THE ALUMINOTHERMIC PRODUCTION OF EXTRA LOW CARBON FERROCHROMIUM FROM LOW GRADE CHROMITE ORE

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ABSTRACT

With the objective of study some of the parameters affecting on the possibility of utilization of a low grade chromite ore for the production of extra-low carbon ferrochromium, pilot plant experimental heats were carried out to determine the optimum condition to get the highest recovery and metallic yield using the aluminothermic process.

An optimum recovery of chromium and metallic yield of 79% and 76% respectively can be attained by adjusting the total input energy, the flux composition and amount as well as the amount of reductant relative to that of the ore.

The results were successfully applied on semi-industrial scale for the production of extra low carbon ferrochromium (O.02%C) containing 61% chromium.

1   INTRODUCTION

The increased demands for high quality alloy steels necessitate the large scale utilization of ferroalloys of special quality. Extra-low carbon ferrochromium is considered one of the ferroalloys necessary for the production of some high quality steel grades specially the corrosion- resistant and high-temperature oxidation-resistant steels.

The basic principle in obtaining the ferroalloys is to process the available raw materials, i.e. ores, ore concentrates, and/or ore sinters, using the suitable technology. This basic principle is applied for the production of low-carbon ferrochromium. The most widely used technique at present time is the silicothermic process. Although much work has been carried out to study, improve and develop the silicothermic process, it is characterized by technical complications and relatively high contents of carbon in the ferrochromium produced ($\approx 0.2\%$ C)[1].

The aluminothermic production of metals and alloys has been widely studied. However, its application for production of extra—low carbon ferrochromium has not been given the due attention of researchers in developing countries despite its technical simplicity and the low capital investment it requires [2]. The reduction reaction of oxides by aluminum can be generally, represented by the following equation [3]:

$$2/y\ M_xO_y + 4/3\ Al = 2x/y\ M + 2/3\ Al_2O_3 \tag{1}$$

Where MO represents the reducible oxides in the ore or concentrate.
The most important consideration with development of satisfactory aluminothermic reaction is that the self-propagating reaction which occurs throughout the charge shall produce enough heat to melt the products of the reaction and to allow separation of the metal and slag. The aluminothermic reduction process usually proceeds outside the furnace when the reaction temperature exceeds the melting point of the oxides being reduced [4]. If the amount of heat evolved from the reduction process is insufficient for melting of the charge, external sources, such as energizers or preheating the charge, are used to supply the charge with additional energy.

The amount of energizer required for the aluminothermic reduction process can be calculated by the following formula [5]:

$$G_{eng} = \frac{\delta H(G_{ore} + G_{Al} + G_F) - Q_{red}\,x100}{\Delta H_{eng} - \delta H(1 + g_{Al})} \, x \, \frac{1}{C_{eng}}$$

(2)

Where

δH : the heat required for the process, *2615* kJ/kg[4]
G_F: weight of flux used, kg
G_{eng}: weight of energizer, kg
G_{ore}: weight of chromites ore, kg
G_{Al} : weight of aluminum, kg
ΔH_{eng}: heat liberated from 1 kg of energizer, kJ/kg
g_{Al}: weight of aluminum for reducing 1 kg of energizer, kg
C_{eng}: percentage purity of energizer
Q_{red}: heat liberated from the reduction of oxides per kg of reduction mixture, kJ/kg

In addition, some other factors, such as aluminum amount, particle size of the charge constituents and flux additions will determine the success of an aluminothermic reaction.

This work aims at study some of the parameters affecting the possibility of utilization of low grade chromite ore for the production of extra-low carbon ferrochromium by aluminothermic reduction process. In previous study [6], a limited concentration ratio of the low grade chromite ore was obtained which attributed to its complex mineralogy. The replacement of Fe and Mg to Cr in the spinel structure acquires more or less similar magnetic properties to the ore constituents rendering their magnetic separation impossible. Thus, the concentration of this ore was found to be useless. Therefore, the study was carried out on the low grade chromite ore without concentration.

