

# Smelting Technologies for Ferrochromium Production – Recent Trends

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## ABSTRACT

*The conventional process for producing high carbon ferrochromium by smelting chromite ore in a submerged arc furnace is reviewed and its limitations highlighted with regard to (a) product quality through impurity removal, and (b) high power consumption for a given raw materials supply. The trends towards (i) utilization of medium grade ore fines by agglomeration, and (ii) pre-reduction of chromite ore prior to arc smelting are examined in terms of their effectiveness in accomplishing substantial savings in power consumption. A technoeconomic evaluation of the conventional smelting practice in the Indian context makes obvious the need for adopting improved technologies for better cost-competitiveness and survival in this era of economic liberalization.*

**Keywords :** Ferro chromium, Smelting, Submerged arc furnace.

## INTRODUCTION

More than 80% of the world production of ferrochromium is used in stainless steelmaking. There are four grades of ferrochromium produced commercially, characterized broadly in terms of their carbon and chromium contents :

High carbon ferrochromium	(Cr : >60%,	C : 6–9%)
Charge chrome	(Cr : 50–60%,	C : 6–9%)
Medium carbon ferrochromium	(Cr : 56–70%,	C : 1–4%) and
Low carbon ferrochromium	(Cr : 56–70%,	C : 0.015–1.0%)

The demand for low-carbon ferrochromium, produced by reacting Fe–Cr–Si alloy with a  $\text{Cr}_2\text{O}_3\text{CaO}$  based slag, has decreased dramatically during the last two decades mainly due to the commercial development of AOD and VOD processes which allow removal of carbon from stainless steels with acceptable loss (oxida-

tion) of chromium<sup>[1]</sup>. These low and ultra-low carbon ferrochromium grades are used mainly for final adjustments of composition and for super alloys which are melted in coreless induction furnaces. The ultra-low ferrochromium, produced by aluminothermic reduction of chromite, is relatively pure but very expensive and consequently, not widely employed in the steel industry.

As a result the high-carbon ferrochromium has become the most widely produced and consumed grade of chromium-containing ferroalloys. The production of high carbon ferrochromium is based on reduction smelting of chromite ore with coke in the presence of silica in a submerged arc furnace.

In this paper the performance of the conventional submerged arc smelting process in producing quality ferrochromium alloys and its technoeconomics are examined in view of the prevailing raw materials situation and thermodynamic constraints, and the existing market conditions.

Later, the new technologies, especially those based on smelting of pre-reduced chromite feed, are briefly reviewed and their distinct advantages, already proven in terms of process economy, furnace productivity and product quality, are highlighted.

## Raw Materials

The natural ores of chromium are mainly composed of spinels,  $\text{FeO}\cdot\text{Fe}_2\text{O}_3$ ,  $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ ,  $\text{MgO}\cdot\text{Cr}_2\text{O}_3$  and  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ , all in solid solution in the chromite mineral, and accompanied by gangue frequently composed of serpentine ( $\text{MgO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$ ). with suitable concentration treatment, it is possible to remove most of the siliceous gangue rendering a concentrate containing  $\text{Cr}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  with nearly stoichiometric amounts of FeO and MgO i.e., moles of  $\text{R}_2\text{O}_3$  equal to moles of RO<sup>[2]</sup>. Indigenous chromite ores, mostly from Orissa's Sukinda Vally, fall into two broad categories :

- a) high silica hard lumps from igneous rock, containing serpentine ( $\text{MgO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$ ) as the principal gangue with an overall Cr/Fe ratio of approx. 3. These siliceous ores are generally amenable to beneficiation by gravity methods.
- b) ferruginous friable ores from limonite deposits rich in secondary iron oxides.

Since the chromite ore contains gangue, it is not possible to produce low carbon, low silicon ferrochromium in the conventional single-stage submerged

arc furnace smelting process. In general, additional silica must be included in the charge as a flux to facilitate formation of a fluid slag during the smelting operation.

