PYROMETALLURGICAL RECOVERY OF CHROMIUM FROM SLAGS

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ABSTRACT

The dissolution and reduction of chromite particles entrapped in high carbon ferrochrome slags were investigated. Statistically designed experiments were conducted in an inductively heated reaction furnace at 1600°C. The effects of slag basicity and Al_2O_3 */MgO ratio were determined. The dissolution-reduction rate changes with change in slag basicity. A high degree of slag boiling was observed at low basicity. The optimum basicity for recovery was in the range of B= 0.6 to 0.8. The effect of* Al_2O_3 */MgO ratio changed with slag basicity. The input masses of* Al_2O_3 *and MgO at a fixed ratio altered the extent of recovery.*

INTRODUCTION

In South Africa the yield of chromium in ferrochrome production is limited to 80 – 92% depending on the type of operation. Commercially AC Sub-Arc operations produce slag containing 11 – 17% Cr_2O_3 in acid slag operations and 8 – 10% in basic slag operations. Due to higher volumes of slag produced in basic operations the given figures do not necessarily indicate lower losses in basic slag operations. The recovery of chromite or chromium oxide would be beneficial not only in saving a large amount of chrome, but also avoiding possible pollution by chromium containing slags. Currently, entrapped metal in the skimmed slag of metal ladles and in the overflow slag pot at the taphole is being recovered by jigging and/or other mineral processing methods. However, pyrometallurgical recovery of chromium from the bulk slag has not been attempted due to costs involved.

Investigations on slags obtained from plants showed that more than 60% of the chromium in the slag was in the form of undissolved or partially reduced chromite particles [1, 3]. Experimental studies showed that slags having higher MgO and Al_2O_3 contents had lower capacity of dissolving chromite [2]. Increase in slag basicity from B=0.3 to 0.8 was reported to increase the dissolution-reduction percentages of chromite [5]. In a study on the kinetics of reduction of chromium oxide from industrial ferrochrome slags to carbon saturated iron, it was found that 90 – 99% of chromium could be recovered in a reasonable time [6]. The mass transfer of chromium from the slag to the metal/slag interface was said to be the rate controlling process. In another study chemical dissolution of chromite in the slag was found to be the rate limiting factor [7].

EXPERIMENTAL PROCEDURE

The tests were conducted in a stable 50 kW, 3kHz induction unit. In all experiments the slag was contained in an A5, 34 cm *ID* graphite crucible. Type B(Pt-6% / Pt-30%Rh) thermocouple was used for temperature measurements. The slag was heated, melted and cooled under a protective argon atmosphere that was purged through a deoxidisation furnace, silica gel and magnesium perchlorate. The furnace chamber consists of a fused silica tube 500 mm long, with external diameter of 140 mm and internal diameter of 130 mm. The lower end of the tube is closed. The top end is closed by a water-cooled brass plate, with an O-ring between the silica tube and the brass plate to ensure gas tightness. A dense graphite crucible is used as the heating element. The space between the heating element and silica tube, as well as the bottom part of the silica tube is packed with lampblack for insulation. The experimental set-up is shown in Figure 1.

The charge was prepared by mixing 16 % LG6 chromite(-1.00+0.5 mm), and the slag constituents in pure powder form in percentages as listed in Table 1, weighing 200 g in total. The graphite crucible containing the charge was placed into the reaction chamber. The induction unit was switched on and brought to approximately 1200°C and kept at this temperature for 2 hours. This was done to sinter the fine particles. Consequently, the power input of the induction unit was increased sharply to achieve the experimental temperature of 1600°C in a short period that would be taken as the starting time of the experimental run. The graphite crucible was contained in the reaction chamber for the time intervals listed in Table 1. No samples were taken during the experimental period for the reason of inconsistent results due to mass decrease during sampling and air penetration into the reaction chamber. At the end of the experimental period the induction unit was switched off and the molten mixture was brought to room temperature by slow cooling. To minimise the experimental runs for optimal results a four variable three level Box-Behnken design with 27 valid experiments was used as given in Table 1 [8]. The experimental results were fitted into a quadratic response surface model.

