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THE RELATIVE REDUCIBILITIES OF CHROMITE ORES AND RELATIVE REACTIVITY OF CARBONACEOUS REDUCTANTS.

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ABSTRACT

The first part of the study produces a quantified "reducibility rating" for various chromite ores in a way that eliminates the influence of various factors such as temperature and particle size, resulting in a relative reducibility scale in which the rating of haematite (Fe_2O_3) is 100 and that of pure chromic oxide (Cr_2O_3) is O. Fixed quantities of oxide were reduced using spectrographic grade graphite as the solid reductant under controlled conditions in a thermogravimetric analysis (TGA) apparatus. The second phase evaluates the reactivity of various industrial reductants in terms of their ability to reduce a standardised chromite ore sample under controlled conditions, again using TGA.

It is envisaged that the adoption of this technique would permit the rapid characterisation of different ores and reductants and thereby provide a tool to optimise furnace charge blends.

INTRODUCTION

The need to develop a reproducible method of comparing the reducibility of various chromite ores and the reactivity of the various carbonaceous reductants used in the production of ferro-chromium alloys had been expressed at various times over the two decades in which the Pyrometallurgy Research group of the University of the Witwatersrand, in close cooperation with the Ferro-Alloy Producers Association (FAPA), has been involved in researching the behaviour of chromite ores. Although the reduction of chromite has been the topic of extensive research, limited work on comparative reducibilities of various ores has been conducted. The most noteworthy exception is the empirical comparisons by Slatter [1], mainly on Zimbabwean chromites. Most of the studies have utilised electro-graphite as the reductant, and again little work has been done to evaluate the reactivity of the various carbonaceous reductants currently utilised on ferro-chrome smelters.

It was therefore considered appropriate that an investigation be undertaken to attempt to consolidate the wealth of information on chromite reduction behaviour accumulated over more than twenty years of research into a simple, reproducible method of comparing the reducibility of chromite ores from any source, in a way that would be comprehensible to users in a similar fashion to the reducibility indices common for iron ores. A parallel study which aimed at classifying reductants in terms of their reactivity (and corresponding suitability as reductants for chromite ores) was also undertaken.

Thermogravimetric analysis (TGA) was selected as the experimental method to be utilized for the following reasons : i) The technique is well known, with many research institutions and organisations having access to TGA facilities, ii) The technique, once the experimental conditions are prepared, is able to provide a large amount of data quickly, iii) The results are reproducible and sufficiently accurate to permit independent comparison of confirmation of results, iv) In terms of pyrometallurgical research techniques it is relatively cost effective, v) It is suitable for use in routine or repetitive evaluation by technicians, vi) The results can be correlated with chemical analyses and microprobe techniques, if required, vii) The equipment is adaptable with respect to operating temperatures and atmospheres.

For the reactivity comparisons, high purity electro-graphite, -38mm particle size, served as the standard. As "primary standard" for the chromite reducibility comparisons, washed Henry Gold chromite (closely sized between 100 and 250mm) was used. This ore is considered fairly representative of the MG-1 (Middle Group, seam 1) type chromite ores commonly used by South African producers of charge chrome. Ores with as wide a range of analyses as possible were obtained with a view to correlating the chemical analysis with the reducibilty. High purity analytical grade iron oxide (Fe_2O_3) and chromic oxide (Cr_2O_3) were used as the terminal "ores" and arbitrarily assigned reducibility ratings of 100 and 0 respectively. The analyses of the various materials are given in Table I.

TABLE I : Analyses of Materials Used in This Study

A : Ores

Description	Cr_2O_3	FeO	Al_2O_3	MgO	SiO_2	CaO
Henry Gould Chromite	45.8	26.5	15.4	9.2	1.5	0.35
Zimbabwean	55.2	8.7	12.9	15.2	4.6	1.0
WCM Lumpy	37.6	22.8	14.7	11.4	9.4	0.9
WCM Screened	38.7	22.8	15.0	10.7	8.6	0.9
Lefco Concentrate	39.6	25.5	15.9	10.3	5.0	0.6

