

A PROCESS FOR THE RECOVERY OF CHROMIUM AND IRON OXIDE IN HIGH CARBON FERRO CHROME SLAG TO OBTAIN CHROMIUM AND IRON IN THE FORM OF SALEABLE METAL

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ABSTRACT

The conventional process for High Carbon Ferro Chrome (Hc FeCr) in sub merged arc electric furnace has got a limitation of recovery of only 84-88% of input chromium in the metal, even after following the best process control methods. 12-16% of chromium is lost as flue dust in the fumes, as metalics entrapped in the slag and as unreduced and partially reduced oxides in the slag. Cr_2O_3 analysed in slag is around 10-14%. Till date no economic method is found to recover chromium lost in the slag, in oxide form.

An attempt is made to develop a process which is described in this paper to recover chromium and iron present in the slag to an extent of 98% by smelting the liquid slag obtained in each tapping from the furnace, with addition of coke and flux in an electric arc furnace promoting reduction by adjusting the slag basicity, to get about 100 kg additional saleable metal from each tonne of liquid slag and discarding final slag with only about 1% to 2% Cr_2O_3 . The final slag could also be used being with higher basicity in the production of Portland cement.

1. INTRODUCTION

With the advent of stainless steel production in India for which chromium is the major additive for its luster and non-corrosive properties HC FeCr production has gained importance. The present annual production capacity of HC FeCr in India is about one million tonnes. The raw materials in the production of HC FeCr consist of chromite ore, which has the requisite chrome and iron contents, metallurgical coke plus anthracite coal or non-coking coal to reduce the oxides present in the chromite ore and fluxing materials like quartz, magnesite or bauxite to get the required composition of the slag formed out of gangue materials in the ore and ash of reductants. The smelted products obtained from the furnace are HC FeCr metal and slag, which are tapped periodically from the hearth bottom. Generally they are collected in cast iron receptacles at regular intervals. The slag production is about one to 1.2 times of the alloy produced, depending on the chemical composition of the chromite ore taken as feed material and ash content in the coke and other reductants used. The melting point of the alloy being about 1550 °C, temperature of the liquid slag composition selected, is about 1600 to 1650 °C for free flow of metal from the furnace.

The main components of slag are SiO_2 , MgO , Al_2O_3 , CaO and Oxides of Cr and Fe.

Typical composition of Ferro Chrome Slag is shown below in table 1.

Table 1: Typical composition of Ferro Chrome Slag

Cr_2O_3 , %	FeO , %	SiO_2 , %	Al_2O_3 , %	MgO , %	CaO , %
14 - 16	2 - 4	26 - 30	22 - 24	24 - 26	2 - 3

As already stated, due to loss of Cr in slag in the present production process of HC FeCr in submerged arc electric furnace there is a limitation of recovering only 84 – 88% of chromium in metal even after following the best practice and process control methods. Though by increasing slag basicity beyond 1.4 is an effective way of reducing the loss of chromium to the slag, addition of lime increases slag volume which causes extra losses and raises up electrical conductivity which is detrimental for the furnace operation ref.[1] and raises the slag temperature too high.

The loss of 14 – 16% chromium is due to:

- (a) about 1.0 - 2.0% loss through flue dust in fumes and handling losses.
- (b) about 2.0 - 3.0% loss in the form of metalics entrapped in the slag and
- (c) about 8.0 - 10% loss in the form of unreduced and partially reduced oxides of Cr in the slag.

In slag analysis the total Cr in slag is expressed as Cr_2O_3 which varies from 12 to 16% and the slag volume varies from 1 to 1.2 times the weight of metal produced, depending on the gangue constituents in chrome ores and ash content in the reductants used in the process. For each tonne of HC FeCr about 2.35 tonnes of Chromite ores are required. The average Cr_2O_3 content in the ore is about 45%. Thus losing 120 to 160 kg of Cr_2O_3 through slag is equivalent to about 260 kg to 350 kg of ore. The present annual production capacity of HC FeCr in India is about one million tonnes. Because of losses in slag, the estimated ore loss is about 0.26 to 0.35 million tonnes which can be termed as excessive depletion of this non replenishable mineral.

Uptill now mostly the efforts have been made only to recover the entrapped metalics in the slag, which are around 2to3% by mechanical means of crushing, grinding and gravity separation by jiggling etc. [2]. Several plants are operating for recovery of metalics from currently produced as well as old dumped slag.