### SUBMERGED ARC FURNACE SMELTING

The conventional smelting process for producing ferrochromium is carried out in electric reduction furnaces having Soderberg electrodes submerged in the burden material. To achieve steady process of the reduction reactions, the gas flow and partition through the burden should be uniform enough to avoid channeling of carbon monoxide gas produced by the reactions. This requires the charges to be primarily comprised of lumpy ore with a minimum of ore fines; also, the ore should not be friable so that excessive degradation of the ore does not occur in the furnace. However, due to increasing mechanization of the ore mining operations and the necessity of using ferrugeneous friable ores, there is considerable generation of ore fines, with grain size smaller than 1 mm, which calls for some form of agglomeration (such as pelletizing, briquetting or sintering) of the feed materials. Another important cost factor of the conventional technology is the high power consumption which is in the range of 4000–4200 KWh/t–FeCr alloy.

### Thermodynamic Considerations

Most of the reduction reactions taking place in the submerged arc furnace are highly endothermic and are listed in Table 1 along with standard Gibbs free energies as a function of temperature<sup>[3-5]</sup>, Table 1 also lists for various reactions the temperature at which the CO pressure is one atmosphere, under standard state conditions for the reactants and products. In actual smelting practice, the reduction temperature will be raised if the reaction oxide is chemically combined in the gangue, and lowered if the reaction product can dissolve in the ferrochromium alloy.

Table 1 : Stability ranges for the carbothermic products

Reduction Product	Stability Range (°C)	Weight Percent Carbon in Product
Cr <sub>3</sub> C <sub>2</sub>	1150 to 1250	13.3
Cr <sub>7</sub> C <sub>3</sub>	1250 to 1600	9.0
Cr <sub>23</sub> C <sub>6</sub>	1600 to 1820	5.7
Cr	> 1820	0

The data in Table 1 indicate that at these smelting temperatures, iron, chromium and silicon form stable carbides. In the case of  $\text{Cr}_2\text{O}_3$ , it first reacts with carbon to form a higher carbide,  $\text{Cr}_7\text{C}_3$ , which reacts back at higher temperatures with  $\text{Cr}_2\text{O}_3$  to form a lower carbide  $\text{Cr}_{23}\text{C}_6$ . This reaction occurs at approximately the same temperature as that required for reducing silica to  $\text{SiC}$  [1].

**Behaviour of Impurity Elements**

*Carbon Content of Ferrochromium*

In submerged arc smelting, the carbon content of the ferrochromium is generally high and varies significantly because of the formation of various chromium carbides such as  $\text{Cr}_3\text{C}_2$ ,  $\text{Cr}_7\text{C}_3$  and  $\text{Cr}_{23}\text{C}_6$ . Fig. 1 shows the standard free energy changes of the chromic oxide reduction reactions as a function of temperature [1].

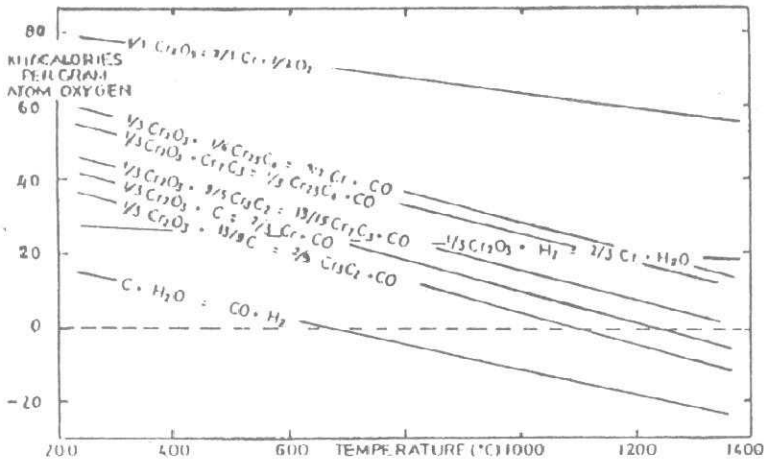


Fig. 1 : Standard free energy changes for the chromic oxide reduction reactions in the temperature range 200 to 1400 °C.