B : Reductants

Description	Fixed C	Vol.	Al_2O_3	SiO_2	MgO	CaO	S	P
Electrographite	100							
Phoenix Coal	55.3	29.7	4.0	7.4	0.2	0.4	0.5	0.005
Newcastle Coke	79.6	1.4	3.7	10.3	0.6	0.7	0.5	-
Vryheid Coke	78.4	1.1	6.2	10.7	0.4	0.2	0.5	0.01
Eikeboom Coal	58.0	26.3	5.2	9.6	0.1	0.1	0.5	0.01

EXPERIMENTAL PROCEDURE

The experimental apparatus is shown in Figure 1. This apparatus is fully described by Soykan, Eric and King [2] and thus details will not be repeated here. The weighed ore and reductant powders were mixed with acetone in an agate mortar, dried and reweighed before adding to the crucible and compacted until firm. The charged crucibles were kept in a desiccator prior to use. Once the basic technique had been settled it was necessary to select the experimental conditions. In order to provide a neutral atmosphere argon gas was used. The argon flowrate was selected as a compromise between economics and productivity : During purging of the system an argon flowrate of 660 cm^3 per minute was maintained for 30 minutes, (four times the dead volume of the apparatus). During reduction runs the flowrate was reduced to 210 cm^3 per minute to minimise bulk mass-flow effects, particularly with ultrafine particles of reductant in the crucibles, while still providing a purge for gaseous reaction products.

Previous reduction work by Soykan, Eric and King [2,3] on the reduction behaviour of chromites had clearly shown that temperature played the largest role in influencing the degree of reduction obtained on a given ore. Very little reduction occurred at temperatures below 1200°C while at 1500°C most chromites exhibited substantial (close to 100%) reduction, so a temperature somewhere between these extremes was indicated Although 1400°C appeared to give better discrimination, it was realised that this temperature was probably above the maximum. operating temperature for most resistance heated furnaces, and 1300°C was consequently selected in order to extend the potential applicability of the technique to as many laboratory facilities as possible Increased temperature also results in an increase in the amount of metalloid reduction and this was a concern when considering the use of high ash content reductants, where self-reduction could occur at higher temperatures

