

# Problems and prospects of carbonaceous reducing agents in ferro alloys production

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## ABSTRACT

*The paper emphasizes the need for development of special carbon reductants for ferro-alloy production. Various physical and chemical properties desired for the carbonaceous reductants are discussed as compared to their present availability and usage in ferro-alloy production.*

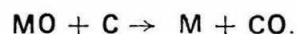
*Establishment of LTC coke plant based on washed coals and production of formed coke should be considered to meet the requirement of ferro-alloy industry. Washed coal with low phosphorus and ash contents will not only help in producing quality ferro-alloys but also contribute to energy conservation measures.*

## Introduction

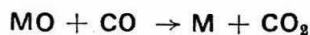
Carbonaceous reducing agents constitute an important feed material in the production of tonnage ferro alloys such as High carbon ferro manganese, High carbon ferro chrome, Ferro Silicon, Silico chrome and Silico Manganese etc. Since the by-product under size screened cokes from blast furnaces were available from the steel plants at the time of the setting up of several ferro manganese plants in India during 1950's usage of these cokes were practised and are being continued in the production of High carbon ferro manganese. As these contain high ash content, they cannot be used in Ferro silicon production and therefore charcoal is being used.

The main role of the carbonaceous reducing agent in the ferro alloys is to reduce oxide ores into its elements by carbon. Due to thermodynamic considerations the reduction temperature involved to reduce the oxides MnO,

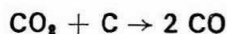
Cr<sub>2</sub>O<sub>3</sub> etc. are very high exceeding 1250°C and therefore the use of carbonmonoxide generated is of no use in the smelting process :



The reaction between CO and MO to form CO<sub>2</sub> is not feasible inside the electric smelting furnace.



This is because any CO<sub>2</sub> formed in presence of carbon becomes unstable above 1100°C and consequently the reaction between carbon dioxide and carbon forming carbonmonoxide becomes predominant above 1100°C.



Thus the otherwise useful potential heat and reducing power of the carbonmonoxide is not useful in submerged arc furnaces and leave the furnace unutilised. The carbonmonoxide generated at best would reduce the higher oxide

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like  $MnO_2$  upto the lower oxide stage  $Mn_3O_4$  and  $MnO$ . Due to the above theoretical considerations the requirement of chemical and physical properties of carbon reductants are different for the production of ferro alloys.

The requirements of carbonaceous reducing agents also depends on the nature of process involved in ferro alloy production. It can be categorised into two types namely for the production of ferro alloys where slag is formed as a by-product and those where no slag is formed. In the first category the production of High carbon ferro manganese, High carbon ferro chrome, silico chrome, silico manganese etc., can be included. In the second category, Ferro silicon, Silicon metal and Calcium silicide are included. This distinction in the process technology makes it necessary to use a very reactive and a very low ash containing carbonaceous reducing agent for the production of ferro silicon and silicon metal as compared to other ferro alloys. As special type of carbonaceous reducing agent containing low ash and low phosphorus is not produced in India, charcoal is used as reducing agent.

In the case of slag making processes a certain amount of ash content can be tolerated since this can be fluxed along with the gangue of the ores with suitable fluxing agent like limestone and dolomite. In view of this, B. P. Metallurgical nut and pearl cokes obtained from steel plants are used in the production of High carbon ferro manganese.

### **Physical and Chemical Properties of Reducing agents**

#### *Fixed Carbon*

The fixed carbon in the reducing agent should be as high as possible but not less than 85%. Any lower fixed carbon in the carbonaceous reducing agents means high ash content or volatile matter and will contribute to more slag volume resulting in increased power consumption per tonne of alloy produced and high Phos content in the metal.

#### *Volatile Matter*

The presence of volatile matter in the reducing agents contributes to higher reactivity. However, it should not be at the expense of the fixed carbon level. Recently in view of the non-availability of low phos cokes or special reducing agents some amount of non-coking coals to an extent of 20 to 30% of the total fixed carbon required are used in the production of High carbon ferro manganese, High carbon ferro chrome & Ferro silicon. The volatile matter released, on heating, oxidises above furnace charge and produces intense heat. This leads to severe heating of furnace super structure by radiation and resulting in water leakages from the pipe joints as well as from the contact clamps. Further, condensation of tar products on electrode clamps and other furnace parts, causes severe corrosion problem leading to expensive maintenance and unproductive shut downs. Therefore, the use of non-coking coals except for nominal requirements should not be practised. However, in view of the non-availability of other cokes having Low phos content, most of the ferro alloy units in India use some quantity of non-coking coals containing high ash content of the order of 16 to 20% and volatile matter 30 - 35%. In principle the non-coking coals get devolatilised and transforms to low temperature carbonised char during the descent to the lower part and takes part in the reduction while the volatile matter simply escapes to the atmosphere after burning. It is worthwhile to note that if suitable low ash non-coking coals are made available, this can be used to an increased amount. The design of the furnace needs suitable modification to accommodate the high volatile matter released by incorporating waste heat boilers and gas cleaning equipments.