2   EXPERIMENTAL

Pilot plant experimental heats were carried out to produce extra-low carbon ferrochromium from a domestic low grade chromite ore using the aluminothermic process. The chemical composition of the used ore is given in Table 1. To determine the optimum condition to get the highest metallic yield and chromium recovery, four series of pilot plant experimental heats were conducted to investigate some parameters that affect the production of extra-low carbon ferrochromium by the aluminothermic process. These parameters included the adding energizer, aluminum amount and flux additions. Unless the parameter under investigation is being changed to find out its effect on metallic yield and chromium recovery, the various experiments were carried out using: preheating temperature 400°C, aluminum powder 32.8 kg/l00 kg ore, sodium nitrate 22.5 kg/l00 kg ore, particle size of aluminum powder - 0.8 mm and for ore -0.25 mm.

The pilot plant aluminothermic reaction was carried out in shaft type reactors. The shell of the shaft was made of steel pipe with 8-10 mm wall thickness. The bottom of the shaft was closed by means of a detachable steel plate. Both walls and bottom of the shaft were lined by ramming magnesite. The thickness of the wall lining was 30-40 mm while that of the bottom was 70 mm.

In each experiment, 10 kg of the ore together with the appropriate additions were thoroughly mixed and the whole charge was charged into the shaft which was preheated to 200°C. The charge was preheated to 400 °C while being in the shaft reactor. The temperature was measured by contact Ni - Ni Cr thermocouple. A mixture of mill scale, magnesium metal, sodium nitrate and aluminum powder was then added to initiate the reaction. Once the reaction started, it proceeds spontaneously. The reaction duration was about 90 seconds in each heat. The reaction products were then left to cool to room temperature. The reactor was emptied and the produced metal and slag were weighed. Representative samples were then selected for the determination of the alloy and slag chemical compositions.

Table 1: Chemical analysis of the used low grade chromite ore.

Constituents, wt.%										Cr/Fe
SiO_2	Fe_{total}	FeO	Fe_2O_3	Cr_2O_3	Al_2O_3	MgO	CaO	MnO_2	L.O.I	
10.34	12.29	12.87	3.26	38.0	8.12	20.55	2.0	0.39	3.20	2.12

Based on the results obtained from the pilot plant scale heats, a semi-industrial heat was carried out using the investigated low grade chromite ore. In this heat, 50kg of the ore was used together with the required charge materials and the aluminothermic process was applied using the same technology previously explained but in bigger size shafts.

Aluminum powder used in these experiments as a reducing agent was produced in situ by atomization method using compressed air. Its aluminum content was not less than 98%.

Ground lime and fluorspar, with grain sizes similar to that of the ore were used as fluxing materials. The chemical composition of the lime was (wt. %): 90 CaO, 5 SiO_2, 2 Al_2O_3, 3 $CaCO_3$, and that of fluorspar (wt. %): 80.5 CaF_2, 12.5 SiO_2, 2 CaO, 2.4 Al_2O_3, 0.35 Fe_2O_3, 2.25 ashes.

Sodium nitrate was chosen as energizer because of its efficiency as heat supplier, comparative cheapness and the favorable fluxing effect of Na_2O resulting from its dissociation.

3 RESULTS & DISCUSSIONS

3.1 Effect of the Heat Content of the Charge

The heat balance of the aluminothermic process for the production of ferrochromiurn is one of the most important factors which affect the productivity of the alloy from its ores. The first set of experiments is designed to investigate the effect of heat liberated from the reduction of the energizer.

3.1.1 Effect of energizer

The results obtained by a previous study [4] showed that the heat required for a successful aluminothermic process for ferrochromium production (δH) is about 2615 kJ/kg. Based on these results, the amount of energizer (sodium nitrate) necessary to fulfill the heat needs for the process was calculated using equation (2) after its modification to the following form:

$$G_{eng} = \frac{\delta H(G_{conc.or.ore} + G_{Al.red} + G_F) - Q_{red} x100 + Q_{preh.}}{\Delta H_{eng} - \delta H(1 - G_{Al})} x \frac{1}{C_{eng}}$$ (3)

Where Q_{preh} is the amount of additional heat input resulting from preheating of the charge at definite temperature.

In this calculation, a preheating temperature of 400°C was chosen as this temperature is lower enough than the melting point of aluminum and causes the least possible dissociation of energizer.

In these smelting experiments, different amounts of energizer, less and higher than the calculated value, were added. The amount of the heat of the process (δH) was calculated depending on the amount of the energizer added in the charge using equation 3.