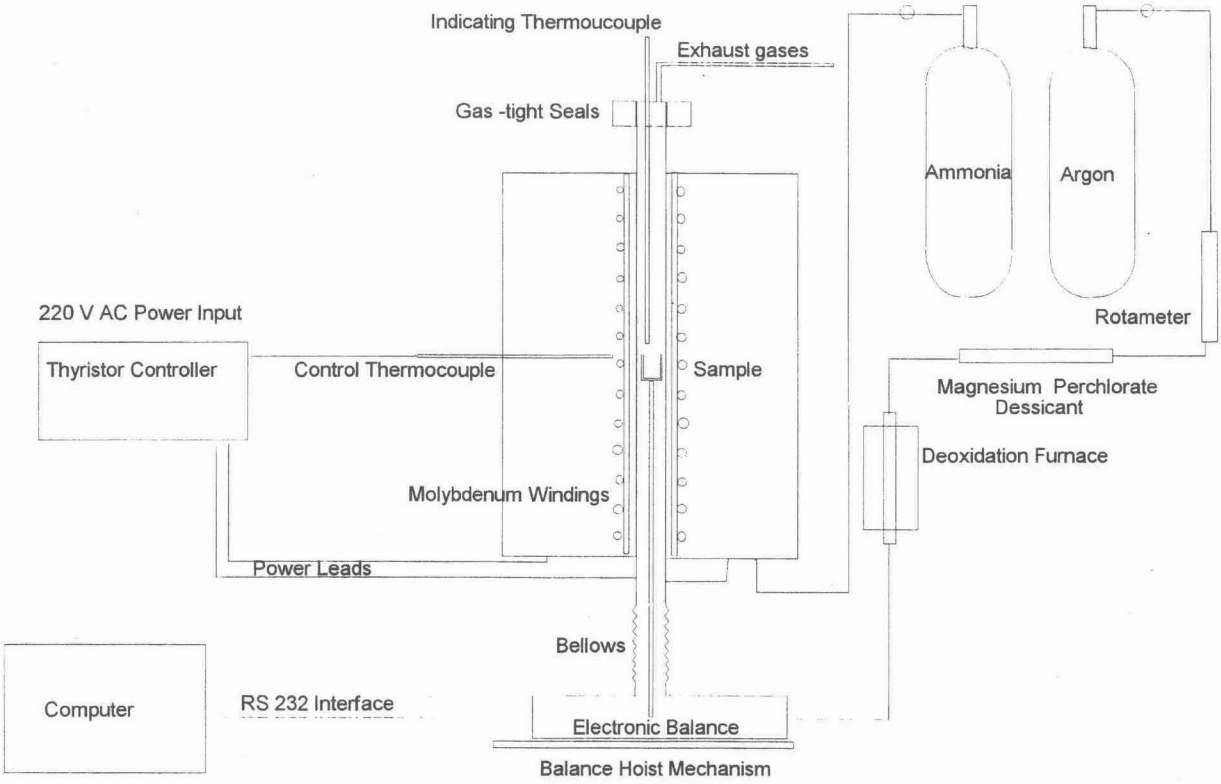

Figure 1: Schematic Experimental Apparatus

Figure 2 shows the effect of temperature on the degree of reduction achieved after 30 minutes on 5 different ore samples in the +90-104mm size range [3]. In this figure, different ores were denoted by their group and seam notations. LG, MG and UG refer to lower group, middle group and upper group respectively. The numbers following the letters indicate the seam. MG-3 for example, refers to Middle Group third seam ore. Upper group ores are the ones nearest to the surface and lower group are the deepest.

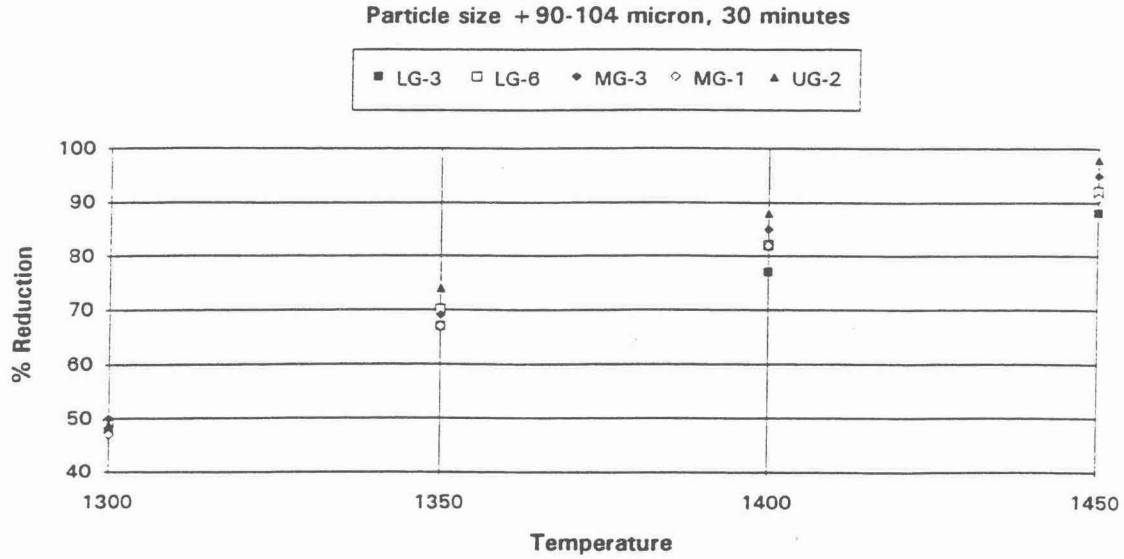

Figure 2: Effect of Temperature

Shorter times produce proportionally lower degrees of reduction as can be seen from Figure 3, which shows the effects of both time and particle size on the LG6 ore reduced at 1416°C [3].

