Production of Ferro-Silicon and Calcium Silicon Alloys

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Part - I : Ferro Silicon Alloys

I.1 Introduction

Initially the process of production of fero-silicon was developed empirically [1]. Ferro-silicon is made by reducing quartzite with metallurgical coke/gas coke/Low Temperature Carbonized coke/charcoal. Quartz, quatzite and chelcedony are the cheapest minerals rich in silicon are used for the manufcture of ferro silicon [2]. In India mainly charcoal is used [3]. The techno-economics of the process of ferro-silicon production improves considerably with the increase of the capacity of the furnace [4]. The feasibility of using plasma smelting of low cost taconite tailings to produce ferrosilicon at a high yield has been demonstrated [5]. Large amounts of ferro-silicon are used for the reduction of various oxides in ferro-alloy production and high percentage ferr-silicon in the form of powder is used as a slag deoxidiser. The scale of operation of ferrosilicon production has increased steadily, and furnace construction and the auxiliary systems for transport, weighing and control have been modernised but the basic process is essentially unchanged. This paper provides an overviw of the raw material requirements, thermochemical consideration, charge calculation, operating conditions, recent developments and, finally, the results of pilot scale trial and industrial plant.

I.2 Raw Materials

Silicon bearing substances namely quartz, rock crystal, amethyst, opal, onyx, cornelian, jasper, snand and mery others are employed in the manfacture of ferro silicon. The cheapest minerals rich in silicon are quartz, quartzite and chalcedony. Quartz is a compact mineral with crystal structure, specific gravity of 2.59-2.65, hardness 7, mostly colourless, white, grey or reddish, depending on impurities. It's SiO_2 contrent is 98% and over. Quartzile is a rock composed of quartz grains, cemented by a subtance mainly containing silicon. It's SiO_2 content should be minimum 96%, preferably 97-99%, Al_2O_3, MgO, CaO content should be minimum possible and P_2O_5 content should not exceed 0.02%. It should have no clay inclusion and its moisture absrption should not exceed 5%. On crushing or heating it should not lose its mechanical strength. Chalcedony is thin-fibrous, sametimes porous, mineral, variously coloured. It contains a lower amount of SiO_2, about 95%, it is inferior to quartz and quartzite and its use is limited.

The reductants employed in the production of ferrosilicon should have minimum ash content, large reactive surface, low volatile matter content, high electric resistance and sufficient mechanical strength. Various carbon bearing materials such as charcoal, petroleum coke, pitch coke, metallurgical coke and coal are used as

reductants. Charcoal having about 68% C, 6-8% ash, 20%volatile matter and 4-6% moisture is a costly reductant and is used mainly for the production of high silicon alloy (~ 90% ferrosilicon) and crystalline silicon. Petroleum coke and pitch cokes containing negligible amount of ash (~ 1-2% or less) and volatile matter and possessing high porosity and reactivity are excellent reducing agents but due to their high cost, they are used only for the production of crystalline silicon. Coals having high electrical resistance, negligible quantities of volatile matter and undesirable inpurities and low ash can be used. Fine coke can replace coals since it decreases the sintering of charge and permits a deeper positioning of electrodes. Some cokes, though having higher ash content and porosity, possess higher electrical resistance and allow for deeper positioning of electrodes. Saw dust, chips and cuttings can also be partially used as reducing agents since they ensure satisfactory gas permeability of the burden and prevent charge crusting, lower the specific electical conductivity of the charge and permit a deeper positioning of electrodes. The timber waste can regulate the penetration of electrodes to a certain degree by varying its amount in the burden mixture.

Iron bearing materials namely iron ore, scales or fillings are used in the burden mixture in varying proportions depending upon the grade of ferrosilicon. The use of scales somewhat improves furnace top operation and ensures fuller evacuation of slag, but entails additional power and increases reductant consumption to reduce iorn oxides. Iron in the form of cuttings, if used, should be free from rust, as rust becomes a source of increasing hydrogen content in ferro silicon. Alloy steel cuttings should not be used since they will become an uncontrolled source of entry of unwanted alloying additions (chrome, nickel, manganese etc.). Cast iron cuttings are prohibited since the entire phosphorous content would pass into the alloy. All cuttings should be finer so as to distribute them in the burden mixture uniformally. The use of greasy cuttings is not advisable as they hamper furnace top operation. The iron content of cuttings should be about 90% and they should be free from impurities, especially nonferrous.