#### *Ash Content*

The ash content should be low since it represents impurities and contributes to higher slag volumes. Each 1% of ash content in coke will increase slag volume by about 10 to 15 kg

per tonne of ferro alloy which in consequence will consume more electric power for its smelting and removal of slag apart from metal losses to slag.

In the production of Ferro Silicon and Silico Chrome, high ash content leads to its fusion and coating of the quartz (source of silicon) with slag. It hampers the progress of reaction, causes more slag formation and disrupts the operation by frequent crust formation and severe blows. It also increases Al content of the ferro silicon. Therefore the ash content should be 8—12% maximum.

#### *Sulphur*

Sulphur content of carbon reductant in the usual range of 0.6 to 0.8% in the production of High carbon ferro manganese or Ferro silicon is not a severe problem because most of it gets volatilised due to high temperature of operation and also gets eliminated in the slag containing manganese. Generally sulphur content of Indian Coals/Cokes is low compared with foreign carbon reductants. However, the sulphur content in High carbon ferro chrome and Charge Chrome has to be kept at 0.03% max, since it is difficult to remove it in stainless steel making. Therefore, care must be taken to avoid coal and coke with higher sulphur content such as raw petroleum coke which contains 3 to 4%.

#### *Phosphorus*

The most undesirable constituent in carbon reductants is phosphorus. About 70 - 80% of the phos input gets reduced and alloyed with the ferro alloy produced. Since ferro alloys are used at the finishing stages of various alloy and stainless steel production, phos cannot be decreased once it is introduced through ferro alloy. Therefore 'P' content in reductants should be 0.02% maximum.

#### **Problems of phos in high carbon ferro manganese & silico manganese.**

During the last few years the availability of by-product metallurgical cokes or beehive hard

cokes have become poor, the cost has become exorbitant while the quality has deteriorated very much. The ash content is about 28 to 30%, Phos content has gone up to 0.17 to 0.19%. It should be noted that the usage of Manganese ores with high phosphorus, has become the order of the day and this has necessitated to look for other carbonaceous reducing agents containing low ash and low phos.

While the Indian Standard Specification for High Carbon Ferro Manganese has increased phos to 0.4% max still many steel plants are using 0.35 max phos and thus the use of low phos containing coke is essential for production of High carbon ferro manganese. If high carbon ferro manganese is to be exported then phos level should be 0.25 max and this requires a very low phos containing carbon reductant. It should be noted that the phosphorus removal in Steel Plants requires extended time of refining, additional amount of fluxes, and energy consumption.

All these can be minimised by using low P cokes in ferro manganese production and supplying low P containing ferro manganese for steel plants.

Since major manganese ores are available in the country are siliceous, these are suitable for Silico manganese production. But due to higher phos content, the use of silico manganese has not been considered by the steel makers in India, as compared to the advanced countries like U.S.A., Japan and other European countries where almost 50% of manganese is used in the form of silico manganese. Further, the ferro manganese slag containing high manganese with low phos 0.03% max which is obtained as By-product during the production of High carbon ferro-manganese can also be utilised in the production of Silico-manganese. Thus if requisite quality of low phos metallurgical cokes are available, the production and use of silico manganese can be adopted which will not only help in conservation of valuable manganese resources but also help in the yield and quality of the final steel products.

## Phosphorus in charge chrome

Since Charge Chrome is mainly used in the production of stainless steels, high chromium alloy steels, super alloy steels, requiring high corrosion resistance and toughness, the phosphorus content should be extremely low. Therefore, the specification for Charge chrome with reference to phosphorus is very stringent. Most of the Chargechrome producers abroad make use of gas coke or other special carbon reductants containing very low ash content, and phosphorus not exceeding 0.015%. The phosphorus content, in Silico Chrome also should be low as this is used in the production of low carbon ferro chrome and Extra low carbon ferro chrome. Therefore, it has become paramount importance now, to have a suitable carbonaceous reducing agent similar to that of cokes available abroad for using it in the production of ferro chrome alloys.