We have come across one application made in 2011 for a Patent given as [4], where the liquid slag from one HC FeCr furnace is being treated with liquid metal with a higher silicon content produced from another sub merged arc furnace, which has about 6 to 8% silicon. So the liquid metal of one furnace is being reacted in a separate reaction vessel /ladle to reduce the Chromium oxide present in the slag of the first furnace. The agitation in the reaction vessel which is in the form of a ladle to get the metal and slag reacted is being done by blowing argon through a porous plug in the bottom of the reaction vessel. So the final slag obtained after this reaction which takes 20 to 40 minutes is having 1 to 2% Cr after the silico thermic reduction.

This process has the following draw backs.

1. Need of having an additional submerged arc furnace for producing high silicon containing HC FeCr metal.
2. Use of argon as the gas for agitation to enable have the reaction between slag and metal, makes the process very expensive as argon is very expensive.
3. Synchronizing of tappings of the two, submerged arc furnaces such that the liquid slag from the first furnace is available at the same time as the liquid metal from the second furnace to pour into the reaction vessel, is difficult.
4. There is no mention about the total Cr_2O_3 content analysed in the slag of the second furnace which produces higher silicon HC FeCr because this slag would also have unreduced and partially reduced Cr_2O_3 content and chromium due to metallic entrapments.
5. There is no mention of usages of inputs and cost of production of the high silicon ferro chrome.

Hence practical applicability of this process, may be difficult.

The object of our study is to find an economically viable method to recover the total chromium now being lost in the slag, by reducing Cr and Fe oxides in the liquid slag obtained from sub merged arc electric furnace with coke adding required flux (calcined lime) in an open arc

electric furnace, by adjusting the slag basicity to promote the reduction reaction, to get Cr and Fe in the form of saleable charge chrome metal.

2. EXPERIMENTAL

2.1. Bench scale studies at National Metallurgical Laboratory, Tatanagar, Jharkhand, India

Since liquid HC FeCr slag was not available the solid slag in the size 10-20mm was taken for the experimental smelting.

Bench scale test was performed in a 50 kVA Electric Arc tilting Furnace having Secondary voltage 80-85 V, Secondary current 0.75 kA with 50-55 kW input power.

7 kg of HC FeCr slag was initially melted in the furnace and after attaining the temperature above 1500°C, started adding mixtures of 620 grams of coke and 4.60 kg of calcined lime in small increments to initiate the reduction reaction. Smelting was completed in about 20 minutes and the melt attained a temperature of about 1700°C. About 50 grams of fluorspar was added to increase the fluidity of the slag. After attaining a temperature of 1750°C and getting the required fluidity of slag, the furnace was switched off and tilted to collect the metal in a graphite crucible and slag in sand beds. Next day, the solidified metal and slag were collected, weighed and analyzed.

Total weight of metal obtained was 911 grams and slag obtained was 10.82 kg.

Analysis of HC FeCr slag used in the study, metal and slag obtained after smelting are given in table 2.1, 2.2 and 2.3 respectively.

Table 2.1: Chemical analysis of HC FeCr Slag taken for study

Cr ₂ O ₃ ,%	FeO,%	SiO ₂ ,%	MgO,%	Al ₂ O ₃ ,%	CaO,%
14.06	4.14	29.18	26.06	23.20	3.36

Table 2.2: Chemical analysis of metal

Cr, %	Fe, % *	Si, %	C, %	S, %
40.70	52.15	1.15	5.98	0.02

* Steel spoon introduced in the melt in furnace for drawing sample could have contributed to higher Fe in metal

Table 2.3: Chemical analysis of slag after smelting

Cr ₂ O ₃ ,%	FeO,%	SiO ₂ ,%	CaO,%	MgO,%	Al ₂ O ₃ ,%
2.28	1.08	26.04	27.16	22.58	15.81

2.2. Studies at Institute of Minerals & Materials Technology (IMMT), Bhubaneswar, Orissa, India

To establish the results in sub-merged arc furnace, conducted trials in a 95 kVA sub-merged arc electric furnace with graphite electrodes at IMMT, Bhubaneswar. The furnace was started with 15 kg of coke in the bottom for initial contact and heating. After about 30 minutes of heating 45 kg HC FeCr slag, 30 kg of lime was added in small increments. Since sufficient coke was given in the bottom, no further coke addition was made. After smelting down the charge, another fresh batch of 45 kg of slag, 15 kg of lime and 4 kg of coke was added in small increments. Lime quantity was reduced in this batch to bring down the slag melting point to get the wider bath because the input

energy could not be increased beyond 45 kW as the size of the hearth was too big to give the intensive energy input required for the high melting point slag required to be made fluid after addition of required lime. Looking at the smelting as the melt could not be spread in wider area beyond the electrodes pitch circle, next batch of 45 kg slag was only added along with 4 kg of coke without any lime addition. Looking at the improvement in the smelting another 45 kg of slag along with 4 kg coke was added in small increments. 5 kg of fluorspar was also added to fluidize the slag. Continued smelting till liquid is formed.