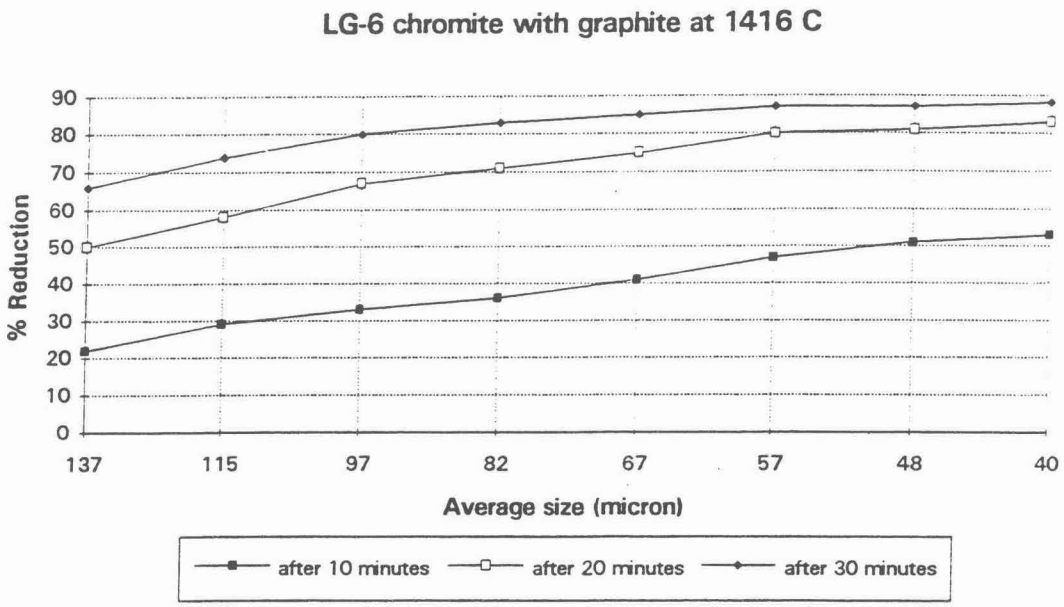

Figure 3: Effect of Particle Size and Time on % Reduction

Figure 4 shows that at a temperature of 1300°C reduction is complete after 40 minutes for the Henry Gould chromite and the iron oxide standard.

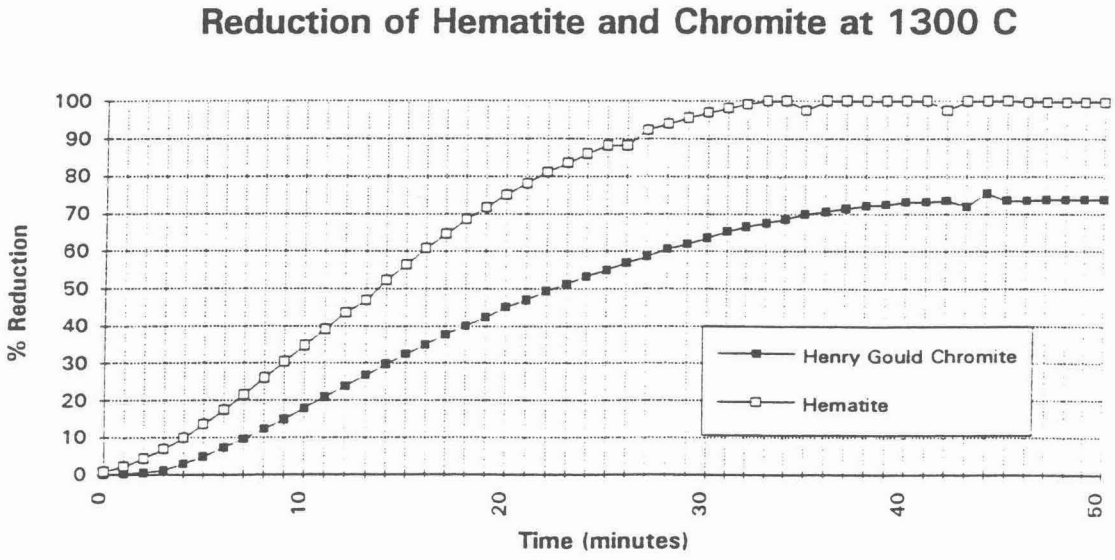

Figure 4: Comparative TGA Curves for Chromite and Hematite

Previous research had also clearly indicated that particle size was the next most important factor after temperature. A particle size of : +90mm-104mm was selected for a number of reasons : i) it is close to the median size of most beneficiated fine chromite ores, ii) the analyses of these size fractions are close to the average for bulk samples, iii) much previous work was conducted on samples of this size, as it was realised that SEM analyses and interpretation were simplified when samples close to 100mm average size were examined.