Table 2 shows the stability ranges for the reduction products and also the carbon contents of the carbides. The data indicate that temperatures over 1600°C are necessary to achieve a carbon content under 9 percent.

Table 2 : Standard Gibbs energies and equilibrium temperatures of reactions during carbothermic reduction of chromite

Reaction	$\Delta H$ 298k kJ/mole	$\Delta G$ , (J/mole)	T K for $P_{\infty} = 1$ atm
$Fe_3O_4 + C = 3FeO + CO$	194.2	200, 595–212.86 T	942
$FeO + C = Fe + CO$	161.5	153, 251–152.08 T	1001
$Cr_2O_3 + 3C = 2Cr + 3CO$	803.1	825, 029–486.0 T	1698
$Fe_3O_4 + 5C = Fe_3C + 4CO$	703.8	670, 083–682.28 T	983
$3FeO + 4C = Fe_3C + 3CO$	509.6	470, 114–469.42 T	1001
$7Cr_2O_3 + 27C = 2Cr_7C_3 + 21CO$	5300.4	5426, 008–3453.5 T	1571
$SiO_2 + 3C = SiC + 2CO$	616.5	624, 559–346.06 T	1805
$3SiO_2 + 2SiC = Si + 4SiO + 2CO$	2256.3		2082
$Cr_2O_3 + 3Cr_7C_3 = Cr_{23}C_6 + 3CO$	956.7		1800

As mentioned earlier, chromite ores contain iron oxides and gangue which have significant effects on the reduction reactions in submerged arc smelting. Studies on solid–state reduction of chromite have shown that the iron oxides get reduced more readily than the chromite oxides [6]. Under such conditions, iron forms only one carbide  $Fe_3C$ , which can dissolve chromium to form a complex carbide  $(Cr,Fe)_7C_3$ . Thus, an ore rich in iron oxide will have high reducibility at relatively low temperatures [7]. Accordingly, the reduction of chromic oxide in such ores will also occur at relatively lower temperatures with the likely formation of a carbon–rich chromite carbide ( $Cr_3C_2$  or  $Cr_7C_3$ ) known to be stable at lower temperatures.

The gangue present in a chromium ore has a significant effect on the temperature of the smelting zone thereby influencing the carbon content of the ferroalloy. An ore having a relatively high  $MgO$  content will require a higher smelting temperature, as can be seen from the ternary phase diagram for  $Al_2O_3$ – $SiO_2$ – $MgO$  system in Fig. 2. Further, if silica flux addition is reduced or lime is added, the liquidus temperature of the slag will increase thus promoting high smelting temperatures [7]. In practice, it has been found that a  $MgO : Al_2O_3$  ratio close to 1.0 forms high smelting slags which promote low carbon levels in the ferro alloy.

It has been argued that, because of their high surface to volume ratio, fine ores react readily at low temperatures forming a product high in carbon. The use of chromite–carbon agglomerates is reported to have produced high carbon

