

# REDUCTION OF CHROMITE FINES IN SOLID STATE USING A MIXTURE OF GASES CONTAINING NATURAL GAS, HYDROGEN AND NITROGEN

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## ABSTRACT

*It is the aim of every metallurgist to innovate and try to adopt processes which will help bring down the over all input of energy in the process of smelting and also to utilize the cheapest form of energy source. Use of electric power in the smelting of **chromium** ores to produce high carbon Ferro chrome is one of the major costs in the inputs.*

*This paper describes the results of the test work carried out for reduction of chromite fines in solid state using a mixture of Natural gas, Hydrogen and Nitrogen. It is planned to feed the pre-reduced fines in the hot state to an electric furnace for production of high carbon Ferro chrome, thereby reducing very substantially the electric power required for the smelting process.*

*The paper also describes the flow sheet of the proposed one **ton** per hour pilot plant to be set up for determination of the most optimum parameters of gas mixture and their pressure and temperature required to be maintained to achieve the maximum reduction and obtain the lowest input of electric power during smelting to produce 'High Carbon Ferro Chrome'. Based on the results obtained in the pilot plant an industrial scale unit would be set up.*

*An application for a patent on the process is pending.*

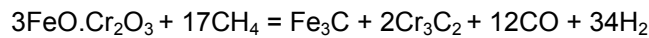
## 1 INTRODUCTION

The largest chunk of income of a producer of Ferro Chromium is taken away by the cost of electric power. So every producer would like to reduce the input of electric power consumed in the process. It is said that up to 39.5% of the energy is used for heating of raw materials and 47% is used on reduction reactions of iron and chromium oxides [1]. Hence if any other form of energy could be utilized which is of lower cost compared to electric power for heating of raw materials and maximum possible reduction before entry to furnace, it would be possible to substantially reduce the cost of production. There is one well-established process for agglomeration and preheating of chromite fines and concentrates which is used by several producers, known as the OUTOKUMPU Process from Finland. Also there is a process for agglomeration, preheating and pre-reduction known as SHOWA DENKO process from Japan. It is being used by few of the manufacturers. This process has been modified by Xstrata; by use of anthracite fines in place of coke fines in the formation of composite pellets, to make it more economical.

With the prospect of new findings of natural gas in our region and the possibility of getting the same at a much lower cost compared to electric power, we started looking at all the possible processes for preheating and pre-reduction.

Apart from the two mentioned above we studied the papers [1] to [5] published on the subject. Most of the processes utilize coke as the reducing agent, by which reduction reaction takes place at a higher temperature. The process with natural gas mentioned in reference [2] does not utilize coke. The reduction reaction of Cr<sub>2</sub>O<sub>3</sub> by methane containing gas is said to be thermo dynamically feasible at a lower temperature. Chromium oxide is reduced by methane through the reaction as mentioned in [6]. This appeared to be of maximum interest to us. So we decided to carryout some tests on chromium

ore fines instead of pure chromium oxide used in their experiments, in a fluidized bed reactor using a mixture of Methane, Hydrogen and Nitrogen instead of argon used by them, since argon is much more expensive compared to Nitrogen. Chromium and Iron Oxides occurring in ore in form of spinel are reduced by methane through the following chemical reaction [6]:



Under standard conditions, this reaction proceeds spontaneously at temperatures above 841°C, which is much lower than the temperatures required for the carbo-thermic reduction of chromium oxide. This makes reduction of chromium oxide by methane quite promising.

## 2 EXPERIMENTAL

The tests were performed in a 6" diameter batch fluidized bed reactor unit. The Nimonic steel reactor vessel was heated in a fluidized bed electric resistance furnace to a maximum temperature of 1200°C. Thermocouples inside the reactor monitored the temperature of the ore sample material, as well as the off-gas and the furnace.

A gas train and pre-heater were assembled to supply the desired fluidizing gas and reducing gases mixture. Fluidizing gas used was nitrogen and reducing gases mixture had nitrogen, natural gas and hydrogen. System set-up included the capability for changeover of one gas to another during any particular run, and/or the use of a mixture of gases during any particular run. The off-gas from the process was filtered through sintered metal filters, a cyclone and finally through a scrubber before release to the atmosphere.