Quartz/quartzite should be crushed into lumps of 35 to 70 mm in size and fines should be sieved through a 20-30 mm sieve for better permeability of the charge. Fines of quartzite may consist of higher percentage of impurities especially alumina. The size of fine coke lumps is chosen in accordance with the rating of the furnace and its secondary voltage. For the furnaces of 7000 to 16,000 KVA with secondary voltage of 140 to 160 V, fine coke in the size 10 to 20 mm lumps is used. The size of fine coke lumps can be further reduced for higher voltages. However, coke lumps of less than 5 mm are not suitable for ferro-silicon production and should be separated out since the deviation in the size of coke leads to serious disturbances in the operation of ferro-silicon furnaces.

I.3   Equilibrium Diagram of the Iron Silicon System
Iron and silicon can be alloyed in any proportion. The silicon-iron equilibrium diagram (Fig. 1) shows the existence of a number of chemical compounds in this system : (i) ε-FeSi [33.3 wt.% Si], (ii) η-Fe$_3$Si$_2$ [25.1 wt.% Si], (iii) ξ-Fe$_2$Si$_5$

[55.68 wt.% Si]. Among these compounds, only FeSi does not decompose at high temperatures and fuses at 1410°C.

Iron-silicon system has three eutectices; the first eutectic α-ε (20 wt.% Si) with a melting point of 1195°C, the second ε-ξ (51 wt.% Si) with a melting point of 1212°C and the third ξ-Si (59 wt.% Si) with a melting point of 1207°C.

The diagram shows that the melting points of standard grades of ferrosilicon do not exceed 1370°C. An alloy of iron with 40-47 wt.% silicon melts at 1260-1370°C and that with 74-80 wt.% Silicon melts at 1320-1340°C. The specific gravity of ferrosilicon alloys [2] decreases with an increase in silicon content as follows :

Si Content	-	45	60	75	90
Specific gravity	-	5.15	4.0	3.27	2.55

I.4 Segregation in Alloys and Disintegration of Alloys

Ferrosilicon alloys with 45% Si, 75% Si and 95 Si have minimum tendency to disintegrate. However they have strong tendency to segregate. As result of segregation, in the same ingot silicon content may very upto 20% or more between its top and the bottom. Larger time interval of ingot solidification leads to more pronounced segregation. Alloys containing 0.03 to 0.04% P and alloys with upto 3% Al do not disintegrate either, whereas their simultaneous presence of 0.03 to 0.04% P and 3.% of Al in the alloy causes its rapid disintegration in moist air. Thus pure iron silicon alloys do not disintegrate in the air and rapid cooling prevents alloy disintegration. This is the reason that maximum thickness of the ingot is kept 100 mm in cast moulds in order to speed up cooling.

I.5 Physico-Chemical Consderations in Ferro-Silicon Smelting

The reduction of silicon from silica occurs by solid carbon at 1500°C [7].

$$SiO_2(l) + 2\ C(s) \leftrightarrow Si(l) + 2\ CO(g); \quad \Delta H^0 = 649623.9\ Joules/g.mole$$
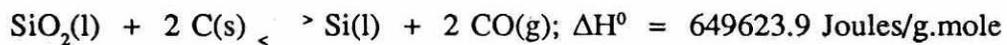
The equilibrium constant of this reaction can be written as follows :

$$K = p^2_{CO} \cdot a_{Si} / a^2_C\ a_{SiO2}$$

With pure starting materials, Silica and carbon are in the free state and both a_{SiO2} and a_C are equal to unity.

$$therefore\ K = p^2_{CO} \cdot a_{Si}$$

6.03

Thus the course of the reaction of silicon reduction is determined by the pressure of carbon monoxide.

In a melt for ferrosilicon, the iron dissolves the reduced silicon and removes it from the reaction zone, thus causing the reaction to proceed from left to right. The partial pressure of carbon monoxide in the reduction zone is slightly above atmospheric while at the top of the furnace the pressure is equal to atmospheric. With a constant value of p^2_{CO}, the equilibrium constant for a 45 percent alloy is lower than a 75 percent alloy, therefore low temperature is required in the reduction zone for 45 percent alloy.

The reduction of SiO_2 by carbon begins at $1500^\circ C$ and the reaction is practically complete at $1800^\circ C$. A further rise in temperature of smelting zone shall lead to intense reduction of silicon but it will be accompained by evaporation. The reduction of silica by carbon in the presence of sufficient amount of iron may take place as

$$SiO_2 + Fe + 2\,C = FeSi + 2\,CO$$

In the presence of excessive amount of reductant in the charge mix, the following reaction may also take place :

$$SiO_2 + 3\,C = SiC + 2\,CO$$
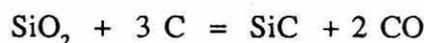
This silicon carbide or carborundum forms in the furnace top and is generally destroyed by iron as