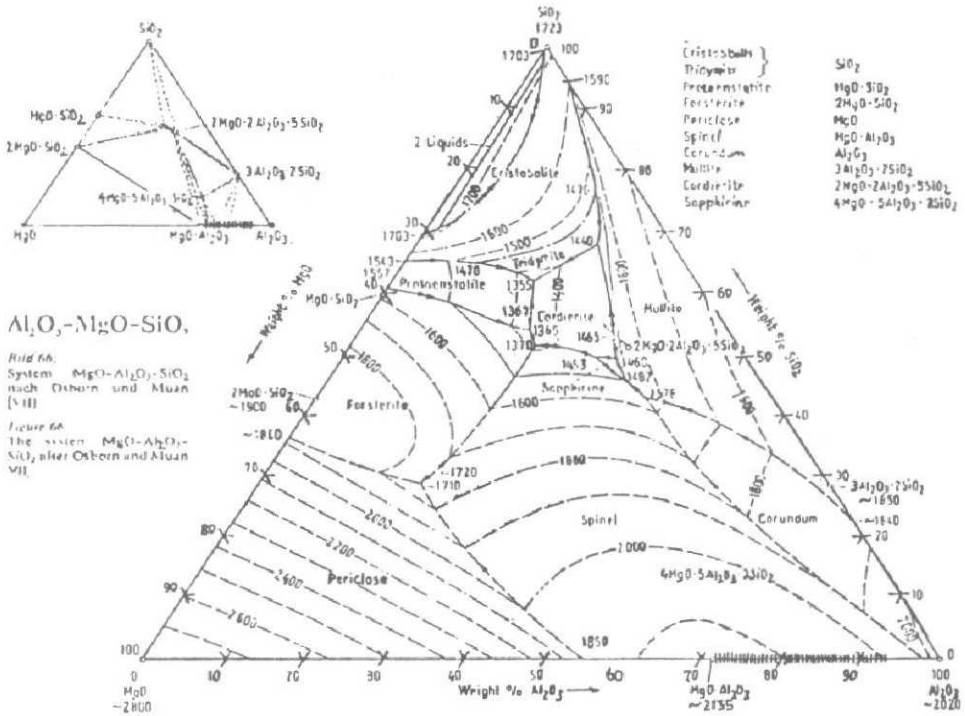


Fig. 2 : Liquids surface for the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system.

ferrochromium since they start reacting at lower temperatures [8]. On the other hand, coarse-sized ores will not be as reactive and thus can survive to a lower depth in the burden and react with high carbon alloy, thereby, promoting a low-carbon ferrochromium.

One method proposed for minimizing the carbon content of the ferrochromium is to create a region in the furnace that is oxidizing to the chromium carbide with the use of a high density-high smelting ore. The high density (approx. 4 g/cm<sup>3</sup>) will allow it to pass through the low density slag (~3 g/cm<sup>3</sup>) and form a chromic oxide rich layer above the molten ferrochromium [9]. Such an ore layer can oxidize the chromium carbides. Further, due to its viscosity it will remain in the furnace even after tapping. This explains how relatively low carbon levels can be obtained with the use of dense, lumpy, low reducibility ores.

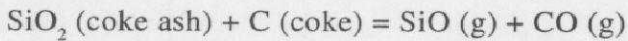
### Silicon Content of High Carbon Ferrochromium

The silicon content of the ferrochromium should be low as it is an undesirable element in stainless steels. A low silicon content is favored by a low operating



temperature, a high carbon content in the ferroalloy and a basic slag. Other impurities are not known to affect the silicon content significantly. In general, the specifications for ferrochromium call for a silicon level below 3 percent. This can be achieved by utilizing the idea, mentioned earlier, of forming a layer of chromic oxide ore in the lower portion of the slag which oxidizes some silicon in addition to carbon <sup>[10]</sup>.

It has been amply demonstrated that, in the iron blast furnace, the silicon content of the hot metal depends on the silica content of the ash in coke in accordance with the following reactions :



Thus, with increase in coke rate, the relative amount of SiO(g), and consequently, silicon in the metal will also increase. It is believed that under the highly reducing conditions in the submerged arc furnace, the silicon content of the ferrochromium would also depend on the silica content of the ash in the carbonaceous reductants used.

High silicon ferrochromium, low in carbon, can be de-siliconized by treatment with a chromite ore–lime slag <sup>[11]</sup>, when it is necessary to produce low carbon ferrochromium.

### *Phosphorous Content of High Carbon Ferrochromium*

Phosphorous is detrimental to both the mechanical properties and corrosion resistance of stainless steels. In the submerged arc smelting of chromite ore, a portion of the phosphorus contained in the charge is vaporized and removed with the off-gas; however, up to 60 percent can be retained in the alloy.

