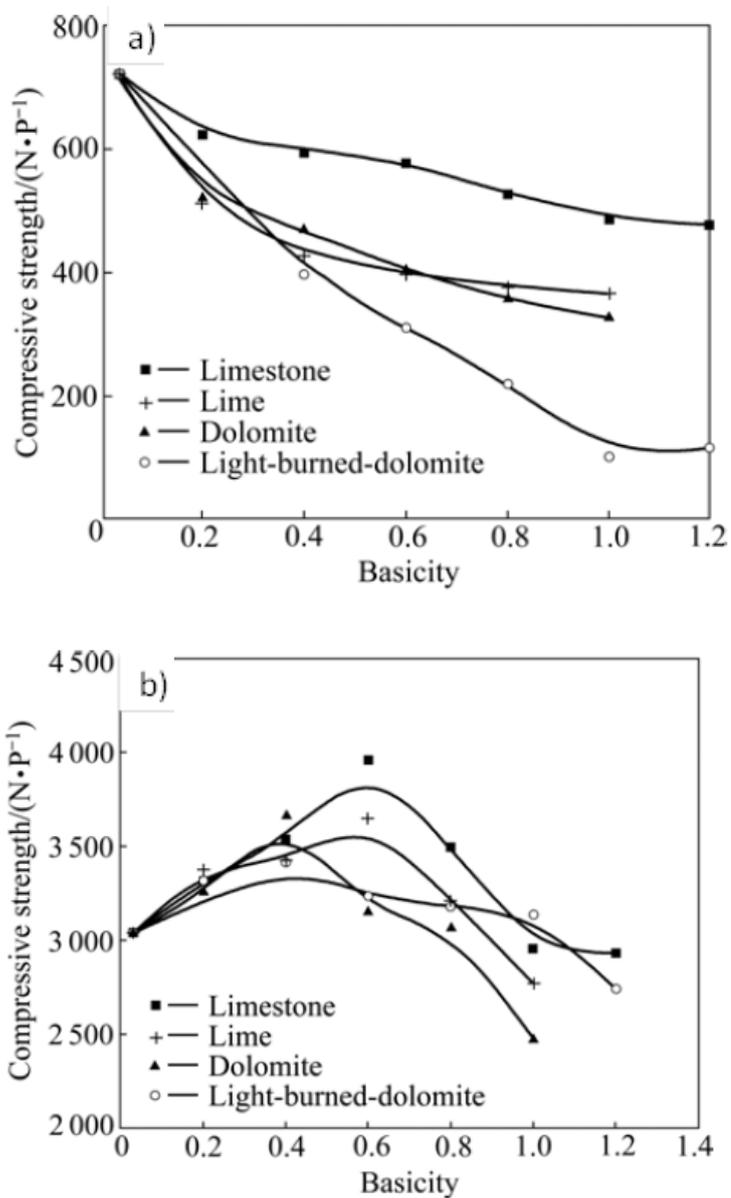


Fig. 17 Effect of limestone addition on the strength of (a) preheated and (b) fired pellets [29]

