SYNOPSIS

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3.	Date of Registration	: 23rd September, 2002
4.	Previous Degree	: M. Tech. (Metallurgical Engineering)
5.	Area of Research	: Process Metallurgy
6.	Thesis Title	: Characterization of Cold-Bonding and Fundamental Studies on Reduction Smelting of Iron Ore-Coal Composite Pellets
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9.	Date of Synopsis submission	: 13th September, 2007
10.	Month and Year of Thesis submission	: June, 2008

For the past hundred years, blast furnaces (BF) have played a dominant role in producing hot metal because of their high efficiency, mass production and high degree of gas utilization. It will remain the most important route for producing iron until metallurgical coke of consistent quality and agglomerated or lumpy feed materials are available at competitive cost. However, scarce availability and high cost of coke/coking coal, high capital cost, large scale of economy and ecological considerations against the conventional BF route have been the main driving force for development and growth of alternative ironmaking process routes. Alternative routes of ironmaking include direct reduction processes producing iron in solid form or smelting reduction processes which produces liquid hot metal directly. A number of direct reduction (DR) processes, both coal and gas based, have been developed and adopted at commercial scale in different parts of the world. Some of the smelting reduction (SR) processes, especially Corex, have also been established at commercial scale.

Indian iron ore deposits are soft and friable in nature and hence, contain quite a good amount of superfines (-200 mesh) rich in iron content (65 pct and above) and low gangue content. These are known as *blue dust.* Enormous amount of coal fines and coke breezes are produced during coal mining and coking of coal respectively. Around 4 Mt of fine slimes (containing 55 to 60 pct iron) are generated every year by ore washing plants in India. Mill scales are produced in large amount by various processes like hot rolling, hot forging, and heat treatment during quenching. These fine concentrates can not be processed in DRI reactors such as Midrex, HyL, rotary hearth and rotary kiln.

Utilization of these fines for extracting metal is of vital concern for resource conservation and pollution control. Industrially fine iron ore concentrate is pelletized into spherical balls of 8-20 mm diameter and then indurated up to 1573 K in an induration furnace to enhance the mechanical strength of pellets. In the induration process, fuel (liquid or gaseous) is consumed to supply the heat, thus CO_2 and other pollutants are emitted. Moreover, the capital cost of the induration furnace is also very high. In order to utilize these fines efficiently and economically, a novel concept of cold bonding is developed.

In the cold bonding concept, the fines of iron bearing oxides and carbonaceous materials are mixed with a suitable binder and optimum quantity of moisture. The mixture is then pelletized into balls of appropriate size. In cold bonding process, the pellets are hardened due to the physico-chemical changes of the binder in ambient conditions or at slightly elevated temperature (400 to 500 K). The challenge in cold bonding is to find a good binder that ensures the proper physical and mechanical properties of the pellet.

The term composite pellet is being employed here to mean pellet containing mixture of fines of iron bearing oxide and carbonaceous material (coal) which has been imparted sufficient green strength for subsequent handling by cold bonding technique. The prepared cold bonded pellet should have sufficient mechanical strength to withstand high temperature and stresses in reduction furnaces.

Interest in ore-coal composite pellet technology had been there for many years without any significant application in iron making. The principal technological problem was to produce pellets with sufficient strength at low cost. Advances in cold bonding technology have brightened the prospects. Cold bonded iron ore-coal/coke composite pellets are very promising feed materials in smelting reduction processes. Interest in composite pellets has grown from the decade of 1980s because of the following advantages:

i) utilization of cheaper resource and pollution control,
ii) very fast reduction due to intimate contact between reductant and oxide particles,
iii) reduction in energy consumption because cold bonded composite pellets do not require induration,
iv) promising prospect for iron making at small scale with higher production rate,
v) because of their uniform size and convenient form, pellets can be continuously charged into the furnace leading to higher productivity, and
vi) consistent product quality as the chemical composition of composite pellets (input material) does not change.