For the run, 12.5 pounds of chromite ore fines ground to below 75 microns were loaded into the unit. Nitrogen was used to fluidize the material at a linear velocity of 20ft/min. The reactor was lowered into the fluidized bed furnace at ambient temperature. The furnace was then heated to 1200°C over a 7-hour period. As the temperature inside the reactor increased, the fluidizing gas flow was decreased to maintain a constant linear velocity.

When the material bed temperature reached 1100°C, the nitrogen gas was replaced with the reduction process gas, a combination of methane, hydrogen and nitrogen 30, 20 and 50% respectively. The reactor was run under these conditions for approximately 100 minutes. The concentration of the methane was then increased to 33% (hydrogen concentration decreased to 17%). After another 75 minutes when twice the calculated quantity of methane was passed and the reaction was expected to have been completed the concentration of methane was reduced to 20% in the mixture before completely cutting off methane and hydrogen. The reactor was held under these conditions for another 25 minutes. The fluidizing gas was then returned to full nitrogen and the reactor unit removed from the furnace. The bed was maintained under the full nitrogen flow for approximately 2 hours.

Figure 1 shows the recording of process temperatures. It may be observed that when the sand bath and furnace body temperatures came to 1200°C, the bed temperature of the ore fines sample was only 1100°C. As soon as the reduction gases mixture was passed the bed temperature came down, indicating the endothermic reduction reaction absorbing the thermal energy. After the reaction was completed, the temperature of the bed became stable and came again to about 1100°C