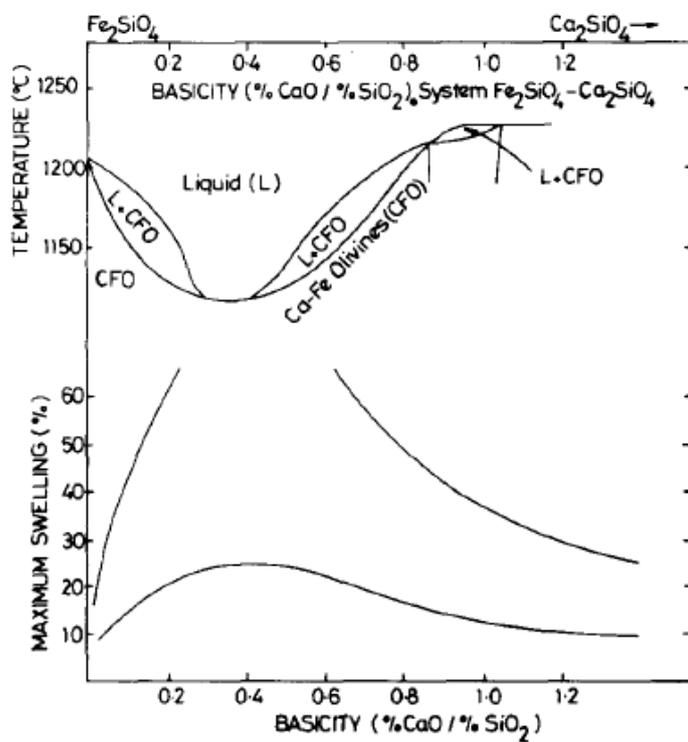


Fig. 18 Effect of pellet basicity on their swelling behaviour [30]

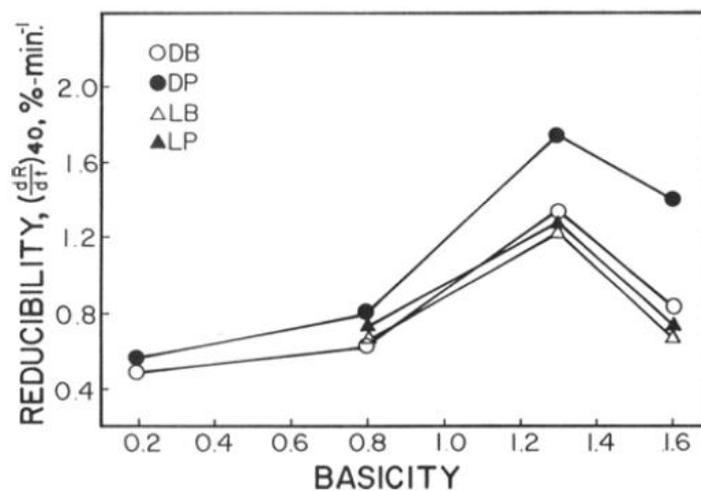


Fig. 19 Effect of pellet basicity on their reducibility [34]

2.2.2 Effect of MgO in the form of dolomite on the pellet quality

When dolomite is added to the pellets as fluxing agent, its calcination to CaO and MgO, is followed by the formation of magnesioferrite ($\text{MgO}\cdot\text{Fe}_2\text{O}_3$) by solid state reaction at temperature more than 700°C [27].

In the dolomite fluxed pellets, after calcination, first reaction takes place, in solid state, between $\text{CaO}\cdot\text{Fe}_2\text{O}_3$ and $\text{MgO}\cdot\text{Fe}_2\text{O}_3$. As the MgO has less solubility in calcium ferrites, the former enter joins the slag phase only after the formation of calcium-iron-silicates [28].

MgO after calcination enters and stabilizes spinal structure by forming magnesioferrites. CaO combines with silicates to form calcium silicates and also forms calcium ferrites at high basicity. Dolomite fluxed pellets with 1.5% MgO at 0.8 basicity showed superior reducibility at high temperature, as shown in **Fig.20**, due to porous structure and presence of calcium ferrites [35].

Work done by Gupta and W-K Lu, indicated that dolomite addition increases the pellet strength after induration and low temperature reduction (at 550°C) but increases the swelling [36].

Dolomite fluxed pellet at 0.8 basicity results in the formation of magnesioferrite and slag phase of two types, one high in Fe and MgO and the other rich in CaO and SiO_2 .

Dolomite addition also results in higher porosity due to the formation of less slag as MgO raises its liquidus temperature [34]. Reducibility also found to increase at 1.3 basicity with dolomite addition, due to high porosity of the pellets.