$$SiC + Fe = FeSi + C$$
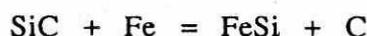
At higher temperatures [$1500-1800^\circ C$], the reduction of silica takes place by carbon

$$SiO_2 + 2\,C = Si + 2\,CO$$
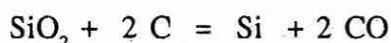
This liquid silicon is quite volatile and it gets evaporated considerably during smelting. The high temperature near the arc zone [$> 1800^\circ C$) promotes the reaction between SiO_2 and SiC, forming Si, SiO and CO

$$SiO_2 + 2\,SiC = Si + SiO(g) + CO(g)$$
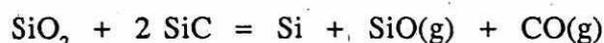
This SiO(g) rises up through the charge. A minor portion of it reacts with the carbon of the reductant forming SiC at about $1500^\circ C$

$$SiO + 2\,C = SiC + CO(g)$$
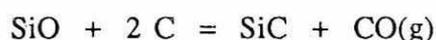
This reaction will slow down when a layer of SiC covers the surface of the reductant. The remaining larger part of SiO will react within the mix partly with the

CO rising together according to the reactions

$$SiO + CO = SiO_2 + C$$
$$3SiO + CO = 2SiO_2 + SiC$$
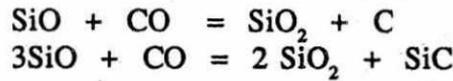
Another part will condense according to reaction

$$2SiO = Si + SiO_2$$
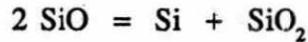
At corresponding temperatures, silicon carbide can be destroyed by iron forming FeSi

$$SiC(s) + Fe(l) = FeSi(l) + C(gr)$$
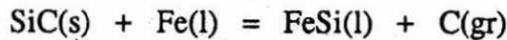
Along with the reduction of silica, the oxides of aluminium, calcium and iron are also partially reduced. As a result ferro-silicon may contain upto 2% Al and 1.5 Ca.

I.6 Formation of Slag during Smelting

Though ferrosilicon smelting is a slagless process, yet slag formation takes place because of the impurities in raw materials namely aluminium oxide, calcium oxide, magnesium oxide, which are not reduced completely. Shortage of reducer in the charge mix also leads to more amount of slag. Slag composition varies widely depending upon the charge composition, purity of charge materials and smelting conditions. Slag is generally viscous and hard to fuse. Its melting point is around 1700°C and viscoisty at 1700°C is 30-35 poises. Due to its high viscosity, some slag always remains in the furnace and causes accretions which decreases the yield of the furnace and increases the specific power consumption. Thus the amount of slag in the smelting of ferrosilicon can be prevented by strict control of raw materials and sufficient amount of reductant in the charge mix. If excess slag accumulates in the furnace, it can be removed by addition of lime to furnace hearth. The lime shall dilute the slag and permit its tapping.

I.7 Basis of Charge Calulation for the Production of Ferro Silicon Alloys

The charge calculations are being done on the basis of the following assumptions :

1. The main reduction reactions during the smelting process are

$$SiO_2 + 2C = Si + 2CO$$
$$Fe_2O_3 + 3C = 2Fe + 3CO$$
$$Al_2O_3 + 3C = 2Al + 3CO$$
$$CaO + C = Ca + CO$$
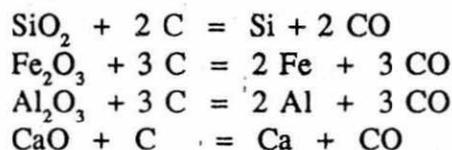
2. The oxides of the charge mix are distributed into metal and slag as follows during smelting process.

Oxides	Oxides reduced joining metal	Oxides Slagged
SiO_2	98%	2%
Fe_2O_3	99%	1%
Al_2O_3	50%	50%

3. For normal grade of ferro-silicon, the reduced oxides are distributed between metal and stack losses as folows :

Reduced element	Reduced Oxides joining metal	Reduced Oxides joining stack losses
Si	94%	6%
Fe	99%	1%
Al	90%	10%
Ca	70%	30%

4. Half of the consumed electrode is utilized for the reduction of oxides.
5. Stack lossses of reduced elements are more for higher grades of ferro silicon.
6. The amount of reductant in the charge mix is used about 10 to 15% in excess to that of stoichiometric requirement.