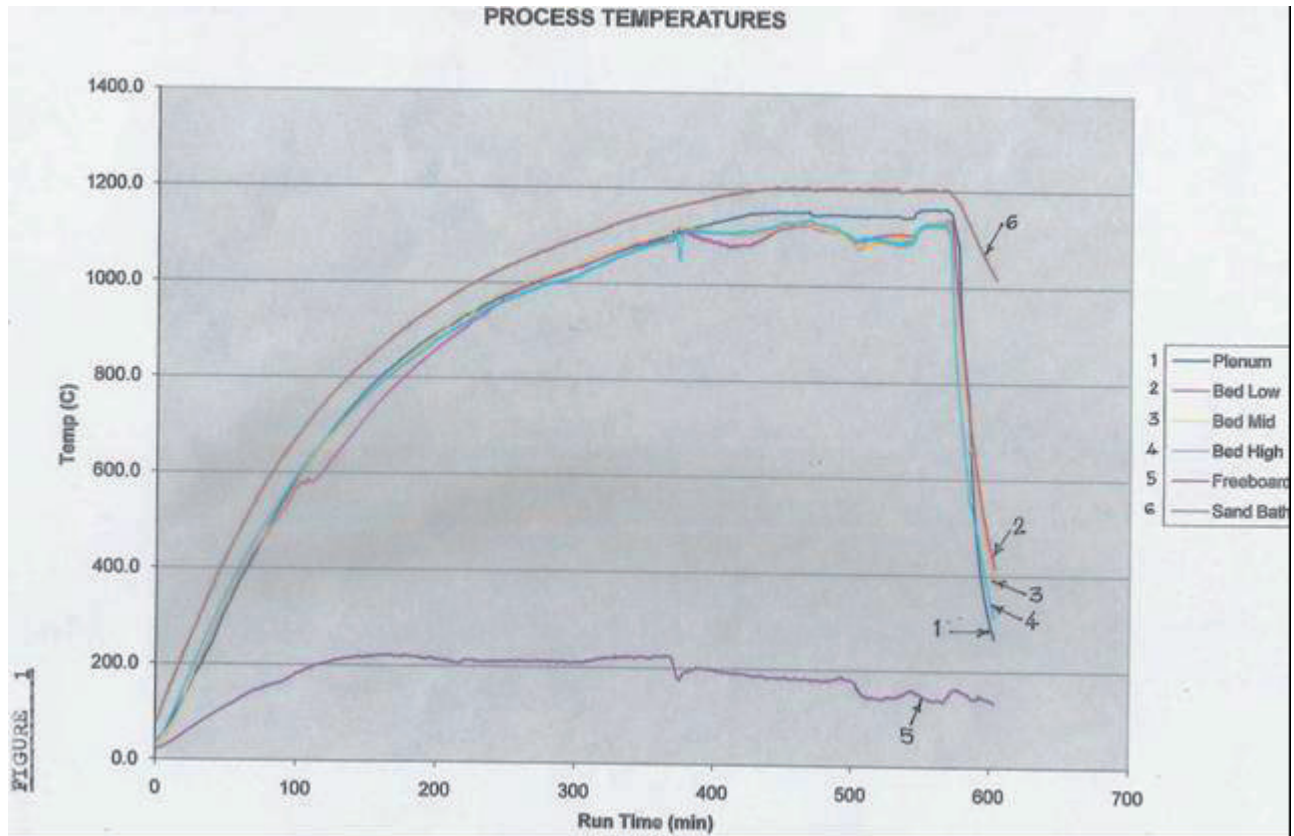


Figure 1:

The reactor was opened and emptied the next morning. The majority of the material inside was free-flowing powder. There were a few friable chunks of material sitting on the distributor plate. The weight of the product recovered from the reactor was 10.2 pounds. A sample of the material, which had changed color from reddish brown to dark grey, was sent for analysis.

Analysis of the feed material was as per Table 1. Analysis of the reduced material produced during the test is as per Table 2. Preliminary results indicated nearly complete reduction of the chromite ore, and achievement of the desired product. The prospect of fluid bed reduction of the chromite ore fines at a commercial scale is thus favorably indicated.

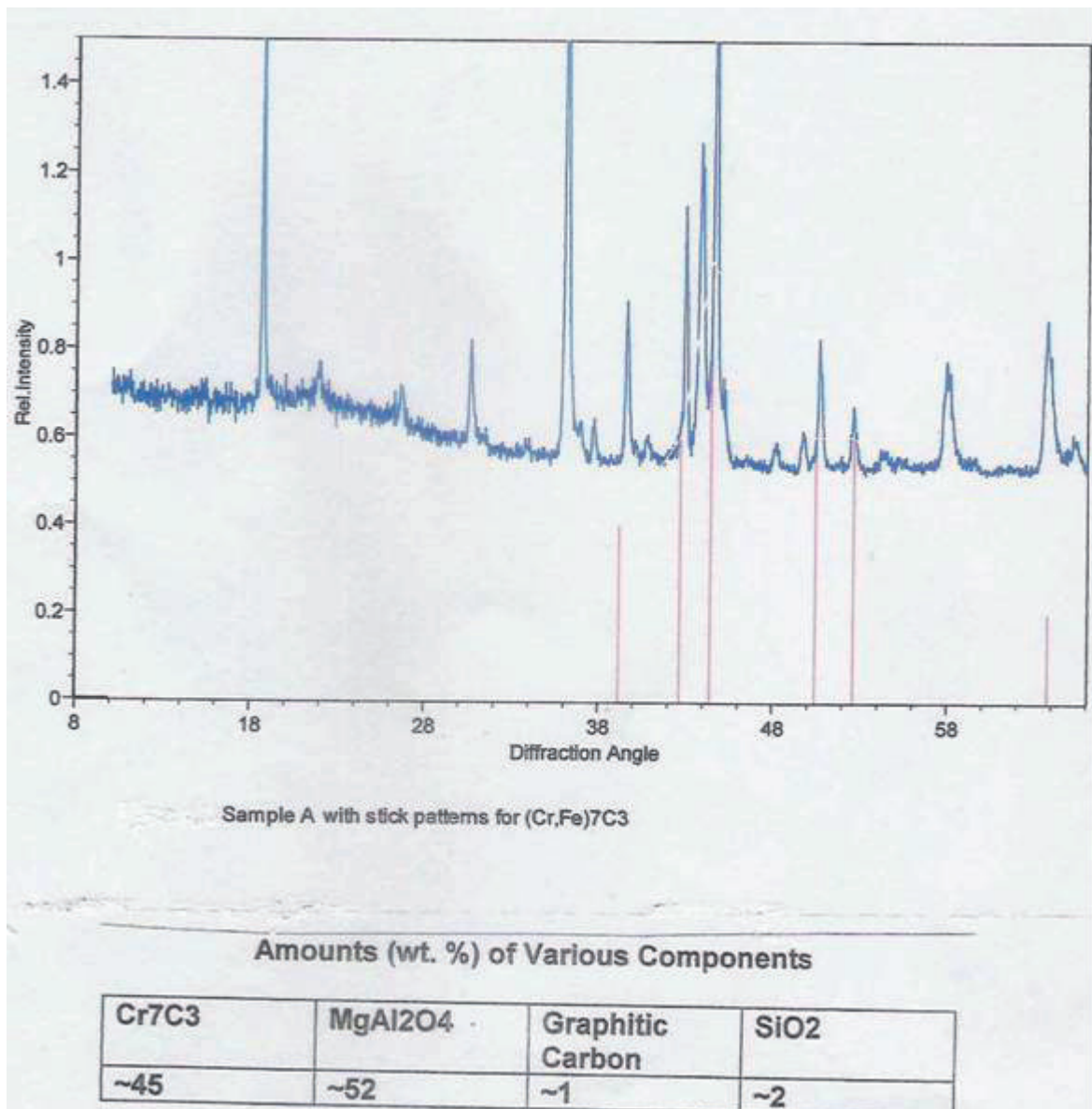
Table 1:

Constituent.	%
Cr <sub>2</sub> O <sub>3</sub>	52.50
FeO	16.53
SiO <sub>2</sub>	4.70
CaO	0.34
MgO	11.70
Al <sub>2</sub> O <sub>3</sub>	11.75
LOI	1.56
Eq.Cr	35.92
Eq.Fe	12.85
Cr:Fe ratio	2.79

Table 2:

Constituent	%
Cr	38.66
Fe	13.97
C	5.47
S	0.032
N	0.2337

The reduced ore sample was sent for XRD analysis, the result obtained and the diffraction pattern are given in Fig. 2.



**Figure 2:**

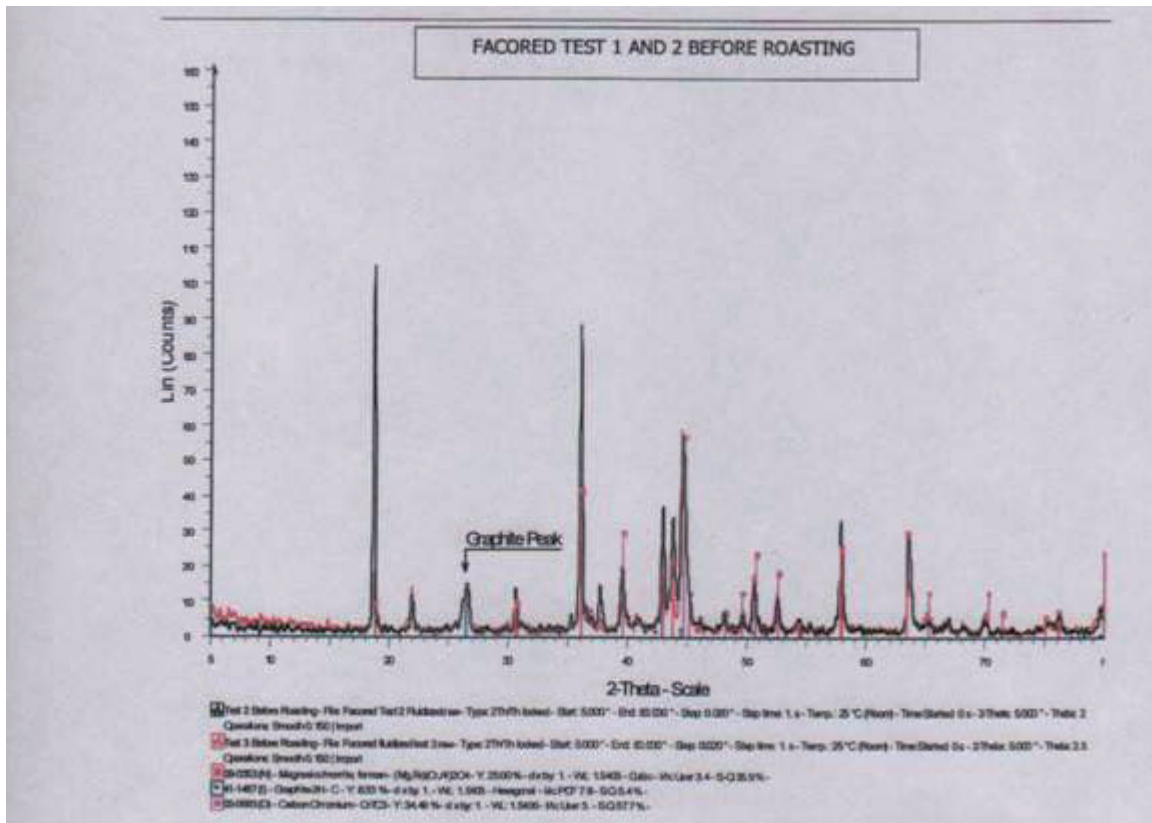
Further tests in the fluidized bed reactor were carried out changing the mixture of reducing gases by increasing methane and reducing hydrogen as well as reducing the initial preheating temperature. But it was found that the reduction reaction does not accelerate. On the contrary the free carbon content increases in the reduced ore but the extent of reduction of chromium oxide does not increase. It was not possible in the available equipment to carry out reduction reaction at higher material bed temperatures of 1150°C or 1200°C, due to limitation imposed by the material of construction of the reactor vessel .