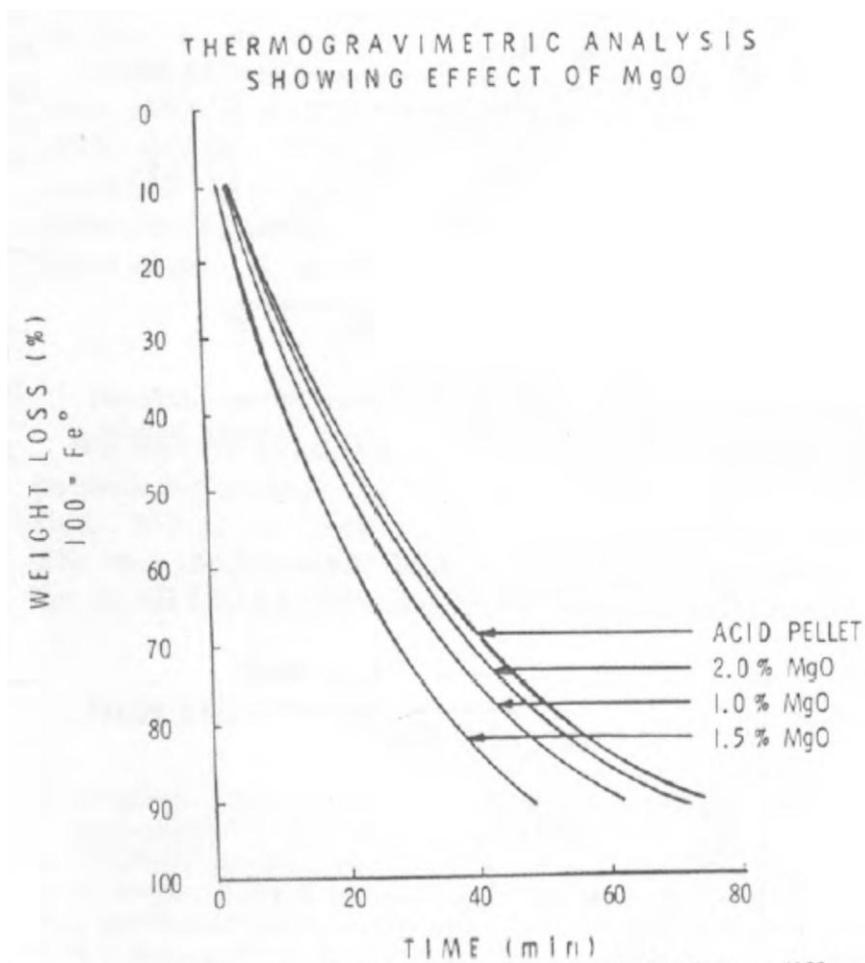


Fig.20 Effect of pellet MgO on its reducibility at 1.3 basicity [35]

2.2.3 Effect of MgO in the form of magnesite on the pellet quality

The degree of reduction of pellets increases with increase in the MgO/SiO₂ ratio as shown in **Fig.21**. When MgO is added in the form of magnesite, the pellet porosity is expected to increase due to the decomposition of magnesite thereby improving the reducibility.

The swelling tendency of pellets also decreases with increasing MgO/SiO₂ ratio of pellets as shown in **Fig.22**. Low swelling could be due to the fact that magnesioferrite, during reduction, does not cause volume increase as it has a spinal structure with a cubic system which is same as wustite. Hematite is the primary cause for swelling and it was calculated that 1 wt.% hematite in the pellets leads to 0.15% increase in volume. The volume is including the volume caused by transformation of hematite, cracks caused by it, sintering among iron oxide particles, and solid solution of gangue minerals into iron oxide [37].

From phase diagrams (FeO-SiO₂-MgO and SiO₂-CaO-MgO), it is understood that slag phase with high MgO/SiO₂ ratio has high melting point irrespective of its FeO content. Cao content should be as low as possible as it lowers the slag formation temperature [38].