I.8 Operating Considerations

1. The submerged arc furnaces with rotating baths reduce the power consumption by 3-4%, raises the productivity, saves raw materials and reduces the need for labour for furnace top operation.
2. Closed top furnaces are most important for ferrosilicon smelting because the furnace gases from closed top furnaces have good heat value, 2500 Kcal per cubic meter.
3. An optimum diameter of electrode circle is needed for efficient smelting operation. The diameter of electrode circle is carefully selected for the smelting of high grade ferro-silicon.
4. Feeding should be continuous, by small portions, as fast as the charge sinks. The hottest zones of the furnace are charged first.
5. The liquid slag should be regularly present at each tapping.
6. The electrode penetration is more for higher grade ferrosilicon.
7. The charging should be through furnace bins and chutes, located around the electrodes, however the number of charges per shift are decided by furnace power consumption and specific power consumption per charge.
8. The silicon losses from evaporation are considerable, therefore deep and stable electrode positioning and uniform evolution of gases over the whole charge surface are essential to minimize the silicon losses.
9. The electrical parameters namely electrode secondary voltage and electrode current considerably affect the performance of the furnace, hence they should be appropriately selected.

10. The furnace resistance is adjusted by increasing or decreasing the conductivity of the charge mix and by increasing or decreasing the electrode circle.

11. The reduction reactions as well as the heaviest gas evolution occur mainly around the electrodes.

12. Electrode crucibles are high temperature zones formed at the tips of the electrodes. When the furnace runs hot, the lower parts of the crucibles join to form a comman crucible. The colder mixture in the upper part of the crucible sinters and roofs over the crucible. The walls and roof of these crucibles melt down continuously and are replaced by new portions of the mixture.

13. The flow of hot gases through a cold mixture causes the vapour of silicon and silicon monoxide to condense. Poking at regular intervals to the maxium depth is necessary to provide uniform distribution of the escaping gases at the furnace top, as well as to prevent sintering and the appearance of hot spots.

14. Lack of reductant in the charge mix leads to the crusting of the furnace and the operation of tap hole becomes difficults, while the excess of reductant in the charge mix leads to the high positioning of the electrodes, absence of slag, freezing of the furnace top and sharp drop in the productivity. Excess of reductant in the charge mix for a prolonged period of time will lead to the formation of carborundum.

15. The tap hole should be opened wide enough to permit full evacuation of slag from the furnace. In normal conditions, slag should be evacuated from the furnace at each tapping of alloy since slag accumulation in the furnace casuses a breakdown in the operation of the taphole and leads to a general disturbance in the furnace run.

16. Ferrosilicon is tapped directly into moulds, since rapid cooling reduces the segregation of silicon down to 2% and that of aluminum practically to nil.

17. The silicon losses increase with higher grades of ferro-silicon. The silicon losses can be decreased by a proper choice of optimum electrical operating conditions, stable composition of the charge and correct operation of the furnace top and furnace tap hole.

18. Correct carbon balance, correct electrode position, sufficient porosity of the charge and good tapping conditions are the four main criteria for good smelting operation.

I.9   Illustrations
I.9.1   Pilot Scale Trials at NML Jamshedpur [6]
Ferro silicon was smelted in a pilot scale open type 500 KVA submerged arc furnace at NML [Figure 2] using quartzite, charcoal and scrap iron. The charge mix consisted of good quality quartzite, lower grade charcoal and scrap iron. Ferro-silicon of varying grades [51 to 66% Si content] was produced continuously for more than 4 days, six tapings per day. The slag produced was insignificant in most of the tappings which clearly illustrates that the production of ferro-silicon can be taken as slag-less process. The average amounts of metal and slag produced per tapping were 60 kgs and 3 kg repectively and the percentage recovery of silicon varied from 50 to 89%. Higher recovery of silicon is achieved by the appropriate choice of raw materials and precise control of furnace operation. The average specific power

consumption [~ 14000 KWh/tonne of ferro-silicon], was on much higher side, in comparison to that observed in commercial operation on account of excessive heat losses from the surface of the charge.

I.9.2 Industrial Scale Production of Ferro-Silicon at Soviet Works [7]

At Soviet Works, ferro-silicon was made in a closed type three-phase furnace of a power of 21,000 KVA, operating at a voltage of 145-175V. Normal operating conditions were established in 2 to 2.5 days from the begining of charging. A little amount of slag was tapped together with the metal through the same taphole. The charge mix consisted of quartzite, coke and iron turnings. A typical composition of slag was 35-39% Al_2O_3, 22-26% SiO_2, 9-18% CaO, 7-13% BaO, 1-3% MgO, 7-14% SiC and 0.2-2.0% FeO. The melting temperature of the slag was 1650-1700°C and that of ferrosilicon was around 1350°C. Ferro silicon contained upt 2% Al and upto 1.5% Ca. The typical data on the consumption of raw materials and electric energy for smelting 65 percent ferrosilicon were as follows:

Quartzite	1678 kg/t
Coke	765 kg/t
Iron Turnings	402 kg/t
Electric energy	7639 KWh/t

The cost of electric energy amounts to more than 40 percent. Proper choice of operating voltage and careful prepration of charging materials can ensure normal furnace run and lower energy consumption.

