REDUCTANT CHARACTERIZATION AND SELECTION FOR FERROCHROMIUM PRODUCTION

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ABSTRACT

A variety of carbonaceous reductant materials are being used in the production of ferrochromium such as coke, char and coal. Matching the correct carbon reductant for each specific process and product requirements has become a vital function in the ferrochromium industry. This selection process however has become increasingly difficult. In many cases the substitution of a reductant with a new one, despite being similar in all relevant chemical specification characteristics to previous material has resulted in different performances relative to that expected.

This experimental investigation has been performed to determine a reliable model for characterizing the reductants according to their reactivity performance and to use the model parameters to be able to choose the appropriate reductant. Sintered chromite or was reduced with the reductant under investigation in a thermo-gravimetric analyzer (TGA) at different temperatures. The experimental data was then fitted into the Arrhenius model to obtain the indication of the reactivity of the reductant through the calculated activation energies. The results were also confirmed at actual operational plant level tests. The TGA tests suggested that the Vietnamese anthracite had the highest reactivity with the lowest activation energy.

A generalized rate model was also used to describe the reduction of chromite which has shown that at a given particle size the rate of reduction was controlled mainly by interfacial area chemical reaction up to a reduction level of 40%, after which the rate control was dominated by diffusion.

1 INTRODUCTION

Various smelters in South Africa produce high carbon ferrochrome by smelting chromite or with fluxes such as limestone and serpentine and with reductants such as char, coal and coke together with silica in a submerged arc furnace. The electric arc and the electrical resistance of the charge generate the heat required for smelting. The heat is most intense at the electrode tips and this is where most of the smelting reactions occur. The smelting reactions involve the reduction of metal oxides to the metallic state with the formation of a slag. Coal and coke are the main source of carbon for reduction reactions. The increasing cost of coke and the fact that metallurgical grade coke (and hence coal) is dwindling have lead ferroalloy producers to search for alternative sources of carbon. Such alternatives include char, bituminous coal and anthracite. This has also lead to some changes as to the suppliers of such alternatives which now include China, Argentina and Vietnam for the South African operations.

Most of the previous investigation concentrated mainly on alternative cokes and hence their performance. This investigation, however, was initiated with the aim of substituting coke with anthracite which is cheaper than coke. Although the alternative anthracite might be of similar chemical analysis when compared to, for example, China nuts coke, other physical properties (reactivity, resistivity, strength) considered to be important parameters with regard to desirable burden characteristics will differ considerably.

One of the most important properties of a reducing agent used in submerged arc furnace is electrical resistivity of the material. This property depends on the type of material, processing conditions, material sizing, operating temperatures and pressures within the furnace mix. High burden resistivity is necessary for good overall heat distribution. It depends on resistivity of the reducing agent, a stable coke bed at the tip of the electrodes, volume fraction of the reductants, carbon content and particle size.

Reactivity of reductants towards reduction of oxides plays an important role in many metal smelting processes. In general, reactivity decreases with the increase in the degree of graphitization. In addition, the presence of carbon atoms in the amorphous phase or in aliphatic side chains also leads to an increase in reactivity. The combustion/gasification rate for different reduction materials can therefore be significantly different. As combustion proceeds, reactivity decreases due to loss of volatile matter, enhanced thermal annealing and decreased concentration of active site [1]. In addition to structural order, physical characteristics such as pore size distribution and surface area, composition and concentration of ash impurities present in the carbonaceous material also play an important role. With respect to determination of the reactivity of carbonaceous material, a common method is the exposure of packed bed of reductant containing 200g of 20mm diameter particles to flowing CO_2 at 1100°C for two hours. The percentage mass loss (by the Boudouard reaction) is quoted as the coke reactivity index (CRI). While it is feasible to predict and measure CRI values, it is not obvious what values of these indices are desirable for reductants used in ferroalloy production. Given the apparent importance of CO generation, it appears that a high reactivity would be required. On the other hand, the primary electrical contact between the electrode and charge is through a coke bed directly beneath the electrode tips [2] which would favor the use of a less reactive reductant. Such counteracting requirements partially explain the general use of a mixture of reductants in ferroalloy production. Moreover, the CRI measurements completely ignore the behavior and hence reducibility of the ore in use.