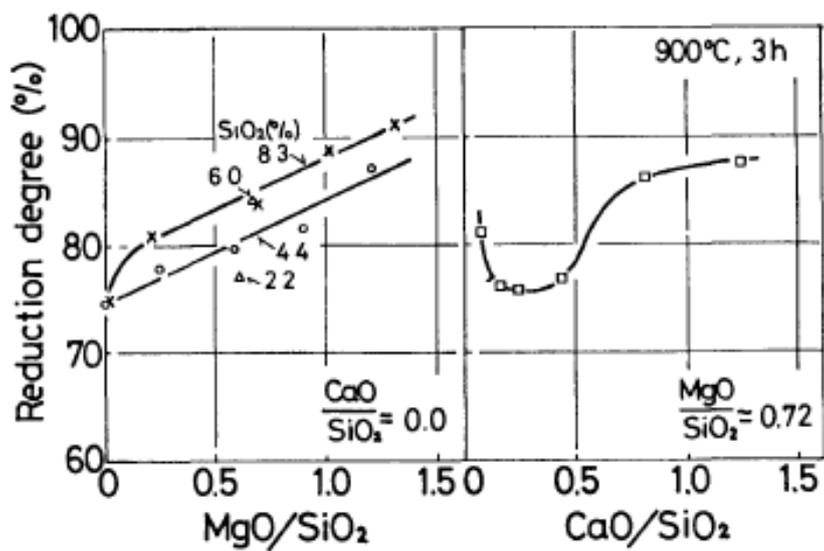


Fig.21 Effect of MgO/SiO₂ ratio on reducibility of pellets [37]

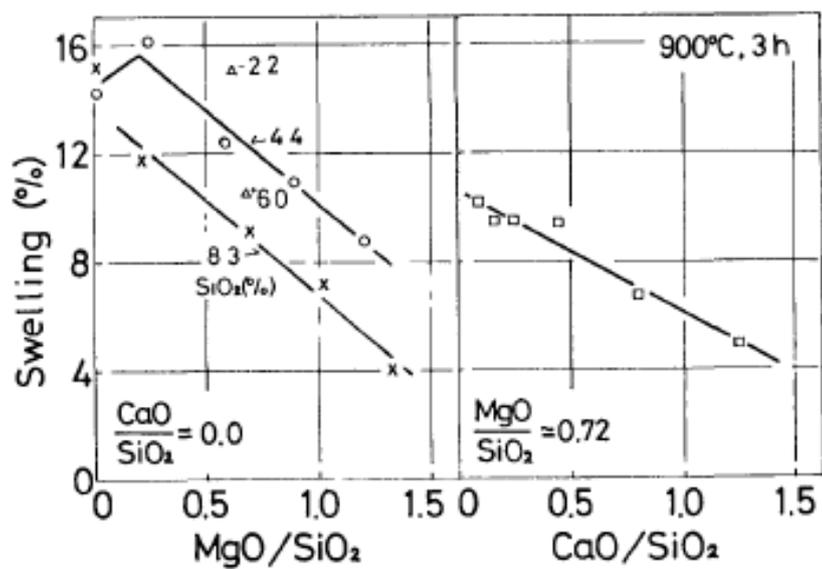


Fig.22 Effect of MgO/SiO₂ ratio on swelling of pellets [37]

The reduction degree of CaO-free MgO pellets, at high temperature (1250°C), increases significantly when the MgO/SiO₂ ratio is more than 0.4 as shown in **Fig.23** [39]. In CaO fluxed pellets, reduction degree drops steeply up to 0.3 CaO/ SiO₂ ratio and increases thereafter. Liquid slag formation that causes volume contraction during the reduction, influences the reducibility to a great extent. Acid pellets, during reduction, form more amount of low melting point (~1200°C) fayalite slag leading to closing of pores and hence low reducibility. With increasing MgO/ SiO₂ ratio, amount of liquid slag decreases due to the formation of high melting point (~1500°C) olivine. In CaO fluxed pellets, up to 0.3 CaO/SiO₂, formation of low melting point (~1250°C) anorthite increases leading to closure of pores.

Pellet softening temperature increases with increasing MgO/SiO₂ as shown in **Fig.24**. In CaO fluxed pellets, lowest softening temperature occurs at 0.45 CaO/SiO₂ ratio. Softening degree of pellets below 1100°C is more affected by the strength of iron oxides than the slag phase [39], whereas above 1100°C, it is more affected by the pellet chemistry and slag phase. Softening properties of pellets can be improved by increasing the amount of solid slag.