The diameter of the furnace work tube (45mm internal diameter) dictated the maximum crucible size. 36mm OD by 56 mm high sintered alumina crucibles were used. This in turn restricted the maximum total sample mass that could be used to about 10 grams.

Again in the interests of utilising previous results and to ensure that reduction reaction can go to completion it was decided that the amount of graphite reductant used would be calculated on the basis of 20% excess over stoichiometric carbon. Stoichiometric carbon had previously been defined as sufficient to ensure 100% metallisation of Fe and Cr and formation of Fe_3C and Cr_7C_3 carbides after reduction reactions between carbon and the iron and chromium oxides to produce carbon monoxide (CO) as the reaction product. Percentage reduction had been defined previously [3] as :

$$R = \frac{Mass\ of\ CO\ evolved}{(28/16)\ x\ mass\ of\ original\ removable\ oxygen.} \qquad 1$$

RESULTS AND DISCUSSION

Reproducibility of the Technique

In order to determine the reproducibility of the technique, four samples of Henry Gould chromite were reduced by electrographite under similar operating conditions except that the runs were conducted at different times of the day, and there were very small differences in the samples masses. The TGA reduction curves are shown in figure 5. The analytical results are collected in Table II. The reproducibility is satisfactory and it is within 2.0% for iron metallization and within 2.5% for chromium metallization.

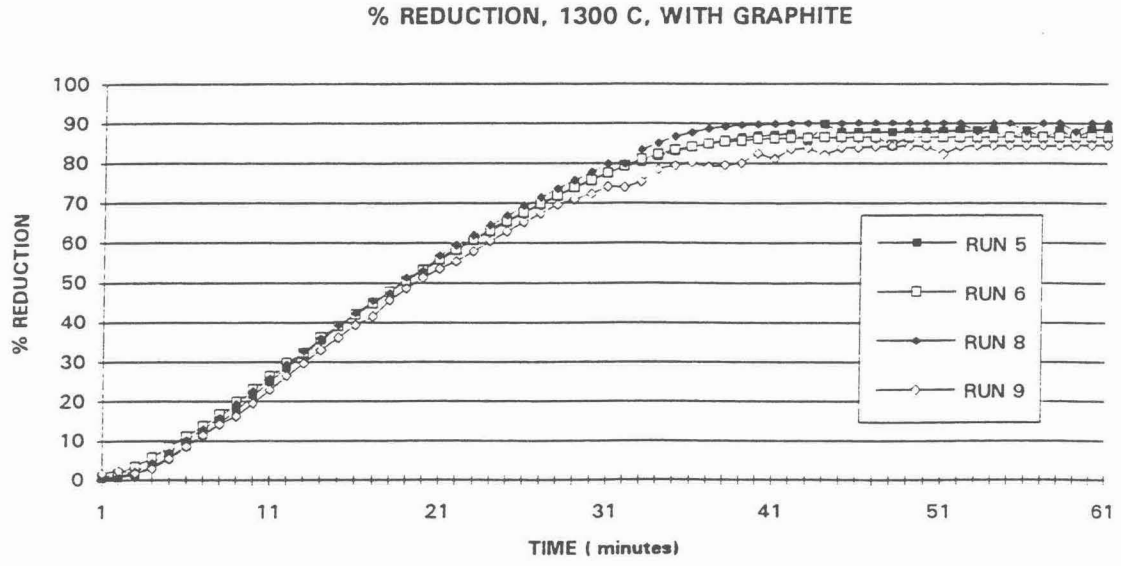

TABLE II: **Results of Reproducibility Tests**

Run No	Cr Tot	Cr Met	Fe Tot	Fe Met	C	% Cr Met	% Fe Met
5	31.9	25.3	25.5	24.2	10	79.31	94.90
6	34.1	26.3	28.4	26.6	9.3	77.13	93.66
8	33.6	27.6	24.5	23.5	10.6	82.14	95.92
9	32.7	25.9	22.8	21.0	11.2	79.20	92.11

Reactivity of Reductants

The various reductants consisted of two coke samples, one from Iscor, Newcastle and the other from Vryheid, in Northern Natal. The analyses are similar with the Vryheid sample showing a slightly higher alumina content, and marginally lower fixed carbon. The coal samples were from the Phoenix and Eikeboom Collieries in the Western Transvaal (both bituminous coals) and again differed only slightly in analysis. The Phoenix coal has a slightly higher volatile content, lower ash and lower fixed carbon. On the basis of the reproducibility results, 3 identical samples were prepared from each reductant. A decision was made to prepare all the samples in the same mass % fixed carbon as the first series of chromites with graphite reductant, namely 8g ore to 2g carbon. As the % fixed carbon varies slightly with each reductant the mass of reductant added varies between 2,5 and 2,6 g per 8 g chromite.