The reacted slag samples of slag were separated from metallic globules and particles and subjected to wet chemical analysis for the constituents of Cr_2O_3, Fe(total), FeO, SiO_2, CaO, MgO and Al_2O_3 at the MINTEK laboratory.

Table 1: Initial composition and time of experimental runs

No.	% Al_2O_3	% MgO	% SiO_2	% CaO	Time (min)
1	25	15	30	30	110
2	5	5	50	40	110
3	25	5	30	40	110
4	5	15	50	30	110
5	25	10	20	45	110
6	5	10	65	20	110
7	25	10	45	20	110
8	5	10	40	45	110
9	25	10	30	35	200
10	25	10	30	35	20
11	5	10	50	35	200
12	5	10	50	35	20
13	15	15	30	40	110
14	15	15	55	15	110
15	15	5	30	50	110
16	15	5	55	25	110
17	15	15	40	30	200
18	15	15	40	30	20
19	15	5	40	40	200
20	15	5	40	40	20
21	15	10	30	45	200
22	15	10	30	45	20
23	15	10	55	20	200
24	15	10	55	20	20
25	15	10	40	35	110
26	15	10	40	35	110
27	15	10	40	35	110

EXPERIMENTAL RESULTS AND DISCUSSION

The analytical results were inserted as mentioned earlier into a quadratic response surface model which yielded a regression coefficient of R = 0.935. The obtained equation is as follows:

$$\%\ Cr\ recovery = 7.260109 - A*0.576988 + M*4.343974 + B*91.884157 + T*0.510475 + A^2*0.044609 - A*M*0.02382 - M^2*0.185625 - A*B*0.36958 - B*M*1.847521 - B^2*49.521827 - A*T*0.001824 + M*T*0.008011 + B*T*0.086607 - T^2*0.002036 \tag{1}$$

where,

A: Al_2O_3 content of slag in wt % (range 5 to 25%)
M: MgO content of slag in wt% (range 5 to15%)

B: Basicity of slag calculated according $B = \dfrac{\%CaO + \%MgO}{\%SiO_2 + \%Al_2O_3}$ (range 0.4 – 1.2)

T: Time in minutes(range 20 to 200 min).

Although the dissolution + reduction process involves two steps, it is difficult to determine the degree of dissolution in the presence of carbon, as the dissolution and reduction process seem to proceed at the same time. If indeed the dissolution rate of chromite in the slag is the rate determining factor, the reduction rates obtained from experiments should be close to the rate of dissolution [7]. In this work, the presented results are total dissolution-reduction rates as a result of decrease of chromium oxide from the slag.

In almost all experiments as listed in Table 1, chromium recoveries up to and above 90% was obtained within 160 minutes of reaction time. Figures 1 to 3 show recoveries as a function of the Al_2O_3, MgO percentages and slag basicity. The recoveries were calculated according:

$$\%\text{Recovery} = \frac{\%Cr_t}{\%Cr_o} \text{x}100 \tag{2}$$

where, $\%Cr_t$ is the time dependent Cr content of slag and $\%Cr_o$ initial Cr content of slag. It is seen that recoveries at B=0.8 are higher than at B=0.4 and lower at B=1.2 than at B=0.8.

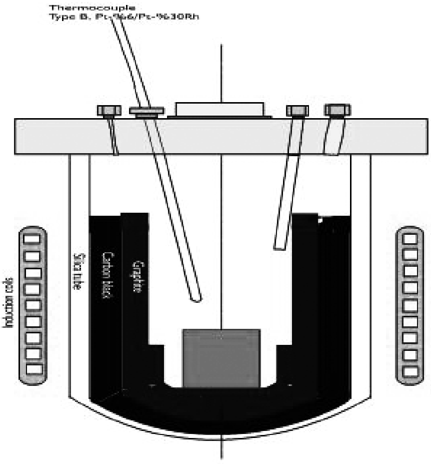

Figure 1: Schematic representation of experimental set-up

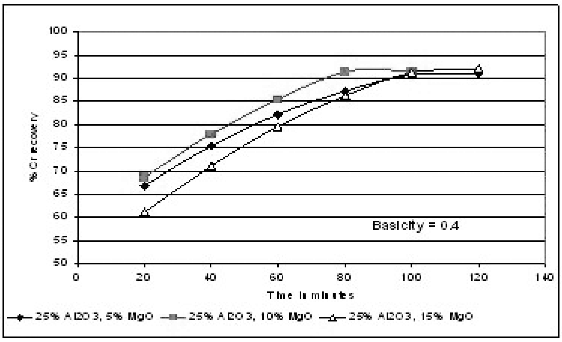

Figure 2: Graph showing the effect of MgO content at 25% Al_2O_3 content and slag basicity of B=0.4 on the chromium recovery percentage at 1600°C