In this investigation an alternative testing of reactivity was utilized. This method involves reducing the sintered chromite ore with a chosen reductant in a thermogravimetric analyzer (TGA) at different temperatures. In this method reactivity was redefined as the inherent capacity of the reductant to induce the reduction reactions of the ore or the resistance to the reduction process. In this regard the simple Arrhenius Model was utilized:

$$R_T = R_{To} \exp\left[-\frac{\Delta E}{R} \left(\frac{1}{T} - \frac{1}{To} \right) \right] \qquad (1)$$

Where R_T and R_{To} are the rates (in units/sec) at temperatures T and To respectively. ΔE (J/mol) is the activation energy of the reaction which in this case will be the measure of the capacity of the reductant to induce the reduction reactions. R(J/mol.K) is the gas constant.

Previous investigations done by Eric [3] on the solid state reduction of chromite ore has suggested that the reaction mechanism involves both the chemical reactions and the diffusion of ionic species. This has lead to the development of a generized mixed rate control model with the following important relationships

$$k = \frac{\rho Fp Vp}{Tb Ap}, \quad \text{chemical reaction rate constant} \qquad (2)$$

$$De = \frac{kVp}{2\sigma_S^2 Ap}, \quad \text{effective diffusion coefficient} \qquad (3)$$

$$\mathrm{T} = \frac{t}{t*} \qquad (4)$$

where; ρ is the density (kgm^{-3}), Fp is the shape factor (3 for spherical particles), Vp is the volume (m^3) = $\frac{4}{3}\prod r^3$ (r : particle radius), T is temperature, Ap is the cross sectional area (m^2) = $4\prod r^2$, b is the stoichiometric factor ($\frac{1}{4}$ for the reduction of $FeCr_2O_4$ spinel), t is time and t* is the total time for a chemical reaction controlled process, σ_S^2 is the ratio of dimensionless time for a chemical reaction controlled process to dimensionless time for diffusion controlled process. The fraction of the reduction of the ore (Xi) was calculated using the following:

$$Xi = \frac{mass\ of\ CO\ evolved}{\frac{28}{16}\ x\ mass\ of\ original\ removable\ oxygen} \qquad (5)$$

The chemical reaction rate constant; k (in s^{-1}) and the effective diffusions coefficient; D_e (in m^2s^{-1}) obtained at different temperatures are then fitted into the Arrhenius equation (1). The reactivity of the reductant will then be obtained from the fit of the data to the Arrhenius equation yielding the activation energy. The results would then be confirmed at actual operational plant lever tests.

2 EXPERIMENTAL PROCEDURE

Thermogravimetric analysis (TGA) was carried out with a Simultaneous Thermal Analyzer STA 409 PC Luxx. The reaction mixture consisted of sintered chromite ore, chemical analysis of which is given in Table 1, and the reductant under investigation. These were China nuts coke (88.85% fixed carbon, 9.73% ash, 1.42% volatiles), Argentina coke (88.16% fixed carbon, 10.48% ash, 1.36% volatiles), Vietnamese anthracite (92.86% fixed carbon, 4.03% ash, 3.11% volatiles) and Springlake anthracite (80.10% fixed carbon, 10.83% ash and 9.07% volatiles).

Table 1: Chemical analysis of the sintered chromite ore

Species	Cr	Fe Total	Fe^{2+}	SiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Zn
%	30.2	19.2	2.2	3.1	12.9	11.0	0.39	0.10	0.12	0.12