The effects of δH (as a function of the amount of the added energizer) on the metallic yield and chromium recovery are represented in figure1. Both the metallic yield and chromium recovery increase by increasingthe amount of δH to a maximum value equals 3205.3 kJ/kg. Further increase in δH is accompanied by a general decrease in both metallic yield and chromium recovery. The different values of optimum δH obtained in this investigation comparing with that of published data [4] may be attributed to the different chemical compositions of the used charge.
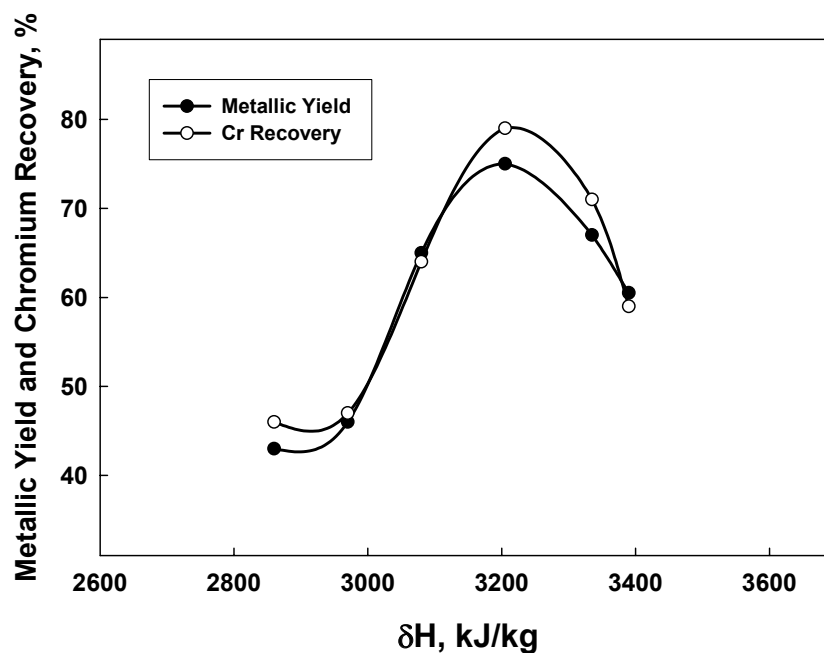
Figure 1: Effect of δH (as a function of the amount of energizer) on the metallic yield and chromium recovery

The increase of the metallic yield and chromium recovery with the increase of the amount of energizer and consequently the amount of heat of the process could be attributed to the increase of molten bath temperature. This increase of the temperature leads to the formation of more fluid slag which in turn enhances the settling process of the formed alloy droplets. The gradual decreasing of both metallic yield and chromium recovery when increasing the amount of energizer more than a certain value in the melts is suggested to be due to the resultant of the following:

- The decrease of the amount of the remained aluminum for the reduction process due to the greater consumption of aluminum by the reduction of energizer.
- Increasing the amount of heat losses due to increase of the amount of N_2 gas evolution from the energizer reduction by aluminum.