## Physical Properties

In Electric furnaces, the carbon reductants not only serve as reducing agents but also as conducting material for the passage of electrical current and contributes to ohmic resistance. Deep penetration of the electrodes is required to ensure smooth functioning of the furnace and high recovery of metals like silicon. The production of Ferro silicon and Silico Chrome requires cokes of high reactivity and high electrical resistance.

Since the electrical resistance is a factor depending on the porosity, particularly the micro-porosity of coke and since the reactivity of coke increases with an increasing internal surface area, a specifically light coke is needed both from the point of view of reactivity and high electrical resistance.

For these reasons the coke should be light charcoal with high porosity.

The following is specified :

- 1) Apparent specific gravity : 0.8 gm/cc

- 2) Bulk density : 450 - 500 kg/m<sup>3</sup> for 10 - 40 mm size.
- 3) Porosity : 25 - 35%
- 4) Though very high strength as that required for cokes used in blast furnaces are not necessary in electric furnaces due to its small height, it should be high enough to withstand transport and mechanical handling operations and to lead to minimum generation of fines of less than —6 mm.
- 5) The fusion point of the ash should be high so that it will not melt at low temperature and cause surface coating of the raw materials and impair the reduction of oxides by promoting slag formation. In Ferro Alloy production, the main reduction takes place in solid state between ore and carbon except in Mn alloy production.
- 6) Electrical resistivity : Specific electrical resistance should be 70 - 100 Ohm cm/cm<sup>3</sup> (measured at room temperature 7 - 15 mm size)

## Reactivity of Special Carbon Reductants

The concept of reactivity of carbon reductants is somewhat different in ferro alloy production. Originally metallurgical cokes were used where reactivity was understood as the rate of combustion with oxygen. Since metallurgical coke is used in blast furnaces and cupola where it is oxidised with air from tuyeres, the usual determination of reactivity by critical air blast method or CO<sub>2</sub> method, is useful enough. But in ferro alloy production especially ferro silicon and silicon containing ferro alloys, the reactions involved are different since formation of silicon monoxide constitute an important intermediate reaction gas amounting to about an equal proportion as that of carbon monoxide. The SiO raising from bottom of the electrodes disproportionates by condensation into Si metal, plus SiO<sub>2</sub> at the less hotter top portions. Also it reacts with carbon to form silicon carbide

which again reacts lower down with  $\text{SiO}_2$  to form Silicon Metal.

Therefore, the carbon reductants must have the ability to promote the condensation reaction which ascends at a fast velocity from the furnaces. Otherwise there will be great loss of silicon. Usually the silicon recovery is about 80 percent only in ferro silicon production and thus about 20 percent of silicon is lost as  $\text{SiO}$  which immediately oxidises to submicron size silica fumes on contact with infiltrated air in open and semi-closed furnaces. This leaves as dense white fumes from furnace chimneys.

### Reactivity Measurements

Since the concept of reactivity is different for Blast furnace cokes and carbonaceous reducing agents used for ferro silicon alloys, several methods have been evolved for determination of reactivity such as SINTEF. Norwegian technical University of Trondheim has evolved a method called SINTEF METHOD for determining the  $\text{SiO}$  reactivity of various carbon reductants. In this test, a known mixture of  $\text{SiO}$  and  $\text{CO}$  is allowed to flow by use of Argon as a carrier gas at  $1650^\circ\text{C}$  over a  $20\text{ cm}^3$  sample of material of grain size  $-6.35 + 4\text{ mm}$ . The reactivity number is measured in ML of  $\text{SiO}$  gas left unutilised during reaction. Several carbonaceous reducing agents have been measured by this method and the values are indicated as follows: the Rexco Semi coke is ranging from 950 to 1200 ML on this scale, charcoal in 450 - 700 ML range, metallurgical coke in 1500 - 2000 ML and petroleum coke and Anthracite 2000 - 2500 ML range.