### I.10 Recent Developments in the Production of Ferro-Silicon Alloys

Gero, Rath and Metalmann, H Otto [8] discussed the experience obtained during the production of ferro-silicon and silicon metal with a view to (i) improve the equipment and overall operational control (ii) utilize the recycling and waste products as well as the heat content of the process gas and (iii) shift the production units to locations of higher cost savings. Dosaj, V.D. et al. [5] conducted a two-stage plasma smelting experiment to explore the feasibility of producing 75% ferro silicon from taconite tailings. The taconite tailings are used in briquette form with starch as binder. They consist of 11.4% FeO, 18.9% Fe_2O_3, 56.4% SiO_2 and small amount of Al_2O_3, MnO, CaO and MgO etc. The feasibility of converting taconite tailings to ferrosilicon in a closed, direct current plasma-arc-furnace was determined and the potential for commercialisation of this technology was evaluated [9]. Halvard Tveit and Aasgeir Valderhaug [10] have focussed both improvements in furnace operations and theoretical studies of the process and major improvements have been achieved in furnace production.

## I.11 Conclusions and Remarks

Ferro silicon alloys are generally produced by reducing quartz/quartzite with carbon in three phase submerged-arc-furnaces. Any iron bearing material in the burden mixture is added in varying proportions to give the alloy of the desired grade. The physico-chemical conditions of ferro-silicon smelting and charge calculations for different grades of ferro-silicon alloys are well established. However, silicon losses during smelting and specific power consumption are to be minimized by choosing quality raw materials, correct carbon balance, sufficient porosity of the charge and optimum smelting conditions. Attempts are being made to produce ferro-silicon using taconite in a closed, direct current (dc) plasma arc furnace and commercialise the technology.

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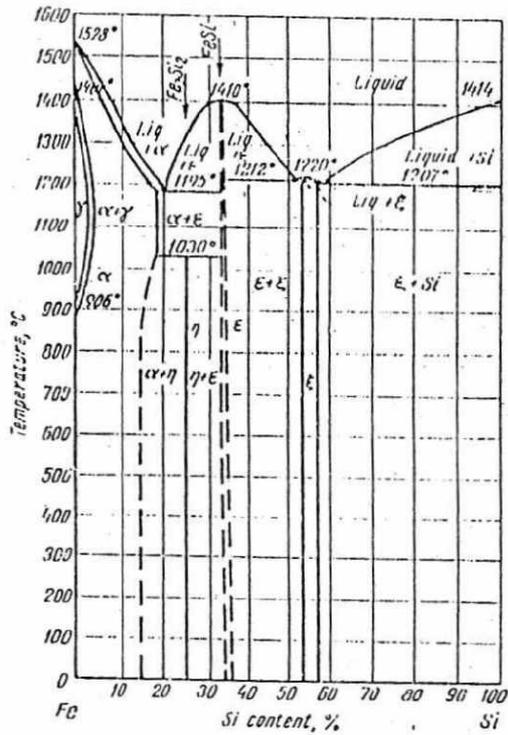
Fig. 1. Equilibrium diagram of iron-silicon system
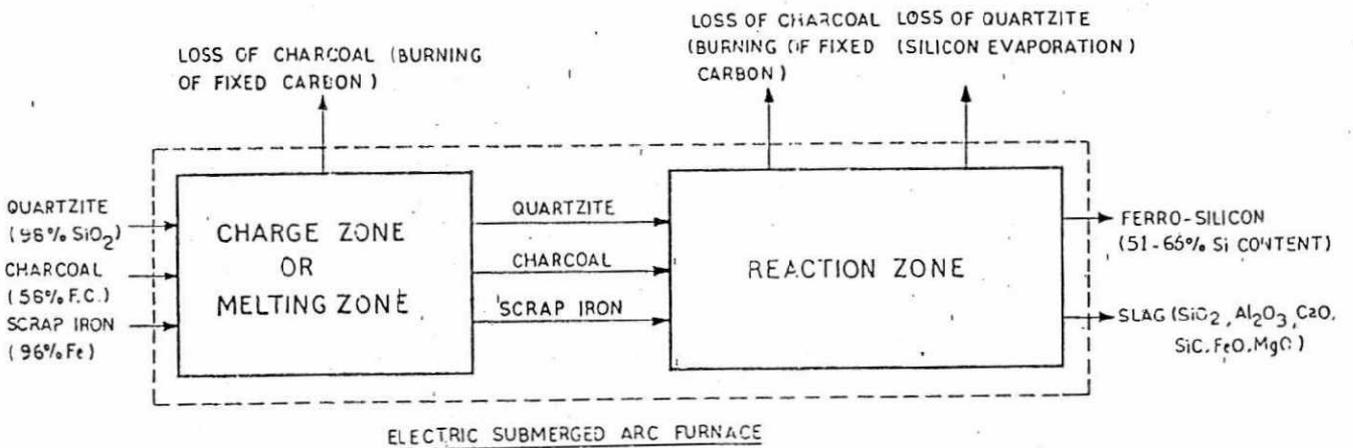
FIG: 2. FLOW DIAGRAM FOR THE PRODUCTION OF FERRO SILICON.