$$6NaNO_3 + 10Al = 3Na_2O + 5Al_2O_3 + 3N_2 + \Delta H \qquad (4)$$

- The resulting Na_2O will form a complete range of solid solution with SiO_2 present in the slag [7] which in turn decreases the free SiO_2 in the charge and hence decreases the silicon recovery in the alloy. This effect of Na_2O on the silicon recovery is confirmed in figure 2, which illustrates the decrease of silicon recovery with increasing the δH value, i.e. increasing Na_2O in the slag. The overall result will be a decrease in the metallic yield and chromium recovery by increasing the value of δH beyond the optimum value.
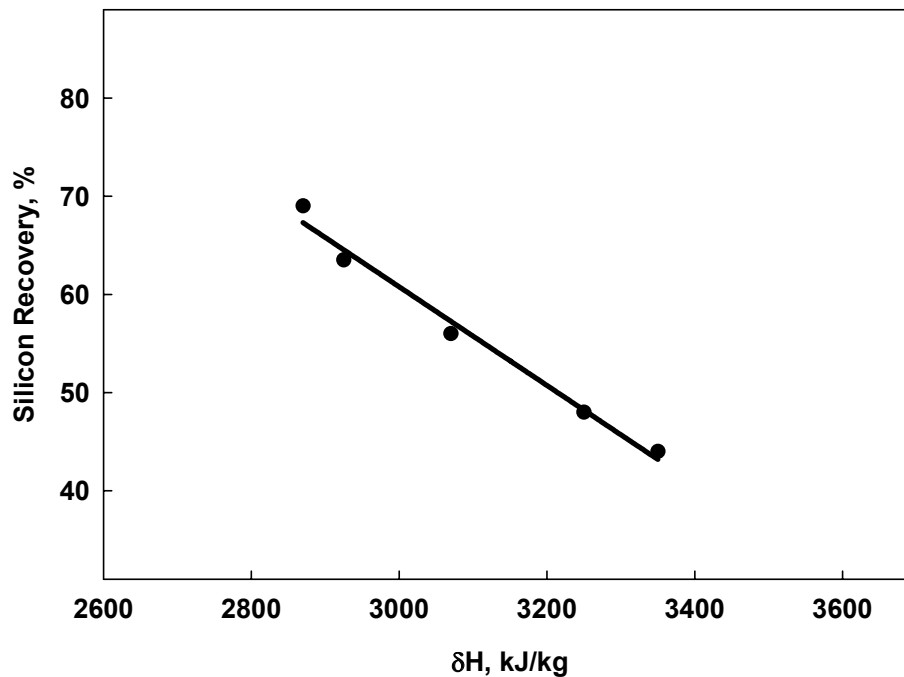
Figure 2: Effect of δH (as a function of the amount of energizer) on the silicon recovery

3.2 Effect of Amount of Reductant

The effect of aluminum amount on the metallic yield and chromium recovery is studied at constant δH (3205.3 kJ/kg of the ore). Based on the material and heat balance calculations, the amount of calculated aluminum necessary to get the highest metallic yield and chromium recovery was found to be 32.8 kg

The effect of aluminum amount on the metallic yield and chromium recovery is represented in figure 3. In this figure, the ratio of the added amount of aluminum to the calculated one is plotted against the metallic yield and chromium recovery.

Steady increase in metallic yield and chromium recovery, is accompanied the increase of the aluminum amount in the charge until a certain amount of aluminum ($\approx$ 1.16 ratio) after which the increase is unremarkable in metallic yield and negligible in the chromium recovery.

Increase of the amount of aluminum needed for the ore more than the stoichiometric value to obtain the highest metallic yield and chromium recovery may be due to the higher contents of refractory oxides such as MgO and SiO_2 which need more energizer and aluminum. Furthermore, the amount of heat liberated during the aluminothermic process of the ore is high, which can lead in turn to the volatilization of greater amount of aluminum as well as the possibility of reducing the relatively hardly reduceable oxides, such as SiO_2, to a certain extent.

As the aluminum content beyond the optimum ratio is consumed in reduction of relatively hardly reduceable oxides such as SiO_2 which is clearly indicated in Table 2. So, it is not surprising that the metallic yield slightly increases and the chromium recovery remains constant.

In previous study [8], an optimum reductant content, near to the stoichiometric value necessary for the reduction, was found to give the maximum metal recovery in the metallothermic process. Additions of more reductant resulted in a decrease of the recovery of obtained metal which was attributed to the decrease of the density of the alloy with the result of worse conditions of separation of metallic and slag phases and loss of metal particles in the slag. However, in our study, this negative effect of excess aluminum additions was not observed may be due to the settler addition. Settler amounts 2 kg/100 kg of ore, composed of two parts mill scale and one part aluminum powder by weight, was added onto the molten surface of the slag for complete separation of metallic droplets from the slag to the produced alloy.

Table 2:   Effect of aluminium amount on the silicon recovery.