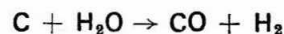
The reaction  $2\text{C} + \text{SiO}(\text{gas}) = \text{SiC} + \text{CO}(\text{gas})$  is very important above the temperature  $1520^\circ\text{C}$ . The more reactive the coke, the less silicon monoxide gas will escape through the furnace.  $\text{SiO}$  gas from furnace also contains intense electrical heat energy. By using a carbon reductant of high surface area and reactivity, the power consumption per ton of ferro silicon can be brought down and increased recovery of silicon can be obtained. While in Norway and other

countries gas cokes and special carbon reductants such as Rexco Semi-coke, Auschar, etc., with low ash content and low phos. are used in ferro alloy production, such special cokes with high reactivity are not available in India and therefore wood charcoals are mainly used especially in Ferro Silicon production. However, the charcoals obtained from different areas contain varying proportions of volatile matter due to improper carbonisation, and phosphorus due to the types of wood used and the soil from which the trees are grown. The charcoal is very fragile and generates considerable under size rejects during loading and unloading operations, transportation, storage etc. Due to its high adsorption property, it contains very high moisture if exposed to rains. Also it being very reactive, oxidises faster on the surface of the charge and therefore a higher fixed carbon will be required per tonne of Ferro silicon.

It may be mentioned that in slag forming processes such as high carbon ferro chrome or chargechrome, high carbon ferro manganese etc, such high  $\text{SiO}$  reactivity values are not required.

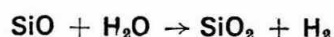
### Moisture

High moisture content disturbs the carbon balance. Uniformity in moisture content is more important without frequent or sudden variations. High moisture content results in higher requirements of fixed carbon and also power consumption. Moisture not only consumes electric power for evaporation, but also consumes carbon from electrode and carbonaceous reducing agents.



Usually the Hydrogen content goes up in the furnace gases if water leakages are there or moisture in coke is very high.

Silicon monoxide also reacts with  $\text{H}_2\text{O}$  to form



The above two reactions are endothermic and therefore results in excess power consumption in ferro silicon production. The moisture content should be uniform and should be maximum 4.0% in B. P. Cokes, coals etc., In lighter types like charcoal it should be 8.0% max.

After having briefly reviewed the necessity for using special carbonaceous reducing agents the chemical and physical properties desired for ferro alloy production is indicated in Table.

**TABLE**  
*Chemical & Physical Properties desired for carbon reductants*

Fixed carbon	85% Min (drybasis)
Volatile matter	3% max "
Ash	12% max "
Phos	0.015% max "
Sulphur	0.6% max "
Moisture	6.0% max "
Size	10 - 40 mm $\pm$ 5%
Bulk density	400 - 500 kg/m <sup>3</sup>
Ash fusion point°C	1250 - 1450°

#### Requirements of Carbonaceous Reducing Agents

The requirement of carbonaceous reducing agents for Ferro Alloy industry in India would amount to about 6,00,000 tonnes which is based on an average 70% fixed carbon, 10% moisture, 15% rejects due to handling loss and under size materials. In actual practice this will be much more due to wide variation in the above parameters. However, if special carbonaceous reducing agents are used, there will be less consumption.

As compared to Blast furnaces, where large quantities of metallurgical coke are required, the amount required for ferro alloys is not much. For instance for the newly proposed Visakhapatnam Steel Plant, the coke requirement would be 2.2 million tonnes for 3.4 million tonnes of ingot steel capacity. Thus it can be seen that it is not beyond the means of the coal authorities or other Government agencies to set

up suitable plants to produce special carbon reductants.

Talcher and Singareni coalfields are having abundant reserves of non coking coals. The superior grade coals can be earmarked for conversion into special cokes for electro metallurgical industries.

The following steps are worth considering :

- 1) Since the quantum of coal required for special coke production is not much, mining of low P, low ash coals from Bottom Sections of the basal seam in Talcher and other coal fields should be pursued and intensified.
- 2) The mined coal should be segregated with regard to low phos and ash content and reserved for ferro alloy production and the balance only should be allotted to thermal power stations, railways, fertilisers, cement, paper and other industries where it is used as fuel. As compared to the total demand estimate of about 9 million tonnes of Talcher coal during 1984-85 and about 28 million tonnes during 1989-90, the demand for making special cokes would be 0.6 millions only per annum. This can be reserved from the coal production from the underground mine in Talcher.
- 3) As the demand for coal for production of special cokes is not much as compared to the overall demands, setting up of suitable coal washeries would be highly rewarding. To obtain 0.6 million tonnes, assuming 25% rejects as middling and waste, a washery capacity of 0.8 million is required with a daily capacity of 3000 tonnes per day. Depending on the economics, either two or three coal washeries can be set up at different locations. The main objective of this washery would be to bring down the ash less than 8.0% and P to less than 0.010%.
- 4) There was some proposal to set up a formed coke plant by SAIL with a capacity of 2

lac tonnes per annum at Talcher with an investment of Rs. 30 crores, but this was dropped since it was not found economically viable. Even at that time the ash content of formed coke was not considered to be less than 16.0%. Tests conducted at CFRI with formed coke at low shaft furnaces contain ash content of 22%. This type of formed coke will not be suitable for ferro alloy production. If non coking coal after washing is used to produce formed coke, this will be a suitable material for ferro alloy production.