To see the effect of preheating the material to a higher temperature before injecting the reducing gases mixture, some tests were carried out in a rotary kiln and a quartz tube fluidized bed reactor at MINTEK, South Africa. The test results are given below in Table 3. It was evident that in the rotary kiln the contact between the sample particles and reduction gases was not enough. But in the case of preheating the sample material to 1150°C in the quartz tube fluidized bed reactor, the carbides in the reduced ore sample were found to be 58% compared to 45% in the earlier tests according to the XRD test results. The reduced ore samples were showing a higher content of graphite (free carbon). So they were roasted in a muffle furnace at 500°C. As seen from the result of test 2, the graphite content reduced from 5% to 2%, but the carbides content also reduced from 58% to 55%. These tests proved that the higher preheating temperature resulted in a higher degree of reduction of Chromium Oxide.

**Table 3:** Semi-quantitative XRD and C (by LECO) analysis of reduction test products before and after roasting at 500°C

Test No.	XRD Analysis Before Roasting(%)			XRD Analysis After Roasting (%)			By LECO C
	Spinel	Carbide	Graphite	Spinel	Carbide	Graphite	
Kiln	-	-	-	55.0	25.0	3.00	6.54
Fluidbed 1	54.0	42.0	4.00	59.0	39.0	2.00	6.49
Fluidbed 2	37.0	58.0	5.00	43.0	55.0	2.00	4.04

The diffraction pattern of the XRD tests in the reduced ore samples before and after roasting is shown in Figures 3 and 4, given here below.