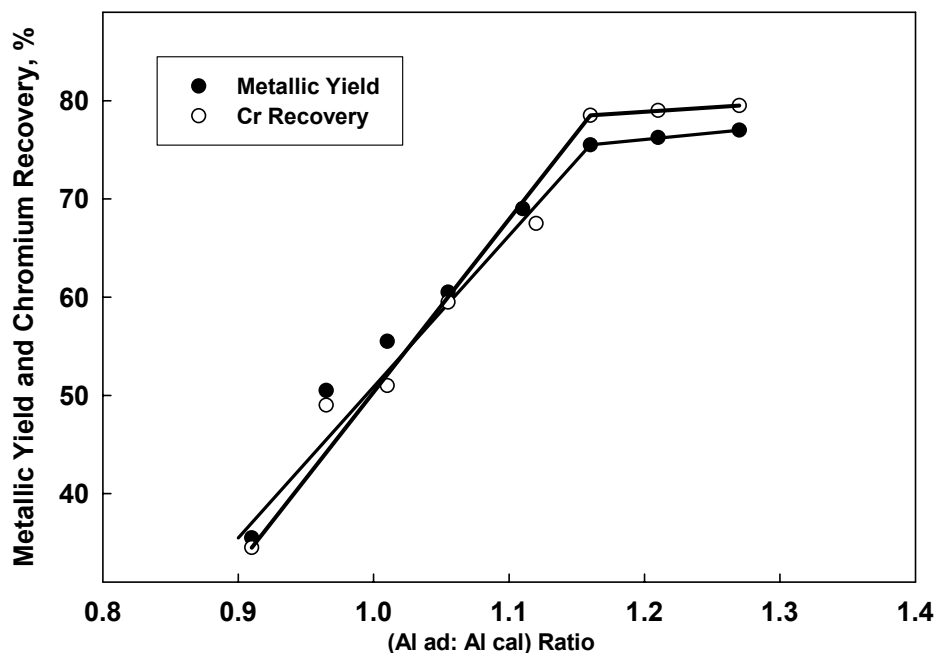| (Al$_{ad}$: Al$_{cal}$) Ratio	Silicon Recovery,%
1.11	56
1.16	68
1.21	77
1.27	83

Figure 3:   Effect of the amount of reductant on the metallic yield and chromium recovery

3.3   Effect of Fluxes

The effect of lime addition on the metallic yield and chromium recovery is represented in figure 4. In these experiments, δH was deliberately maintained at 3205.3 kJ/kg. The metallic yield and chromium recovery decrease by increasing the content of lime in the charge. This detrimental effect of lime is suggested to be due to increase of both viscosity and basicity of slag. The viscosity of the slag increases rapidly as the solubility limit of calcium oxide in high alumina slag is exceeded [9], and consequently the metallic particles separation and settling is opposed, leading to a decrease in both metallic yield and chromium recovery. Furthermore, the slag basicity will also increase as calcium oxide in the slag increases with the result of decreasing the activity of chromium oxide due to the formation of chromites of the basic oxides [10], and consequently decreasing the chromium recovery and metallic yield.

The high tendency of decreasing both metallic yield and chromium recovery with increasing of lime may be explained by the existence of higher percentage of refractory oxides, MgO and Al$_2$O$_3$. These refractory oxides form with CaO a series of high melting temperature compounds and viscous state. The formation of these compounds retards the reduction process, growth of the molten droplets and the separation of new phase. The effect of slag basicity, expressed as (CaO + MgO + Na$_2$O)/ (SiO$_2$ + Cr$_2$O$_3$) weight ratio, on the chromium recovery and metallic yield illustrated in figure 5. As it is clear from this figure, increase of slag basicity up to 1 improves both the chromium recovery and metallic yield. However, further increase of slag basicity results in a decrease of both chromium recovery and metallic yield.

The positive effect of the slag basicity on both chromium recovery and metallic yield may be attributed to the behavior of Cr_2O_3, as amphoteric oxide, reacting as basic oxide in acidic stags with the result of increasing of its activity in the slag as the slag basicity increases up to 1. Further increase in slag basicity leads to decrease of the chromium recovery and metallic yield as Cr_2O_3 behaves, in these basic slags, as acidic oxide and its activity will be decreased with increasing of slag basicity.