Both the ore and the reductant were ground and sized to -53+75 microns. The reaction mixture was heated in an alumina sample holder of the TGA from room temperature to selected reaction temperature at a rate of 10°C per minute, and then held for 120 minutes. The selected temperatures were 1190°, 1240°, 1290°, 1340° and 1390°C. The TGA furnace was flushed continuously with high purity nitrogen gas at a flow rate of 700 Nml.min^{-1}. The mass loss caused by the loss of volatile matter from the reductant and the evolution of CO gas by the reduction was measured continuously by the TGA apparatus. According to literature [4] the reduction of chromite ore starts around 900°C. Using 900°C as the reference for the purposes of this investigation, the mass loss due to the volatiles is calculated from the observed mass loss measured from room temperature till 900°C which correlated very well with the analysis of the reductants. The mass loss due to CO evolution is calculated from the observed mass loss from 900°C till the end of specified reaction time (after 120 minutes at the selected temperature). The percentage reduction at a given time and selected temperature was then calculated by equation(5). It must be mentioned here that the total removable oxygen in the sintered chromite ore due to its chemical analysis and stoichiometry is 21.874mg/100mg of ore. In all the experiments 20% excess carbon over that required for the removable oxygen is used. The use of 900°C as the reference requires a correction to be made to the calculation of fraction reduction (Xi) by equation (5) to take into account the reduction that occurs from 900°C to the selected temperature. Correlation of the fraction reduction with temperature has been found to be in the following form [5]:

$$X_{corr} = a(T\text{-}900) + b(T\text{-}900)^2 + c(T\text{-}900)^3 \qquad (6)$$

when T is temperature in °C. The data obtained by means of the TGA as a function of temperature for each reductant was fitted into equation (6) using an appropriate curve fitting procedure with very highR^2 values.

3 RESULTS

Through the use of equation (6) all the data were analyzed to yield the coefficients summarized in Table 2 and Xcorr values illustrated in Table 3. A typical plot for Argentina coke is shown in Figure 1.

Table 2: Derived coefficients of equation (6) from TGA data for each reductant.

Reductant	a	b	c	R^2
Argentine coke	3.581×10^{-4}	1.849×10^{-6}	3.881×10^{-9}	0.968
Springlake anthracite	4.065×10^{-4}	2.291×10^{-6}	4.587×10^{-9}	0.989
China nuts coke	2.723×10^{-4}	1.439×10^{-6}	3.372×10^{-9}	0.971
Vietnamese anthracite	3.683×10^{-4}	1.661×10^{-6}	3.026×10^{-9}	0.989

Table 3: Values of Xcorr at different temperatures for each reductant.

Temperature(°C)	Xcorr			
	Argentine coke	Springlake anthracite	China nuts coke	Vietnamese anthracite
1190	0.042953	0.037093	0.040196	0.040909
1240	0.060482	0.053674	0.058774	0.052128
1290	0.088555	0.082196	0.087354	0.070473
1340	0.130083	0.126101	0.128462	0.098213
1390	0.187978	0.188829	0.184628	0.137616

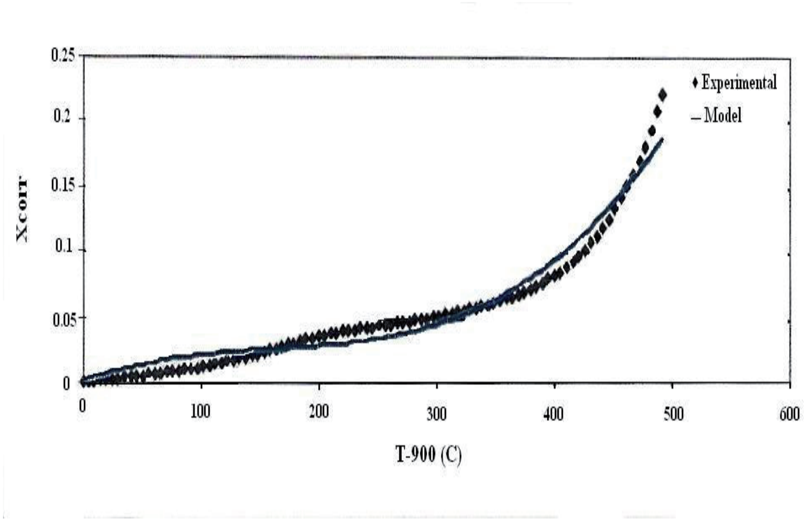

Figure 1: Reduction of Chromite ore using Argentine coke

Thereafter T and б_S^2 values were calculated at each temperature for each reductant. For example for Springlake anthracite used to reduce chromite at 1190°C, X_{corr} is 0.037093 (from Table 3), and hence:

$$X_i \text{ (at 1190°C)} = X_i \text{ (from 900°C)}, - 0.037093 \qquad (7)$$

Where X_i values are less than zero.