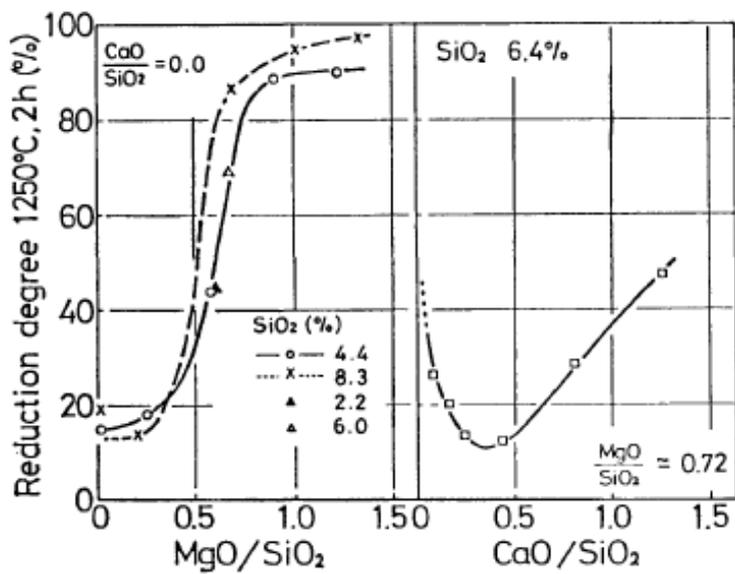


Fig.23 Effect of MgO/SiO₂ and CaO/SiO₂ on high temperature reducibility of pellets [39]

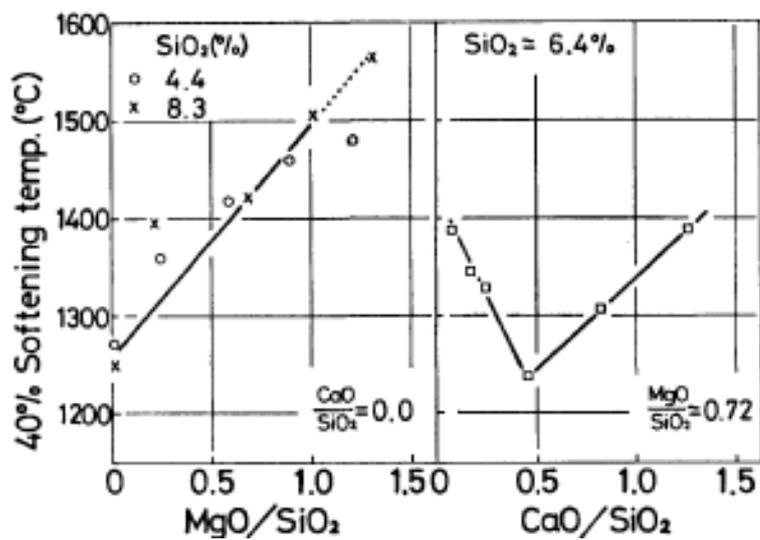


Fig.24 Effect of MgO/SiO₂ & CaO/SiO₂ on softening temperature of pellets [39]

2.2.4 Effect of MgO in the form of olivine on the pellet quality

Addition of MgO in the form of olivine to magnetite concentrate was found to stabilize the magnetite structure by forming magnesioferrite [40]. Magnetic susceptibility of the pellets, in the form of high Fe^{2+} content, increases with increasing MgO/SiO₂ ratio as shown in **Fig.25**. Porosity of pellets also increases with increasing MgO content in magnetite pellets. This is due to the fact that magnetite is stabilized in view of the diffusion of Mg^{2+} ions into the iron oxide lattice, thereby minimizing the heat available from magnetite oxidation, recrystallization and grain growth. Cold strength of the pellets also decreases due to the same reason, as can be seen in **Fig.26**.

MgO addition in the form of serpentine reduces the swelling of pellets made from both hematite as well as magnetite concentrates as shown in **Fig.27**. This could be due to the fact that MgO is dissolved in FeO to form $[(1-x)\text{MgO}.\text{Fe}_x\text{O}]\text{O}.\text{Fe}_2\text{O}_3$ thereby reducing the migration of Fe^{2+} during reduction that leads to no change in volume hence low swelling [41].