Sodium oxide content in the slag seems to play an important role in the smelting process. At a given slag basicity, increase of Na_2O content in the slag to more than 1.5 wt. % enhances significantly both the chromium recovery and metallic yield, as shown in figure 5. This effect of Na_2O may be attributed to the increase of stag fluidity with increasing of Na_2O [11] results in enhancing the metallic separation.
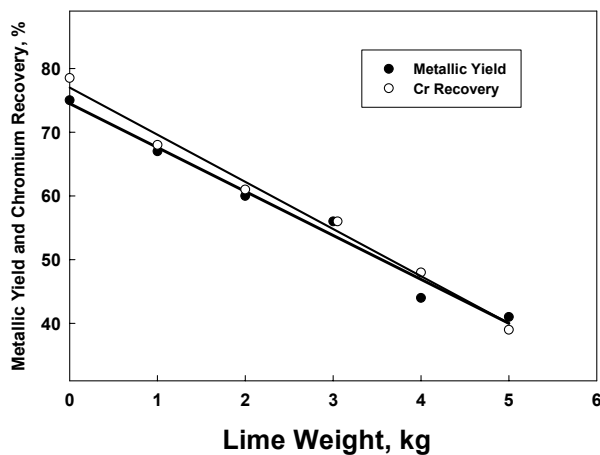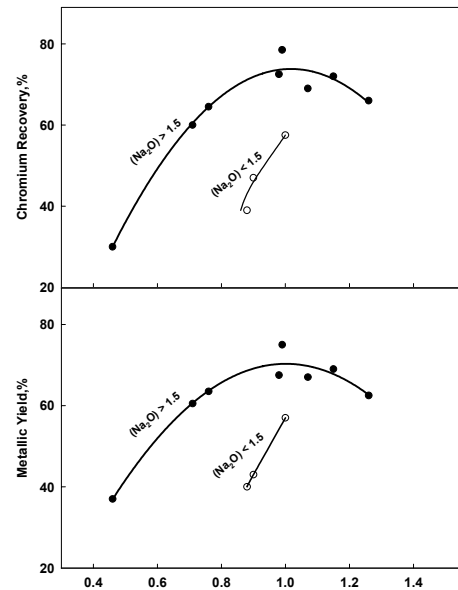

Figure 4: Effect of lime addition per 100 kg ore on the metallic yield and chromium recovery.

$B=(CaO+MgO+Na_2O)/(SiO_2+Cr_2O_3)$, wt. ratio

Figure 5: Effect of slag basicity, expressed as $(CaO + MgO + Na_2O) / (SiO_2 + Cr_2O_3)$ on the chromium recovery and metallic yield of the ore.

3.4 Semi-Industrial Heat

The results were applied on a semi-industrial scale. The data of the semi-industrial heat is given in Table 3. These data clarify the successful suggested aluminothermic process for the production of extra-low carbon ferrochromium (0.02% C) containing 61%Cr from the low grade chromite ore. Chromium recovery of 75% and metallic yield of about 74% are attained.

Table 3: A semi-industrial heat of extra-low carbon ferrochromium production using low grade chromite ore.

Charge weight, kg					Product weight, kg		Metallic yield %	Chromium recovery%	Metal chemical analysis, wt.%			
Ore	Aluminum	Energizer	Mill scale	Fluorspar	Alloy	Slag			Cr	C	Si	S
50	17	10	0.5	2	16	35	73.6	75.1	61.0	0.02	6.50	0.05

4   CONCLUSIONS

From the results of experimental heats carried out to produce extra-low carbon ferrochromium from a low grade chromite ore, using the aluminothermic process, it can be concluded that:

- An amount of energizer should be added to the charge for the heat of the process (δH) to reach an optimum value equals 3205.3 kJ/kg.
- The optimum aluminum amount to be added is 116% of the stoichiometric value.
- Lime addition has a detrimental effect on the chromium recovery and metallic yield.
- Neutral slags with (CaO + MgO + Na_2O)/ (SiO_2 + Cr_2O_3) weight ratio equals 1 is found to be the optimum slag condition for the maximum chromium recovery and metallic yield.
- Sodium oxide seems to play an important role in the smelting process. At a given slag basicity, increase of Na_2O) content in the slag to more than l.5 wt. % enhances scientifically both chromium recovery and metallic yield. This effect may be attributed to the increase of slag fluidity with increasing of Na_2O with the result of enhancing the metallic separation.
- With the optimum reductant addition, heat supply, and flux additions, chromium recovery of 79% and metallic yield of 76% can be attained.
- The results were successfully applied on a semi-industrial scale for the production of extra-low carbon ferrochromium (0.02% C) containing 61 % chromium using the low grade chromite ore without using any further concentration process.

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