For low phosphorous levels (<0.02%) in ferrochromium, the phosphorus content of the raw materials should be as low as possible. Also a relatively low operating temperature will promote removal of phosphorus into the slag phase, especially under oxidizing conditions. However, due to the highly reducing and hot conditions in the submerged arc furnace, there are no easy ways to produce a low phosphorus ferrochromium from high phosphorus ore/coke.

Even though several studies have been made on removal of phosphorus from liquid ferrochromium using fluxes such as CaFe<sub>2</sub>–CaC<sub>2</sub>, Ca–CaF<sub>2</sub>, industrial

practices mostly rely upon the use of imported low-phosphorus metallurgical coke as a preventive measure.

## NEW TRENDS IN FERROCHROMIUM SMELTING TECHNOLOGY

Increasing costs of electric energy and reduced availability of high grade lumpy ores have prompted significant improvements in process technologies. Some of these developments, which have been commercially successful such as those involving pelletization of the ore fines and preheating/pre-reducing the pellets, are briefly discussed as follows:

### The Outokumpu Process

This industrially proven process allows (a) utilization of a feed, comprised mainly/exclusively of ore fines and (b) heat recovery from the arc furnace off-gas (CO) for preheating the burden, Fig. 3. The process involves grinding and pelletizing of ore fines, followed by sintering of green pellets and preheating before smelting <sup>[12]</sup>. The ore and coke fines are normally wet-ground to about 35

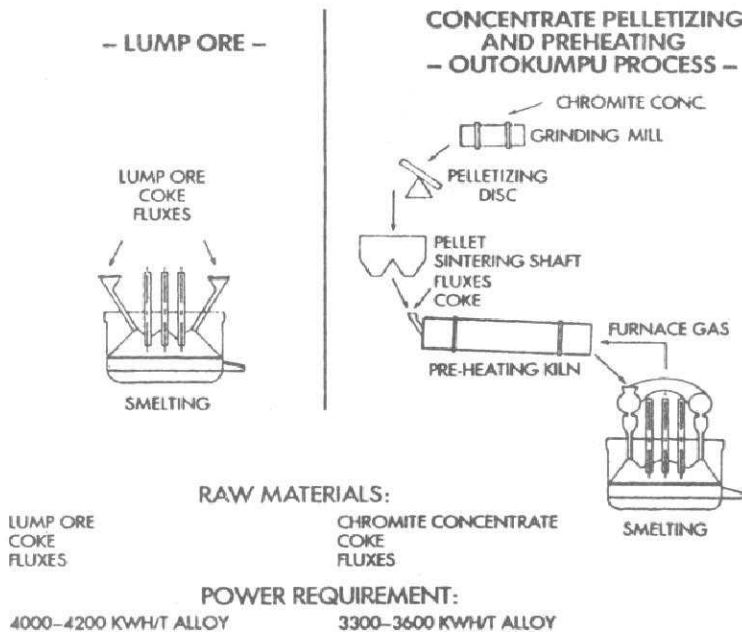


Fig. 3 : Conventional smelting.



– SHOWA DENKO/CMI PROCESS –

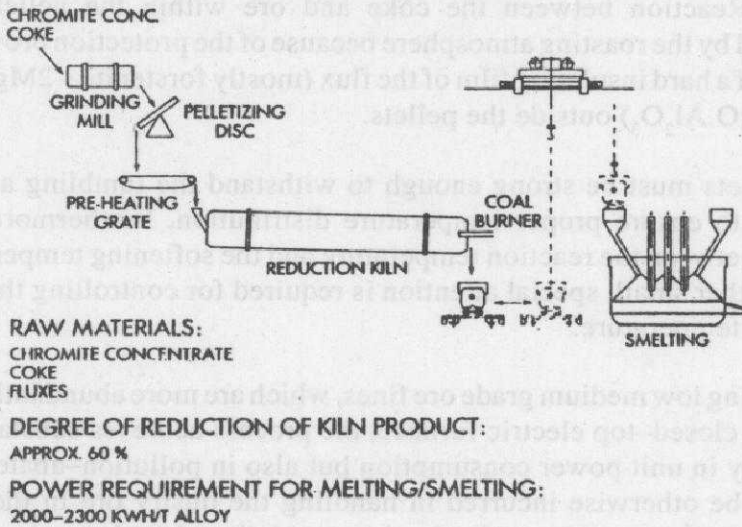


Fig. 4 : Prereduction of pellets and smelting/melting.