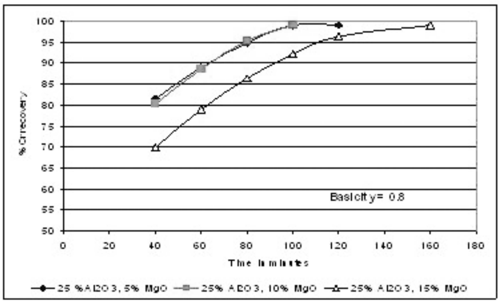

Figure 3: Graph showing the effect of MgO content at 25% Al_2O_3 content and slag basicity of B=0.8 on the chromium recovery percentage at 1600°C

Assuming that the initial reduction rates up to 20 minutes are linear, the recovery rates may be expressed in terms of percent recovery per minute. It must be stated that the given rates will not necessarily represent the industrial operation rates but may however indicate the optimal slag composition for maximum recovery. Figures 4 to 6 show the recovery rates as a function of the Al_2O_3 content and slag basicity at 5, 10 and 15 percent MgO contents. As seen in Figure 4, at 5% MgO contents the highest recovery rate is at B=0.8. The recovery rates at B=0.4 and B=0.8 are very close. At 10% MgO contents the recovery rates at B=0.8 remain same as at 5% MgO containing slags but both rates for B=0.4 and B=1.2 decrease, where the rate at B=1.2 is significantly lower than at B=0.4, as shown in Figure 5. At 15% MgO contents all recovery rates decrease, the rate at B=0.4 equaling to B=0.8 and the rate at B=1.2 being considerably lower, as shown in Figure 6.

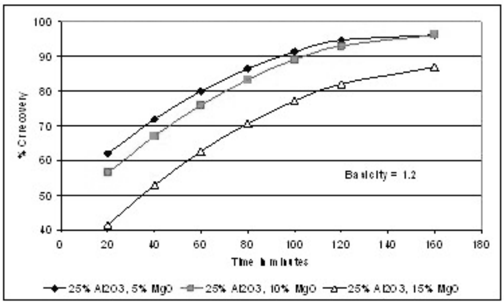

Figure 4: Graph showing the effect of MgO content at 25% Al_2O_3 content and slag basicity of B=1.2 on the chromium recovery percentage at 1600°C

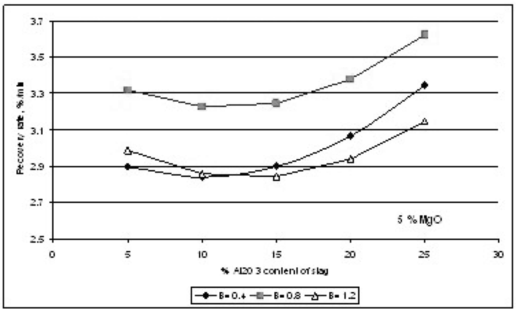

Figure 5: Graph showing the effect of Al_2O_3 content and slag basicity at 5% MgO content on the chromium recovery rate at 1600°C

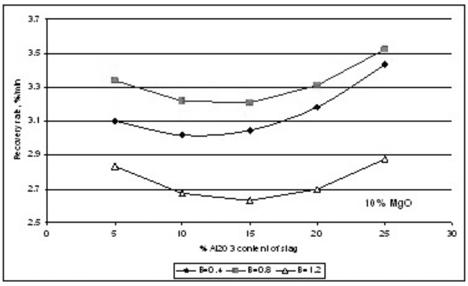

Figure 6: Graph showing the effect of Al_2O_3 content and slag basicity at 10% MgO content on the chromium recovery rate at 1600°C

The highest recovery rates seem to be obtained at high Al_2O_3 and low MgO contents of slag. Figure 7 illustrates a general overview of recovery rates as a function of basicity, MgO content at 25% Al_2O_3 containing slags. In South Africa, industrial ferrochrome slags contain 25 to 32% Al_2O_3 and 15 – 22% MgO due to the nature of the mined chromite and the graph shown in Figure 7 is consistent with the industrial operation practice. Acidic operation practice is at B= 0.45 to 0.8 and an increase in basicity results in production decrease per tap.