Production of Ferro-Silicon and Calcium Silicon Alloys

Part - II : Calcium Silicon Alloys

II.1 Introduction

Calcium silicon is currently imported to meet the requirements in the country. Several methods are reported in literature for the production of calcium silicon [1-5]. These methods are mainly based on the use of different combinations of the following materials viz (i) calcium carbide, silica and carbon (ii) calcium oxide, silica and carbon (iii) calcium carbonate, silica, calcium fluoride and calcium chloride (iv) silicon carbide, calcium carbide and quartz (v) calcium oxide and an aluminium silicon alloy. Aravamuthan et al. [6] studied the production of calcium silicon on laboratory scale using a mixutre of ferro-silicon containing more than 80% silicon and calcium carbonate or oxide and produced calcium silicon having calcium content of 20%, and a silicon content of above 60%. Topilskii et al. [7] showed that ferro-silico-calcium containing 12-15% calcium had a number of advantages over silico-calcium when used for standard purposes. Akerkar et al. [8] discussed the methods of production of calcium silicon by the partial carbide method. Vaish, et al. [9] have conducted smelting trials in a 500 KVA submerged arc furnace following quick lime method with the major objective of producing calcium silicon with 25-30% calcium content.. Patra, et al. [10] produced calcium silicon with calcium upto 32% by carbothermic reduction and proposed a probable theoretical model of the actual operation. Kinnoskuke Okuda [11] conducted a theoretical study on the mechanism of calcium silicon alloy formation. He tried experiements to produce Ca-Si alloy using calcium carbide and proposed models of inner state in the furnace. Calcium silicon is widely employed in the production of high quality steels. It is also used as desulphuriser forming CaS, a very stable compound. In the form of powder it is used for the reduction of slag. Small addition of calcium silicon alters the graphite flakes to almost perfect spheroides with significant improvement in mechanical properties of grey iron castings.

II.2 Raw Materials

The charge mix for the smelting of calcium silicon alloys consists of quartz/quartzite, lime, fine coke, charcoal and coal. The specifications of quartz/quartzite, fine cke, charcoal and coal are the same as in the ferrosilicon smelting practice. The lime should contain at least 90% of CaO. Poorly burned lime sharply raises power consumption, lowers furnace efficiency, causes technology disturbances and shortens furnace life.

II.3 Production of Calicum Silicon Alloys

There are two industrial methods for the production of calcium silicon alloys.

i. **Calcium Carbide Method** : The reduction of silica with carbon takes place in the presence of calcium carbides [13]

$$2\ SiO_2\ +\ 2\ C\ +\ CaC_2\ =\ (CaSi_2)\ alloy\ +\ 4CO$$
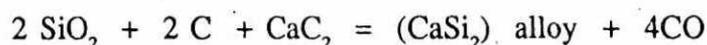
The standard Gibbs energy of this reaction is
$$\Delta G^0 = 14,24,558.7 - 792.97 \ T, \quad Joules/g \ mole$$

The theoretical initial temperature of reduction ($P_{CO} = 1$ atm) is 1520^0C.

In this method calcium silicon is produced in a shaft type electric furnace. The charge mix consists of quartzite, calcium carbide and a mixture of coke with charcoal.

ii. **Quick Lime Method** : Calcium silicon is produced in a single stage, omitting the production of calcium carbide. In this method, production of calcium silicon is based upon the reduction by carbon of CaO and SiO_2 according to the following reaction [13]
$$2 \ SiO_2 \ + \ CaO \ + 5 \ C \ = \ (CaSi_2) \ alloy \ + \ 5CO$$
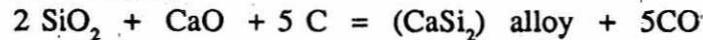
The standard Gibbs energy of this reaction is

$$\Delta G^0 = 18,90,507.60 - 1,020.65 \ T, \quad Joules/g \ mole$$

The theoretical initial reaction temperature is about 1580^0C.