percent under 37 micron (400 mesh) and then pelletized to approx. +15 mm size. The bulk of the fuel for sintering and preheating the pellets is provided by the CO from the submerged arc furnace which must be top-closed so as to recycle the CO gas generated inside. The preheating of the charge, usually in a rotary kiln, results in power saving of about 500–700 kWh/t, <sup>[13]</sup>.

*The Showa-Denko Process*

The logical step, after the Outokumpu Process, in further reducing power consumption was implemented by the Showa-Denko process which includes a pre-reduction treatment of the ore in a rotary kiln downstream of the pelletizing plant, Fig. 4. The hot calcine with about 60 percent pre-reduction is directly charged into the submerged arc furnace. As a result of the pre-reduction, the power consumption is reported to be in the range of 2000–2300 kWh/t alloy <sup>[14,15]</sup>.

Because of a strong affinity during the pre-reduction treatment in a rotary kiln of chromium for oxygen, it is necessary, therefore, to keep the carbonaceous reductant in microscopic contact with the chromite ore particles and allow them to react at temperatures higher than 1280°C <sup>[14]</sup>.

To produce pellets of good strength and reactivity, ore and coke are pulverized to a fine homogenous mixture of size generally less than 100 microns. The pellets are subjected to a roasting treatment in a rotary kiln at temperature 1340 to 1450°C under air. Reaction between the coke and ore within the pellets proceeds unhampered by the roasting atmosphere because of the protection provided by the formation of a hard insulating film of the flux (mostly forsterite –  $2\text{MgO} \cdot \text{SiO}_2$  and spinel –  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ ) outside the pellets.

The pellets must be strong enough to withstand the tumbling action in the rotary kiln to ensure proper temperature distribution. Furthermore, since the difference between the reaction temperature and the softening temperature of the pellets is rather small, special attention is required for controlling the flame and the furnace temperature.

By treating low medium grade ore fines, which are more abundantly available, and using a closed-top electric furnace, the process achieves substantial reduction not only in unit power consumption but also in pollution-abatement costs, that would be otherwise incurred in handling the dusty ore in the open. The Showa-Denko process is credited with two industrial plants, having a total production capacity of 200000 t/yr, operating in Japan and South Africa.

#### *The CODIR Process for Chromite Fines*

The CODIR process, Fig. 5 conceived and tested by Krupp in the 1980's and later commercialized by Mannasman Demag<sup>[13]</sup>, aims at

- \* Direct charging of ores fines into a rotary kiln.
- \* Achievement of almost complete reduction (approx. 90 percent) of chromium and iron oxides in the rotary kiln with the use of cheap non-coking coal as exclusive reductant and fuel.
- \* Hot charging of pre-reduced calcine into an electric furnace for open-bath smelting resulting in a low power consumption of 1050–1200 kWh/t alloy only.

The process is reported to have been in full industrial application at Samancor's plant in South Africa<sup>[16,17]</sup>. The plant employs a rotary kiln, 4.8 m in diameter and 80 m long; rate at 120000 t/yr along with a submerged furnace with a transformer capacity of 33 MVA.