The concept of SR process of iron ore, an alternative to BF technology was initiated around 1970. This concept got evolved due to the progressive measures taken in the development of processes for direct reduction of iron ore. The SR process involving both reduction and smelting are very similar to blast furnace in which all the reactions take pace in a single reactor. Most of the smelting reduction processes involve the removal of oxygen from iron ore in the solid state followed by further removal of remaining oxygen in liquid phase reduction reactions. Ideally, a smelting reduction process should have near 100 pct reduction of iron oxides in the liquid state in a single stage in a single reactor.

There is shortage of coking coal all over the world in general and in India in particular. On the other hand, India has vast reserves of non-coking coal (i.e., approximately 81.7 pct of total coal reserves) which is widely available and cheapest reducing agent for iron oxide. Hence, non-coking coal based iron making technology has special relevance for country like India. In fact, the need to make non-coking coal based iron making units economically viable has resulted in the development of SR processes which do not face sticking problems at high temperature. The SR process exploits faster reduction kinetics at high temperature due to enlarged specific contact area between reactants in a dispersed phase and increased mass transport rates due to convection and thereby improves productivity. The process make use of non-coking coal in a broad range of composition and accept a wide range of materials including iron ore fines, plant wastes or inferior grade ore directly. Their process control is relatively simple and they work out economically at small-scale operation catering to varying demands of the market. The process is environmentally acceptable keeping the demands of coming years in view. Some of the upcoming SR processes are Corex, Romelt, HIsmelt, Ausmelt, DIOS, AISI-DOE, Redsmelt, Fastmet, Finex, Iron Dynamics, ITmk3, Kawasaki Star Process etc. Amongst these SR processes, Corex has already been established at commercial scale and Romelt is in advanced stage of commercialization.

Iron ore-coal composite pellets can be used as feed material for smelting reduction. Rate of production is expected to be much higher with composite pellets due to high degree of pre-reduction to the smelting reactor. There have been a few investigations reported in the literature on smelting reduction of iron oxides in contact with Fe-C melts (mostly in slag phase) under various operating conditions. However, fundamental studies on smelting reduction of iron ore-coal composite pellets in liquid metal bath are not available in published literature. Looking into the above aspect, **the objectives of present investigation are two fold:**

i) To prepare composite pellets using various binders by cold bonding techniques in the laboratory and evaluate their properties; this would be a contribution towards development of suitable binder for cold bonding technology.

ii) Fundamental investigation on reduction smelting of iron ore-coal composite pellets in liquid metal bath, including auxiliary studies as back-up investigations with emphasis on kinetics.

The thesis consists of seven chapters covering all the relevant information about the composite pellets, smelting reduction processes and the work that has been done on investigation on smelting reduction of the composite pellets in liquid metal bath including auxiliary studies.

The first chapter discusses in brief the inherent limitations of the blast furnace technology and the emergence of alternative routes to iron making. It also discusses about the advantages of using cold bonded composite pellets in smelting reduction processes and outlines the objectives and the plan of work of present investigation.

The second chapter covers the literature review pertaining to composite pellets and smelting reduction processes / technologies. It discusses about the preparation, reduction kinetics, advantages and uses of composite pellets in smelting reduction processes. A fundamental knowledge of physical, mechanical and thermal behaviour of composite pellets, concept of cold bonding, smelting reduction processes concepts, foaming slag characteristics, and understanding of mechanism and kinetics of smelting reduction processes are of utmost importance before advancing through the intricacies of the present study. A comprehensive review of smelting reduction processes is done. Some conclusions drawn from literature survey were:

i) Most of the investigations are carried out on solid state reduction of iron ore-coal composite pellets under isothermal conditions. Some studies have also been reported under non-isothermal conditions.
ii) Fundamental studies on reduction kinetics of iron ore-coal composite pellets have been carried out mostly in slag phase.
iii) There are no fundamental studies reported on reduction kinetics and dissolution behaviour of iron ore-coal composite pellets in liquid metal bath and therefore, data is not available on the same.
iv) Not much information is available on binders suitable for the production of high strength cold-bonded composite pellets.