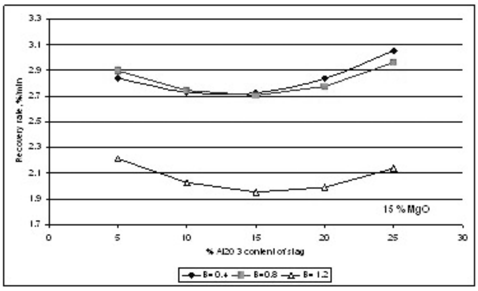

Figure 7: Graph showing the effect of Al_2O_3 content and slag basicity at 15% MgO content on the chromium recovery rate at 1600°C

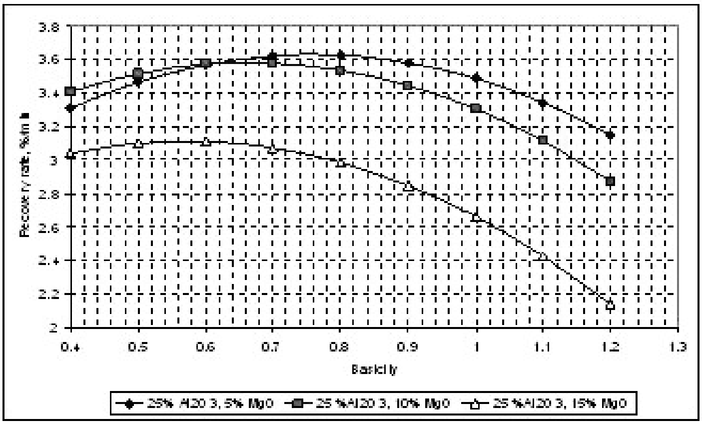

Figure 8: Graph showing the effect of slag basicity and MgO content at 25% Al_2O_3 content on the chromium recovery rate at 1600°C

The nucleation site for CO(g) is limited to the cavities on the graphite walls. Therefore, mass transfer of chromium (divalent or trivalent depending on the slag composition) from the bulk slag to the interface may control the rate of reduction, as suggested by Maeda *et al.* [6]. However, their experiments were conducted for reduction of chromium oxide already dissolved in slag. As per chromite reduction, it seems more likely that chemical dissolution of chromium oxide into the bulk slag is the rate controlling factor as was suggested by Roos [7]. A high degree of slag boiling was observed at experiments conducted at 0.4 basicity. Minor and no boiling occurred for basicities of 0.8 and 1.2 respectively. This is possibly due to increase in slag viscosity with increasing silica content resulting in larger CO(g) bubble growth during its ascend to the slag surface.

CONCLUSIONS

An experimental study was undertaken for the recovery of chromium from ferrochrome slags. The study would also serve for the process optimization of current operations. The obtained results may be summarized as follows:

- Recovery of chromium from slags up to 99% is possible
- The optimal slag basicity for chromium recovery from slag is in the range of B=0.6 to 0.8
- At experimental conditions, highest recovery rates were obtained at 25% Al_2O_3 and 5% MgO containing slags.

The most important factor for the pyrometallurgical recovery of chromium is its economic viability. Initial indications using METSIM (licensed to HATCH Associates LTD. at South Africa) with parameters for typical AC submerged-arc furnace operations shows an electricity consumption of approximately 8000 kWh/t of ferrochrome produced, including 15 percent of heat and electricity losses. In South Africa AC submerged-arc chromite ore smelting consumes in the range of 3000 – 3500 kWh/t_{FeCr} of electricity. Nevertheless, the decrease in the raw material costs may be a substantial advantage.

ACKNOWLEDGEMENTS

The authors acknowledge with thanks the financial support given by the Ferroalloys Producers Association of South Africa and HATCH in Africa for valuable consultation

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