The smelting of calcium silicon according to this method requires a very precise proportioning of the charge. The least shortage of the reducing agent intensifies the formation of slag from CaO and SiO_2, and when it is in excess, the depth of immersion of the electrodes into the charge is reduced very quickly, causing an intensive evaporation of calcium and silicon and cooling of many parts of the furnace. This in turn causes the accumulation of carbides of calcium and silicon.

The quick lime method is preferred compared to the calcium carbide method since it is more efficient.

II.4 Thermodynamics of Single Stage Carbothermic Reduction [Quick Lime Method]
The negative free energy of formation of calcium oxide is the highest of all the oxides of metals, like magnesium, silicon, aluminium, iron etc., and also carbon monoxide at various temperatures [Figure 1]. Since CaO is the most stable of all the four oxides, its reduction by carbon is very difficult.

In single stage carbothermic reduction, both lime and silica are reduced simultaneously. The successful reduction of SiO_2 and CaO to silicon and calcium respectively by carbon is possible only at a temperature when the resultant CO becomes stabler than the reduced oxides. This is attained for SiO_2 at temperature above 1540^0C and for CaO at temperature above 2150^0C. This combined reaction can take place at a temperature considerably lower than the reduction temperature of lime alone owing to the free energy considerations

$$CaO \ + \ C \ + \ Si \ [Metallic] \ = \ CaSi \ [Alloy] \ + \ CO$$
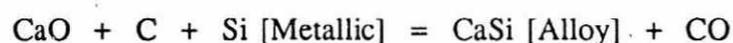
The reduction process is process is facilitated by the formation of silicon at above 1540°C which reacts with CaO in the presence of carbon at about 1600°C only to form calcium silicon. This, lowering of temperature is due to the fact that the process of dissolution of calcium in silicon is strongly exothermic

$$Ca + Si = CaSi ; \Delta H^0 = -1,50,724.8 \text{ Joules/g. mole}$$

This extra generation of heat helps the reduction process to a great extent.

II.5 Physico-Chemical Reactions during Single Stage Carbothermic Reduction of Calcium Silicon

The formation of calcium silicon is not so simple, in reality an easily fusible slag forms at a lower temperature when calcium oxide and silica are available in the ratio of 35-55% and 45-65% respectively. The slag so formed during the process reacts with carbon and produces calcium silicon at 1650°C as follows

$$CaSiO_3 + 3 C = CaSi + 3 CO$$
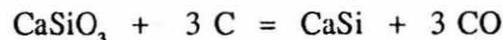
The excess carbon of the charge mix also brings about the formation of silicon and calcium carbides at 1437°C and 1625°C respectively as follows

$$SiO_2 + 3 C = SiC + 2 CO$$

$$CaO + 3 C = CaC_2 + CO$$
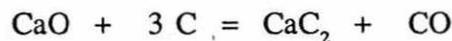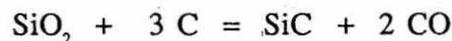
Considerable formation of these carbides leads to the crusting of the furnace. These carbides have very high melting points and they are destroyed periodically by the additions of quartzite at 2023°C and 1792°C respectively according to the reactions

$$2 SiC + SiO_2 = SiO + CO + Si$$

$$CaC_2 + SiO_2 = CaSi + 2 CO$$
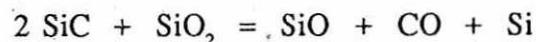
II.6 Basis of Charge Calculation for Single Stage Carbothermic Reduction of Calcium Silicon

1. The coefficients of utilization of calcium and silicon are about 65 percent and 80 percent respectively.
2. Considering significant stack losses of calcium and silicon, lime and quartzite in the charge mix are used 2 times and 1.5 times of that required theoretically.
3. The fixed carbon in the charge mix is used 1.3 times of that required theoretically.

II.7 Operating Considerations

1. Prior to the smelting of calcium silicon, 45 to 60% ferrosilicon is smelted for about 10-15 days to heat up the furnace. Then the furnace is cleaned by smelting lime before changing over to calcium silicon smelting campaign. After

the bath cleaning operation, fine coke is charged on the hearth and the banks before feeding the required burden for calcium silicon.

2. The deepest possible and stable positioning of the electrodes is maintained during the smelting process.

3. The charge level is kept low and the crusting of furnace is avoided.

4. Since smelting process is carried out with excess reductant, the hearth of the furnace gets rapidly crusted with the carbides of silicon and calcium. Therefore special measures are to be taken to destroy the carbides from time to time by charging quartzite around the electrode along its entire perimeter. The addition of quartzite depends upon the degree of crusting.