In the rotary kiln, chromite ore fines and coal react at temperatures approach-

– CODIR® FOR CHROMITE FINES –

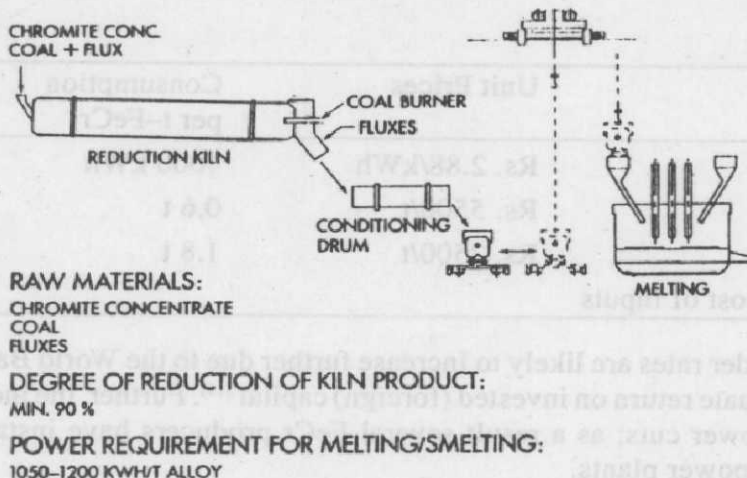


Fig. 5 : Prereduction and smelting/melting.

ing 1450°C to produce a semisolid product consisting of highly metallized ferrochromium, slag, gangue and char. High temperature and intimate contact between the chromite grains and carbon are necessary over the entire residence time in the kiln to achieve a high degree of metallization (>90%). For this purpose, the burden is transformed into a semisolid (pasty) state with some phases molten and other solid, so that only a small portion of the surface of the metallized phase is exposed to air/oxygen, and yet macroscopic phase separation does not take place.

Phase separation is carried out subsequently by melting the kiln discharge in the submerged arc furnace. It has been reportedly recently that the smelter is being upgraded to a 56 MVA furnace for transferring energy to the process/charge via., a DC plasma arc produced by a single hollow graphite cathode<sup>[18]</sup>.

**TECHNOECONOMICS OF FERROCHROMIUM PRODUCTION IN INDIAN CONTEXT**

Production of ferrochrome, and ferroalloy in general, are power intensive. The ferroalloys industry in India is hamstrung by exorbitant power costs (Rs. 2.50–3.00 kWh) not to speak of high prices of coke, coal and ore. Power rates in

India are among the highest in the world and contribute as much as 50 percent to the cost of producing ferrochromium. For the conventional arc smelting of ferrochromium, the cost of power, coke and the ore requirements are estimated as follows :

	Unit Prices	Consumption per t-FeCr	Rs./ton FeCr
Power	Rs. 2.88/kWh	4000 kWh	11520
Coke	Rs. 5500/t	0.6 t	3300
Ore	Rs. 2500/t	1.8 t	4500
Total cost of inputs			19320

Powder rates are likely to increase further due to the World Bank's insistence on adequate return on invested (foreign) capital <sup>[19]</sup>. Further, the industry is facing acute power cuts; as a result several FeCr producers have installed their own captive power plants.

On the other hand the prices of ferrochromium [Cr : 60–65, C : 6–8, Si : 2.0 max.] in the international markets is reported to be about 45% cents per lb of chromium, c.i.f., <sup>[20]</sup>, which works out to Rs. 21700/t-alloy. This calls for enhanced efficiency in transmission, distribution and use of power. It is estimated that the plant load factor could be stepped up by about 5 percent.

Equally important, if not more, the alloy producers must make every effort to reduce power consumption, by adopting better technologies such as those involving pre-reduction of the chromite prior to smelting in the submerged arc furnace as discussed earlier in the paper. In order to maintain cost competitiveness in this era of economic liberalization, it is of utmost importance for the ferroalloy industry to move towards optimization of power requirements by using improved technologies. It has been argued that the cost to benefit ratio for the additional hardware and processing required for agglomerating the ore fines and pre-reducing the chromite feed will be very favourable in view of substantial savings in power costs resulting there from <sup>[21,22]</sup>.

It is encouraging that many of these technologies have already been commercialized successfully in Japan and South Africa.

We at NML have already initiated laboratory studies for the pre-reduction of chromite ores, the preliminary results are encouraging and will be presented later.

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