The data from TGA at 1190°C for this particular case is fitted into the following mixed rate control equation (8) that yields the plot in Figure 2 using the sum of least squares:

$$t_i = \mathrm{T}G(X_i) + \mathrm{T}\ \text{б}_S^2\ P(X_i) \qquad (8)$$

Where

$$G(X_i) = 1 - (1 - X_i)^{1/3}\text{, chemical rate control contribution,} \qquad (9)$$

$$P(X_i) = 1 - 3(1 - X_i)^{2/3} + 2(1 - X_i)\text{, diffusion rate control contribution} \qquad (10)$$

The fit yields $\mathrm{T} = 5238$, $\text{б}_S^2 = 4.694922$ at 1190°C.

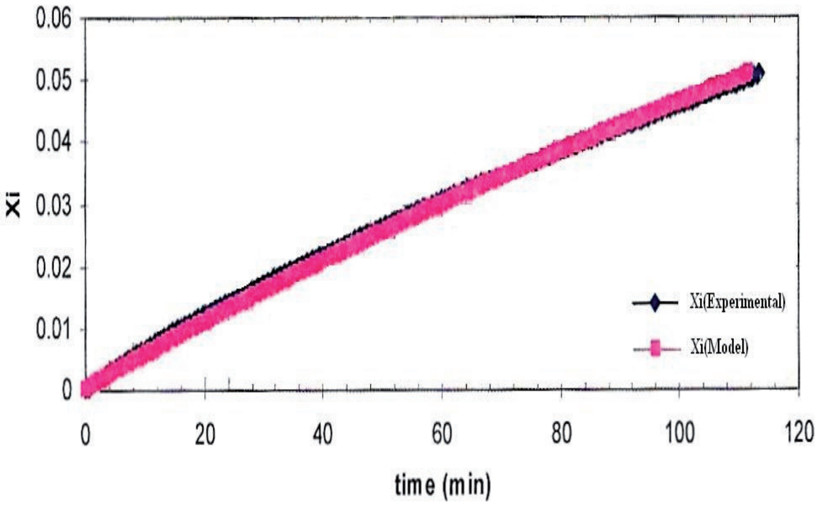

Figure 2: Reduction of Chromite with Springlake anthracite at 1190°C

Once all the T and 6_S^2 values for each reductant at each reduction temperature are calculated from equation (2) and equation (3) the values of the chemical reaction rate constant: k and the effective diffusion coefficient; De are obtained at different temperatures for all the reductants. Then for each reductant the k and De values were fitted into the Arrhenius equation (1) to yield the activation energies for chemical reaction rate and for diffusion.

Figure 3 illustrates the plot for chemical reaction rate constant as a function of temperature for the reduction of chromite with Vietnamese anthracite and Figure 4 shows the plot for diffusion coefficient as a function of temperature for the reduction of chromite with China nuts coke.

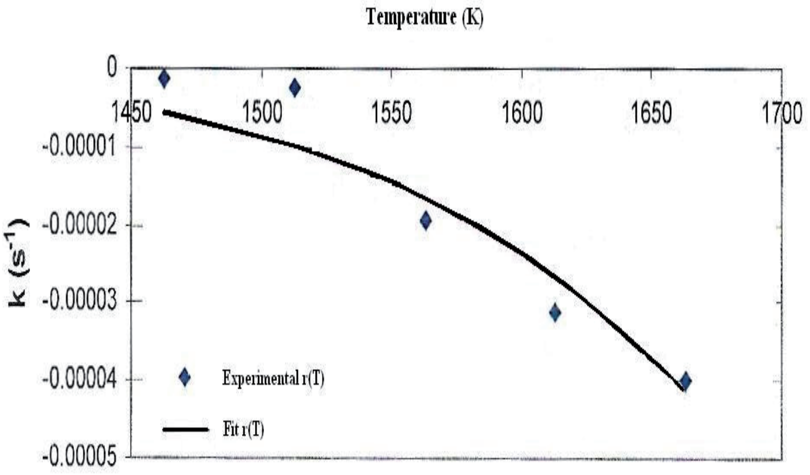

Figure 3: Variation of the chemical reaction rate constant with temperature for the reduction of chromite with Vietnamese anthracite.