**Figure 3:**

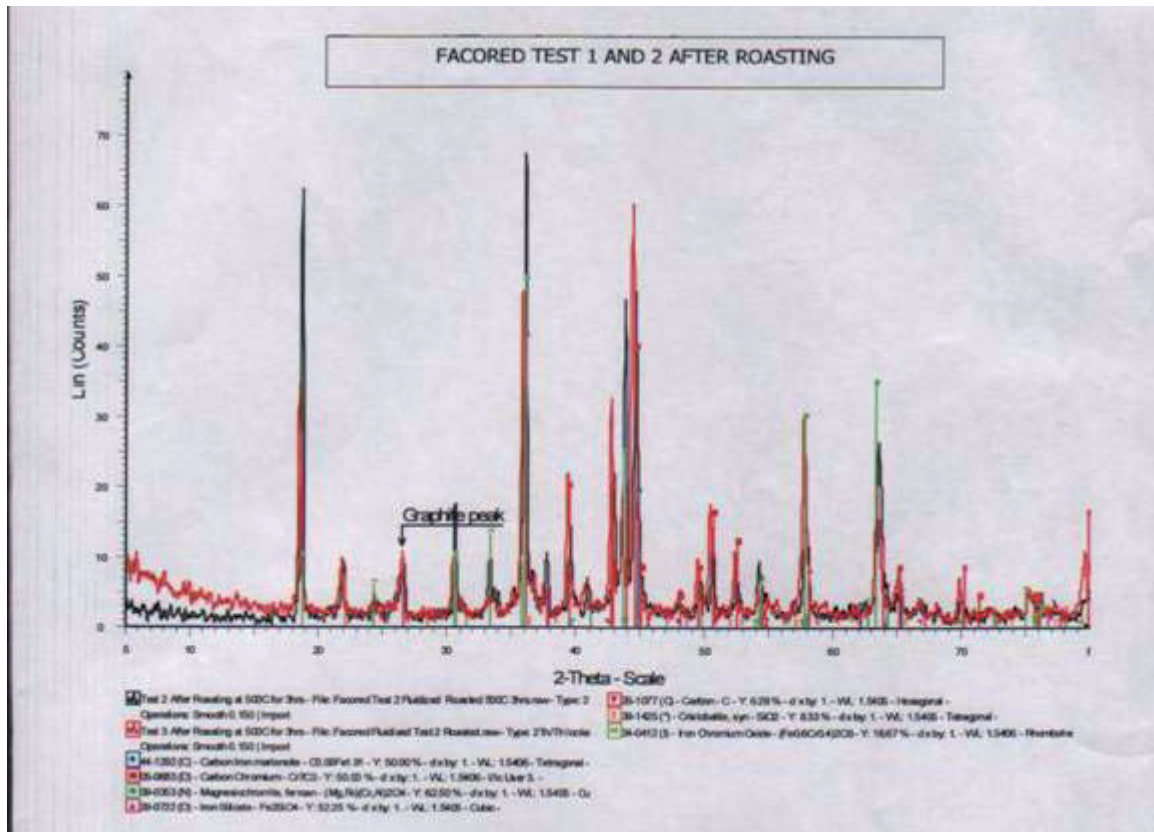


Figure 4:

To attain higher preheating temperatures, it is felt that the fluidized bed reactor has to be built from Silicon Carbide refractory, which can withstand much higher temperatures, and also will have a higher thermal conductivity.

Hence it was decided to put up a pilot plant with a fluidized bed reactor made from refractory bricks so that the most optimum parameters of the process with respect to temperature of preheating and the composition of mixture of reducing gases can be determined. The flow sheet of the proposed pilot plant is given in fig. 5. The supply of natural gas from the authorities is awaited and whenever it becomes available, the pilot plant with a capacity of about one ton/hour will be set up.