The third chapter deals with the mass balance calculations for the melt. An attempt is made to develop a mathematical formulation for mass balance in smelting reduction process. A comprehensive review of different methods, used by investigators in past, for measurement of degree of reduction in composite pellets was done. An empirical relation developed by Wang *et al* was modified to calculate the degree of reduction for composite pellets.

The fourth chapter deals with the raw material characterization (which includes sieve analysis of iron ore and coal, proximate analysis of coal, chemical analysis of iron ore etc.), briquettes and pellets preparation, their test results and discussions, experimental techniques, measurement of degree of reduction, apparatus and procedure. The studies were carried out on cold bonded composite pellets made out of iron ore (of Noamundi

Mines) procured from Tata Steel, Jamshepur, coals procured from Jharia Mines (high ash and low volatile matters), Dhanbad and Bhilai Steel Plant (low ash and high volatile matters), Bhilai. To select the proper binder, cylindrical shaped briquettes (diameter 9.70-9.75 mm and height 13-14 mm) were prepared and tested. Different binders like CaO, $Ca(OH)_2$, slaked lime, dextrose, molasses, sodium polyacrylate etc alone and in combination were used to prepare briquettes/pellets (Fe/C ratio of 2.5, 3.11, 3.5 and 4.0) and their strength properties (compressive strength, drop strength and shatter index) were tested.

It was observed that the highest compressive strength of 357 N/briquette was obtained for briquettes prepared using 10 pct slaked lime and 5 pct dextrose as binder and 6 minutes of CO_2 gas exposure. Similarly, the highest drop strength (84 Nos.) and lowest shatter index value (0.44 pct) were obtained for briquettes prepared using slaked lime plus dextrose as binder and 6 minutes of CO_2 gas exposure.

Therefore, iron ore-coal composite pellets were prepared using slaked lime plus dextrose as binder with Fe_{tot}/C_{fix} ratios of 2.50, 3.11, 3.50 and 4.0 and tested for physical and mechanical properties. Variation in compressive strength was observed mostly by ±15 pct of the average value. For ACP (coal from Jharia mines) pellets, the maximum and minimum strengths of 330 and 212 N/pellet were obtained for Fe_{tot}/C_{fix} ratio of 4.0 and 2.5 respectively. Similarly, for BCP (coal from Bhilai Steel Plant) pellets, the maximum and minimum strengths of 362 and 240 N/pellet were obtained for Fe_{tot}/C_{fix} ratio of 4.0 and 2.5 respectively. With increase in Fe_{tot}/C_{fix} ratio in composite pellet, the strength improved. It was observed that with increase in Fe_{tot}/C_{fix} ratio the porosity of pellet decreased. With increase in porosity both the compressive and drop strengths decreased.

The experiments for smelting reduction of composite pellets were divided into two parts. The first part deals with the investigation on reduction kinetics of ore-coal composite pellets in liquid metal bath. This is done in an induction furnace of 6 kg capacity crucible and 15 kW capacity power panel. The second part deals with the bulk dissolution of pellets into the molten bath and iron recovery (in terms of yield). The thermal behaviour of composite pellets such as decomposition, weight loss, reduction etc was determined by thermal analysis. The non-isothermal reduction behaviour of composite pellets was studied using thermogravimetry and differential thermal analysis (TG-DTA) apparatus. Brief discussion about the facilities such as experimental set-up for smelting reduction, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), TG-DTA apparatus, Energy Dispersive X-ray Fluorescence (XRF) Spectrometer are given in this chapter.

SEM examination of iron ore fines, coal fines and binders were initially carried out to see the morphology (i.e., shape, size and distribution) of the particles. The SEM/EDAX examination of fractured surface of oven dried composite pellets evinced the distribution of iron ore, coal and lime particles reasonably uniform. Reduced pellets were examined by SEM to observe the microstructure of the pellets. XRD test was carried out to identify the phases present in reduced pellets. For measurement of degree of reduction for composite pellets, the weight loss method was used. The loss in weight due to loss of oxygen, carbon and volatile matters were taken into consideration.

The fifth chapter deals with the analysis of experimental data generated on various aspects of the study in accordance with the scheme of experiments presented in previous chapter. It presents results and discussions on non-isothermal reduction of composite pellets using thermogravimetry and differential thermal analysis.