5. The crusting of furnace is indicated by (i) high carbon content in the alloy (ii) absence of slag during tapping (iii) more viscous slag (iv) difficulties in tapping and (v) high positioning of electrodes.

II.8 Microstructure-Composition Relationship

1. The uniform fine grained structure of the metal ingot indicates that the percentage of calcium in the alloy is less than 25 percent.

2. When calcium content in the ingot exceeds 28-29 percent, the fracture of the alloy becomes macrocrystalline and

3. When calcium content in the alloy exceeds 30 percent or more, than columnar structure is observed.

II.9 Illustrations of Calcium Silcon Smelting

II.9.1 Pilot Scale Production of Calcium Silicon at NML, Jamshedpur [9] : Calcium silicon was smelted in pilot scale open type 500 KVA submerged arc furnace at NML [Figure 2] using quartzite, charcoal and calcined lime. The charge consisted of good quality quarttzite, lower grade charcoal and lower grade calcined lime. Multigrade calcium silicon alloys [10-14% Ca content, 14-20% Ca content and 20-30% Ca content] were produced during three week campaign of calcium silicon. It was rather difficult to achieve the grade of 30% calcuim, mainly due to the lime being improperly clacined, although the limestone was good and within the specifications stipulated. The poorly burnt lime caused increase in power consumption, lowering the furnace efficiency and decreasing the yield of calcium. As a result the power consumption increased to more than 19,000 KWh per tonne of calcium silicon. The average consumption of quartzite, charcoal and calcined lime was on a higher side than the standard practice. Further the use of lancing tubes also increased the iron content in the alloy, thereby decreasing the percentage of calcium in the product. With the raw materials of specified compositions and using arcing method for the opening of tap hole, calcium silicon of 30% Ca grade could be produced continuously.

II.9.2 Industrial Scale Production of Calcium Silicon [12] : Calcium silicon is usually smlelted by a continuous process in three-phase furnaces of a power of 10,000-13,000 KVA at a linear voltage of 115-140V. The typical composition of the

slag is 45-50% SiO_2, 15-25% CaO, 10-12% CaC_2, 8-10% SiC and 4-5% Al_2O_3. The density of slag is higher than that of calcium silicon with 30% Ca. On cooling the slag crumbles to powder. The furnace is tapped 12 times a day and the melt is taken in a flat cast iron mould. The typical data on the consumption of raw materials and electric energy for smelting calcium silicon (28 percent Ca) are as follows:

Quartzite	:	1830 kg/t
Lime	:	710 kg/t
Coke breeze (dry)	:	580 kg/t
Coal	:	310 kg/t
Charcoal	:	500 kg/t
Electric energy,	:	12800 kg/t
Electrode mass	:	160 kg/t

The production performance of calcium silicon can be improved by (i) choice of optimum electrical operating conditions (ii) improvement of raw materials quality, (iii) prolonging the campaign of calcium silicon furnaces and and (iv) reduction of alloy losses.

II.10 **Conclusions and Remarks** : The single stage carbothermic reduction [quick lime method] of calcium silicon alloys demands quality raw materials, very precise proportioning of the charge, special operational skills, precise maintenance of temperature in the reaction zones and destruction of carbides from time to time. National Metallurgical Laboratory proposes to demonstrate its technology of calcium silicon production in an industrial furnace utilizing indigenous raw materials.

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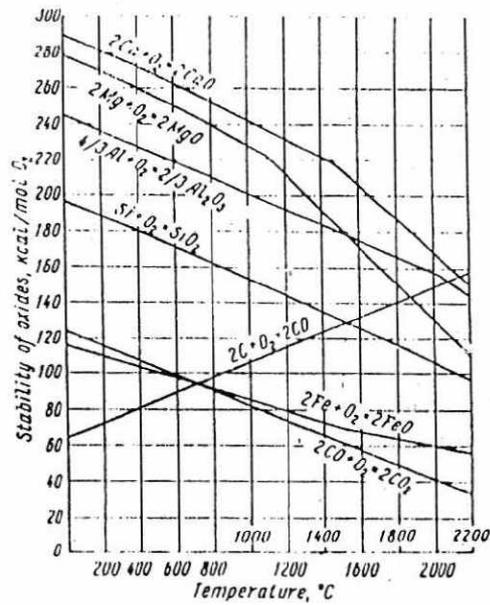
Fig. 1. Relationship between stability of oxides and temperature

PILOT—SCALE ELECTRIC SUBMERGED ARC FURNACE

FIG. 2. Flow diagram for the production of Calcium Silicide.