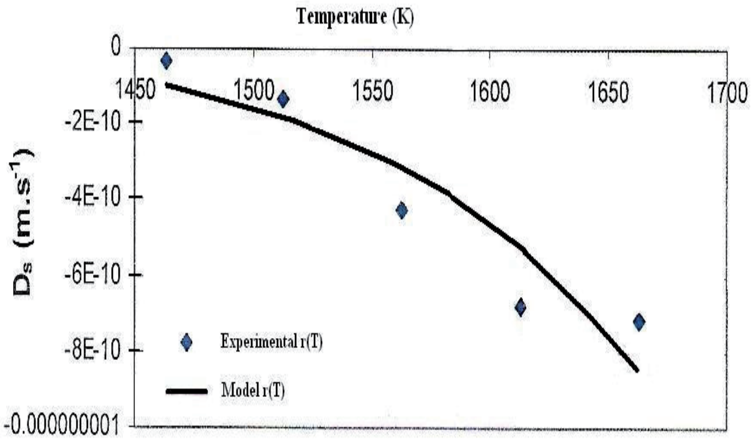

Figure 4: Variation of the effective diffusion coefficient with temperature for the reduction of chromite with China nuts coke.

The activation energies obtained from the experimental TGA data were used to determine the relative reactivity of the reductants. The values of the chemical reaction rate constant and effective diffusion coefficient were used to determine the relative speed at which the reductants can reduce chromite ore. The summary of results of the TGA tests is presented in Table 4.

Table 4: Summary of TGA test results

Reductant	Chemical reaction		Diffusion	
	Δ E(J/mol)	K(s^{-1})	Δ E(J/mol)	De(m^2s^{-1})
Vietnamese anthracite	197024	5.921×10^{-6}	200057	2.846×10^{-10}
China nuts coke	212436	5.129×10^{-6}	213134	1.024×10^{-10}
Springlake anthracite	217508	6.976×10^{-6}	260253	6.021×10^{-11}
Argentine coke	201813	6.010×10^{-6}	305809	9.963×10^{-11}

The results suggest that the Vietnamese anthracite has the highest reactivity since its activation energies are the lowest. The reduction of $FeCr_2O_4$ by activated carbon in argon atmosphere was studied [6] where the activation energy was found as 197kJ/mol which is in excellent agreement to the activation energy obtained in this work.

The results also suggest that the likely rate controlling mechanism is diffusion of species to the reaction site since the effective diffusion constants are much smaller than reaction rate constants. Previously [3] it was determined through a sophisticated generalized mixed rate model that the reduction of chromite was controlled by interfacial area chemical reaction up to a reduction level of 40% at a given particle size and thereafter dominated by diffusion strongly supporting the results of the investigation. The tests also suggest that the Vietnamese anthracite is the fastest to react since its De value is high. The differences in the activation energy values and hence rate constants and diffusion coefficients between the various cokes and anthracites studied here are likely due to the differences in the porosities, specific surface areas and maceral structures of these carbonaceous materials and constitute the subject of another study being undertaken.

4 CONCLUSION

Further tests were also conducted in the smelting furnace to determine if the performance of the reductants were in accordance with the laboratory TGA tests. In these plant scale tests 10 to 30% (in terms of fixed carbon) of China nuts being used in the furnace was substituted with the reductant under study. The sizing of the material was kept at -40+10mm. Overall the results of the tests done in the smelter furnace were in good agreement with those obtained by TGA tests. Hence it can be concluded that the TGA test can be used to determine the reactivity of the reductant with a high degree of confidence. The values of chemical reaction rate constants and effective diffusion coefficients can also be used in a rather qualitative manner in deciding the material size to be used to maintain a stable coke bed. Follow up tests on resistivity of the reductant will have to be performed to establish a better performance profile of the reductants. Overall the investigation showed that anthracite has a significant potential to substitute coke.

5 REFERENCES

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