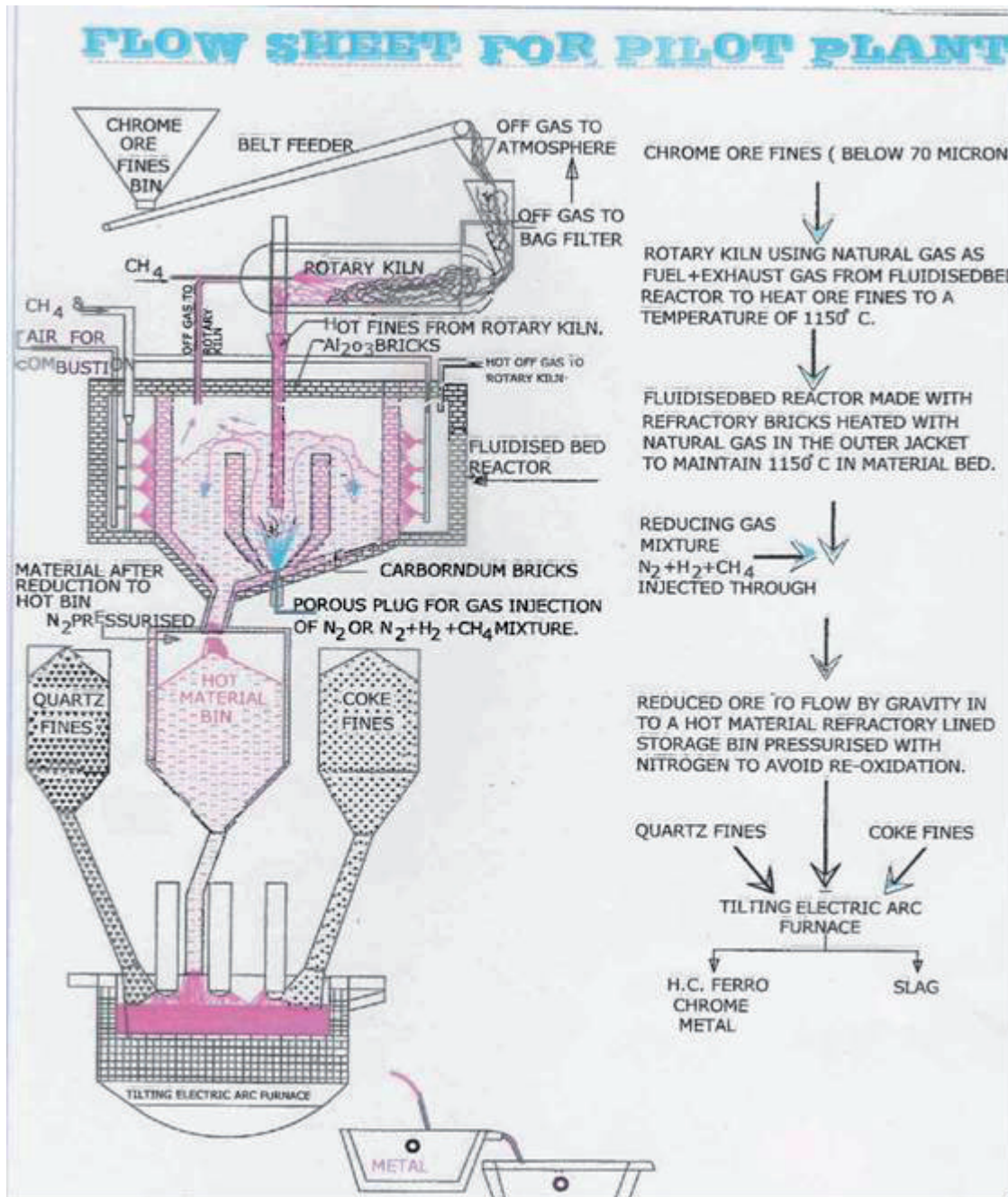


Figure 5:

### 3 CONCLUSIONS

1. The process is expected to bring down the requirement of electric power in the smelting furnace by about 50%, from the present about 3800 KWH/tonne.
2. The requirement of fixed carbon should come down to about one-third from the present about 420kgs/tonne.
3. There will be no need for agglomeration of the ore fines, as pre-reduced free flowing fines at a temperature of over 1000°C will enter the electric arc furnace. Hence expense on agglomeration will be totally avoided. However, there will be some additional cost for grinding to below 75 microns, unless the pilot plant shows that, in larger scale, higher size particles (up to 500 microns, as they naturally occur) can be reduced.

4. The quantity of carbon di-oxide released to the atmosphere from the electric furnace will be much lower per ton of product. The off gas from the fluidized bed reactor will be utilized along with additionally required natural gas, for preheating of Chrome ore fines in the rotary kiln.

### 4 REFERENCES

- [1] 'Factors affecting the reduction of chromite' by N.F.Dawson and R.I.Edwards presented at INFACON 1986.
- [2] 'The Solid-state reduction of Chromite' by M.J.Niayesh and R.J.Dippenaar presented at INFACON 1992
- [3] 'Solid-state Fluxed Reduction of LG-6 Chromite from the Bushveld Complex' by P.Weber and R.H.Eric presented at INFACON 1992.
- [4] 'Reduction of Chromium Oxide by Methane-containing Gas' by O.Ostrovski, Andrew Jacobs, Nathaniel Anacleto and Gregory Mckenzie presented at INFACON 2001.
- [5] 'Direct reduction process using fines and with reduced CO<sub>2</sub> emission' by A.Morrison, S.Hietkamp and D.S. van Vuuren published in Ironmaking and Steelmaking 2004 Vol.34, No.4.
- [6] 'Solid-State Reduction of Chromium Oxide by Methane-Containing Gas' by Nathaniel Anacleto and Oleg Ostrovski published in Metallurgical and Materials Transactions B, Volume 35 B, August 2004-609.