Work done by Bentel [42] revealed that with increasing MgO/SiO₂ ratio, the high temperature reducibility of pellet increases in olivine fluxed pellets. Lingtan K., et al. [43] reported that addition of MgO addition to pellets caused more low temperature breakdown due to the formation of cracks between the reduced magnetite phase and magnesioferrite spinel. However MgO improved the high temperature reducibility of pellets due less liquid slag formation.

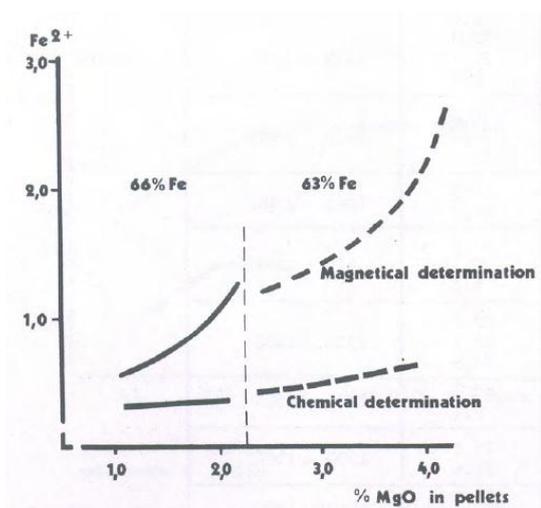


Fig 25 Effect of MgO on the Fe²⁺ content of pellets [40]

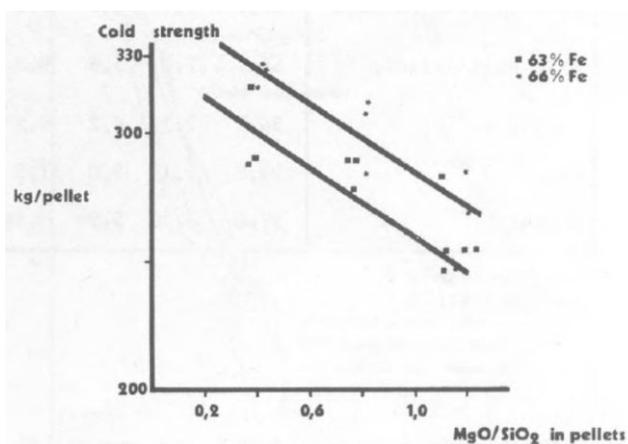


Fig 26 Effect of MgO/SiO₂ ratio on the cold strength of pellets [40]

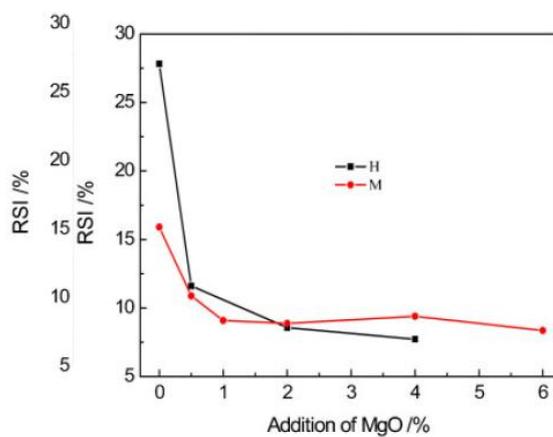


Fig 27 Effect of MgO in the form of serpentine on the swelling of pellets [41]

2.3 Summary of literature review

It has been observed from the literature survey that most of the earlier studies from different workers, on effect of fluxes viz., limestone, dolomite and olivine on the pellet quality, were carried out on iron ore fines that are either primarily magnetite or high grade hematite ores with low amount of alumina.

It is important to note that conditions and parameters of the pelletizing are specific to given ore or concentrate, the results available through literature provide some perception about the pelletizing behaviour for the given conditions but cannot be directly interpreted to the iron ore fines available in the Noamundi region, India. As the Noamundi iron ore fines are distinctly different from the reported ore fines in the literature, especially in terms of high alumina content of the former, there is a pressing need to undertake a detailed study in terms of their characterization, green pelletizing and effect of fluxes on the pellet quality.