After a power consumption of 570 kWh, tapping was attempted. There was a flush tapping initially but most of the metal and slag were left in the furnace as the fluidity of the slag was not sufficient to flow all out. After cooling of the melt, some quantity of metal and slag was taken out to the possible extent by digging from the hearth.

Quantity of metal obtained was 5.82 kg and quantity of slag was 140 kg. Still some more metal and slag were left in the furnace and could not be taken out, as entrapped in lining.

Analysis of HC FeCr slag taken for the test, metal obtained and slag after smelting are given in table 3.1, 3.2, 3.3 respectively.

Table 3.1: Chemical analysis of HC fecn slag taken for smelting

Cr ₂ O ₃ , %	FeO, %	SiO ₂ , %	MgO, %	Al ₂ O ₃ , %	CaO, %
14.06	4.14	29.18	26.06	23.20	3.36

Table 3.2: Chemical analysis of metal obtained

Cr, %	Fe, %	Si, %	C, %	S, %
54.79	31.28	6.81	6.98	0.020

Table 3.3: Chemical analysis of slag after smelting

Cr ₂ O ₃ , %	FeO, %	SiO ₂ , %	CaO, %	MgO, %	Al ₂ O ₃ , %
2.53	1.28	30.80	18.76	21.57	23.46

2.3. Trials at FACOR Steels Limited, NAGPUR, Maharashtra, India.

Looking at the results obtained in bench scale studies at NML and pilot scale experiment at IMMT, we decided to conduct the smelting studies on a larger scale in an open arc electric furnace of tilting type, since tapping of higher basicity slag (CaO + MgO / SiO₂) around 1.6 was found difficult from a submerged arc furnace. With lower basicity, it is not possible to reduce Chromium oxide present in the High Carbon Ferro Chrome slag to the desirable extent probably due to Cr oxide being present in the stable spinel phase ref.[3].

A 20 Mt capacity open arc electric furnace of tilting type, normally used for the production of alloy and stainless steel, is selected for the experimental study. 7 Mt of slag was melted after adding it in small increments and after complete melting of the slag and attaining a temperature of about 1600 °C, started adding the required quantities (as per the stoichiometry calculation) of coke and calcined lime gradually by shovels. Load kept on the furnace was 7 Mw with secondary voltage of 350 V and secondary current of 20 kA. After slag attained a temperature of 1750 °C, spoon sample was collected and checked for the reduction of Cr₂O₃ by observing the weight and colour of the slag. 100 kg of fluorspar was added to further fluidize the slag and the melt was unloaded in a refractory lined ladle. Slag was decanted in slag pot and metal cast in a cast iron chill mould.

After solidification and cooling, the metal cake was crushed and weighed. The quantity of metal obtained was 820 kg. The power consumed for melting the solid slag to liquid was about 1500 kWh per Mt of slag and for smelting was about 5500 kWh per Mt of metal. Analysis of HC FeCr slag taken for smelting, analysis of final slag after completion of smelting and metal obtained are given in table 4.1, 4.2 and 4.3 respectively.

Table 4.1: Chemical analysis of HC FeCr slag taken for smelting

Cr ₂ O ₃ , %	FeO, %	SiO ₂ , %	MgO, %	Al ₂ O ₃ , %	CaO, %
14.06	4.14	29.18	26.06	23.00	3.36

Table 4.2: Chemical analysis of metal obtained

Cr, %	Si, %	C, %	S, %	P, %
55.10	06.25	07.21	0.029	0.020

Table 4.3: Chemical analysis of slag after smelting

Cr ₂ O ₃ , %	FeO, %	SiO ₂ , %	CaO, %	MgO, %	Al ₂ O ₃ , %
0.76	0.42	30.44	27.72	21.56	17.84

3. PROCESS ENVISAGED

The proposed industrial scale process envisaged for the reduction of chromium oxide and iron oxide present in the HC FeCr slag is to reduce these oxides by carbon to a combined chrome iron carbide as given in figure1, which proceeds in the following steps:

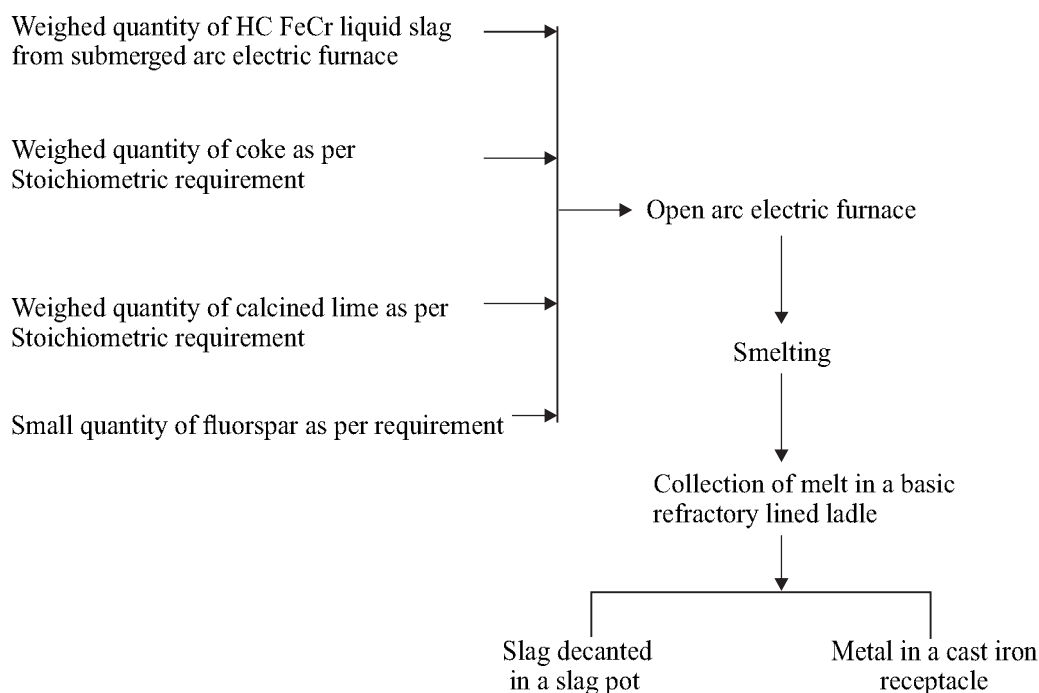


Figure 1: Flow sheet of the envisaged process

1. The liquid High Carbon Ferro Chrome slag collected during the tapping is weighed and poured into an Electric Arc Furnace (EAF).

2. As per the stoichiometry requirement, the coke quantity is calculated, weighed and kept about one third in the furnace bottom and balance for addition later.

3. Calcined lime calculated for maintaining a slag basicity ($\text{CaO} + \text{MgO} : \text{SiO}_2$) of about 1.6 is weighed and put about one third in the furnace with coke and balance kept for later addition after pouring slag.

4. After pouring the liquid slag in the EAF, the furnace is switched on and the arc is stabilized. Then the balance calculated quantities of coke and calcined lime are gradually added to complete the smelting process.

5. After smelting, if required, little quantity of fluorspar is added to obtain the required slag fluidity. Spoon sample of final slag is collected to check for residual Chromium. Sample on cooling will become white instead of green in colour if chromium in it is less than one percent.

6. After attaining the temperature of about 1700°C and ensuring sufficient slag fluidity, metal and slag are poured in a refractory lined ladle. Slag is decanted and metal cast in a cast iron pan. It is crushed and sized after solidification and cooling.

Slag is cast in sand beds and can be supplied to cement plants.

7. Samples of slag and metal are collected for analysis of the required components.

The slag being highly basic can be used like blast furnace slag as a component in Portland cement.

4. CONCLUSIONS

1. Looking at the analysis of metal and final slag after smelting the HC FeCr slag in tilting type electric arc furnace, it is evident that the Cr_2O_3 and FeO contents available in the slag could be further reduced substantially and the metal obtained is of salable quantity as charge chrome.

2. If facility is provided in the existing plant for further smelting of the liquid slag in electric arc furnace of tilting type, power required for melting of the solid slag can be saved and salable alloy (charge chrome) can be produced by consuming about 5000 to 5500 kWh power per tonne of metal plus coke and lime as per stoichiometric requirement.

3. Final slag after smelting being highly basic, can be used like blast furnace slag as a component in Portland cement industry.

5. REFERENCES

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