The reduction studies of composite pellets under non-isothermal conditions using TG-DTA showed that with higher Fe/C ratio in pellets the degree of reduction was found lower which indicates that carbon content more than stoichiometry is required for complete reduction of iron oxide. With increase in Fe_{tot}/C_{fix} ratio, the degree of reduction (α) decreased which is attributed to the lesser amount of reductant present in composite pellet. With Fe/C ratio varied between 2.5 to 4.0, the degree of reduction varied in the range of 64 to 84 pct for ACP (coal from Jharia mines) pellets and 75 to 87 pct for BCP (coal from Bhilai steel plant) pellets. Volatile matters (VM) in coal play very significant role in reduction of iron oxide. For pellets of identical Fe_{tot}/C_{fix} ratio, coal with high volatile matter resulted in both higher degree of reduction (α) and higher rate of reduction (k). With increase in temperature during heating of pellets, the rate of reduction increased. The faster rate of reduction in high temperature region (above 1050 K) shows that temperature plays a significant role in carbothermic reduction of iron oxides. With increase in porosity the degree of reduction increased which is attributed to larger inner surface area available for reduction. The rise in degree of reduction with increase in porosity of pellet is faster in the beginning and sluggish in later stage. The activation energy (E) values calculated for composite pellets of different Fe_{tot}/C_{fix} ratios are in the range of 0.86 to 8.82 and 12.37 to 38.32 kJ/mol for initial and later stage of reduction respectively.

The sixth chapter contains results and discussion on smelting reduction of composite pellets in liquid metal bath at temperature 1723 ± 10 K, and other auxiliary studies carried out in present investigation. During smelting reduction, it was observed that the 16-17 mm diameter pellets completely dissolved in 83 to 90 seconds. The degree of reduction varied in the range of 68-87 pct for ACP (Jharia coal) pellets for 40 seconds and 73-92 pct for BCP (Bhilai coal) pellets for 40 seconds. For BCP pellets immersed in liquid melt for 50 seconds, the degree of reduction varied in the range of 80-98 pct. With increase in Fe_{tot}/C_{fix} ratio, the fraction of reduction (F) as well as rate of reduction (k) decreased for both ACP and BCP pellets. Both the fraction of reduction (F) and rate of reduction (k) are higher for BCP pellets than that of ACP pellets. For identical Fe_{tot}/C_{fix} ratio in ACP and BCP pellets, higher degree of reduction is obtained in BCP pellets, which is attributed to the high volatile matter content in Bhilai coal.

With increase of Fe_{tot}/C_{fix} ratio in composite pellets the iron yield decreased. With increase in Fe_{tot}/C_{fix} ratio the slag weight decreased. For identical Fe_{tot}/C_{fix} ratio of composite pellet, the quantity of slag produced is more with ACP pellets than that of BCP pellets. This is due to the higher ash content in coal from Jharia mines that is used for making ACP pellets. The carbon content decreased in all heats except H1 and H5. The lower carbon content in product metal may be due to the lower Fe_{tot}/C_{fix} ratio than stoichiometric as well as the dilution of carbon as more Fe is coming from reduction of iron oxides of composite pellets. Silicon, manganese and sulphur content decreased in all heats due to their dilution in the melt. Phosphorous content increased in all heats, which is attributed to the phosphorous coming from the iron ore of composite pellets. The tramp elements like chromium, nickel and copper (except molybdenum) decreased in all heats which is attributed to the dilution of these elements occurred during heat.

SEM photomicrographs of reduced pellets revealed a diffused reaction front, cluster of whiskers of iron, sintered structure and surface cracks. Porosity was also observed to increase during smelting due to thermal decomposition of the volatile organics. The tunnel like appearance on the surface clearly indicates the continuous evolution of gas which is due to the presence of high volatiles in coal. XRD results revealed that the reduction occurred topochemically, i.e., stage wise, e.g., $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$.

The seventh chapter contains the summary and conclusions of the present work, and suggestions for further work.