- 5) Presently two low temperature carbonised coke plants have come up namely (i) coal and chemical complex at Ramakrishnapuram, Ramagundam with a capacity of 180 tonnes per day. (ii) Dankuri Coal Complex of Coal India at Dankuri with a capacity of 1000 tonnes per day of L T C Coke.

But these are making use of high ash containing coals to produce smokeless fuel only for domestic purposes without any regard to use low ash, low P coals to produce special cokes. Selective use of low ash, low P coals after setting up of a suitable coal washeries on the pit heads would be a good source of carbon reductants for ferro alloy production.

- 6) Similarly, the proposed LTC Plant of Talcher should use low ash low P coal in their plant to cater to ferro alloy producers after beneficiation of coal.
- 7) In Giridih coking plants hard cokes containing P less than 0.04% used to be produced and supplied to ferro alloy producers. The coking coals used as a feed from nearby colliery has become depleted over these years and these plants are in the process of complete renovation. They can produce about 7,000 tonnes per month. If other low P, low ash coking coals from Bihar are used along with non coking coals containing

low P and low ash, the coke produced can be earmarked to ferro alloy producers.

- 8) Other methods of production for special reactive cokes such as those developed by CFRI or rotary hearth process of Wise-Salem Brosive can be considered.
- 9) The present practice of utilisation of charcoal with wide variations in quality is to be completely eliminated. The charcoals are invariably produced in non scientific way and the forests are denuded indiscriminately causing environmental imbalance without any concern for re-forestation. The special carbonaceous reducing agents based on LTC coke with low ash and low phos will be able to replace charcoal.
- 10) In the case of integrated steel plants, Government has already got convinced and now allow the import of low ash low phosphorus coking coals on long range basis for blending purposes in coke making. Since the quantity required for ferro alloy production is very small compared to the steel industry a certain portion of special coke can be produced by them and supplied to the ferro alloy industry.

Since integrated steel plants are major consumers of ferro alloys, they can derive more benefits by supplying low phos special cokes.

- 11) Government may also permit the import of low phosphorus low ash carbonaceous reducing agents for production of ferro alloys for blending with other cokes or to produce ferro alloys with low phosphorus.
- 12) In conclusion, the main problem faced by the Ferro-Alloy Industry is the non-availability of any special carbonaceous reducing agents containing low P and low ash. Since Talcher coal fields and Central coal fields contain large reserves of non-coking coals with very low phosphorus content these can be used to produce special reductants. The

important aspects would involve setting up coal washeries to bring down the ash content to very low level so that the special cokes produced would not have more than 12% ash. The removal of ash itself would bring down further sulphur and phosphorus levels in the coke. The special cokes can be in the form of formed coke or LTC coke. Until such time the coal washeries are set up and special carbonaceous reducing agents are produced, Government should permit import of low phosphorus low ash cokes. Since ferro alloy production is very power intensive, saving of electric power by use of low ash special carbonaceous reducing agents should be encouraged on top priority.

#### **Discussion**

*A. V. Sortur, VISL, Bhadravati*

Q. What is the effect of volatile matter if coals are used in ferro alloy furnace ?

A. As volatile matter increases beyond the certain point the super-structure, cables and furnace cooling parts will get affected, so one should be very careful about using unlimited coal.

*A. Peravadhanulu, NML, Jamshedpur*

Q. Can beneficiated coal fines by flotation process 8-14% ash content be utilised in Ferro Alloy industry ?

A. I understand may be it is from the coking coal or non-coking coal but whatever may be what we are interested in the ferro alloy production is less costlier carbon reductant. Any of these froth flotation processes will give fine product with requires further processing. Until and unless it has got the special properties of extremely low phosphorus content and subsequently could be used as briquettes or as formed coke then definitely this material can be made use of. It all depends on the economics.