A complication exists in evaluating the results of TGA runs using coal samples containing significant quantities of volatile matter in that the mass loss cannot be equated to reduction or CO evolution. Thus for samples with coal as the reductant the TGA data bears little resemblance to the metallisation data. In order to eliminate this problem it was considered necessary to devolatilise the coals. The metallisation results of the the uncharred reductants are shown in table III.

TABLE III: Metallisation Results on Reductant Tests

Description	% Reduction	% Cr Metallisation	% Fe Metallisation	% Total Metallisation
Vryheid Coke	80	70.81	98.21	82
Newcastle Coke	58	39.86	99.03	65
Eikeboom Coal	69	58.71	91.59	72
Phoenix Coal	50	28.95	89.52	54

After devolatilisation of the coals at 900°C the chars were ground to 100% -45µm and samples were made up using the 20% excess fixed carbon basis,and tested by TGA. These results are displayed in Figure 6 as a % reduction versus time graph.

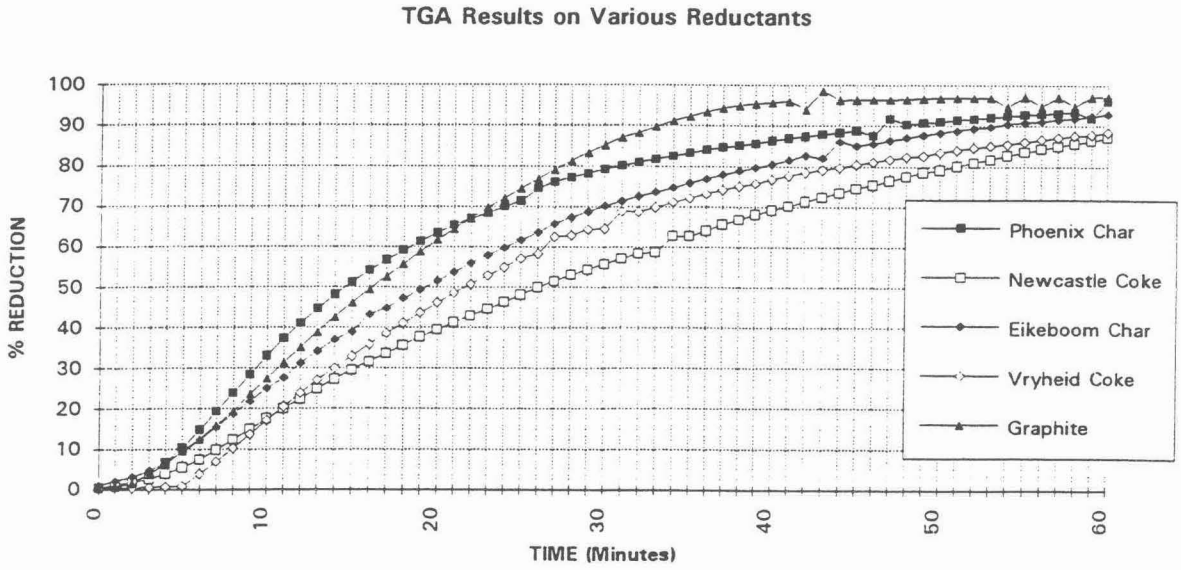

Figure 6: TGA Tests on Various Reductants

Figure 7 rates the reductants on a relative scale in which the regree of reduction of Henry Gould chromite with graphite after 40 minutes at 1300°C is assigned a value of 100. The relatively high reactivity observed for the electro-graphite is thus far unexplained, but is suspected to be related to particle size or specific surface area effects. This is being investigated, but as a separate project.The success of these results has led to a demand for the evaluation of a further 15 potential reductants and the work is continuing.

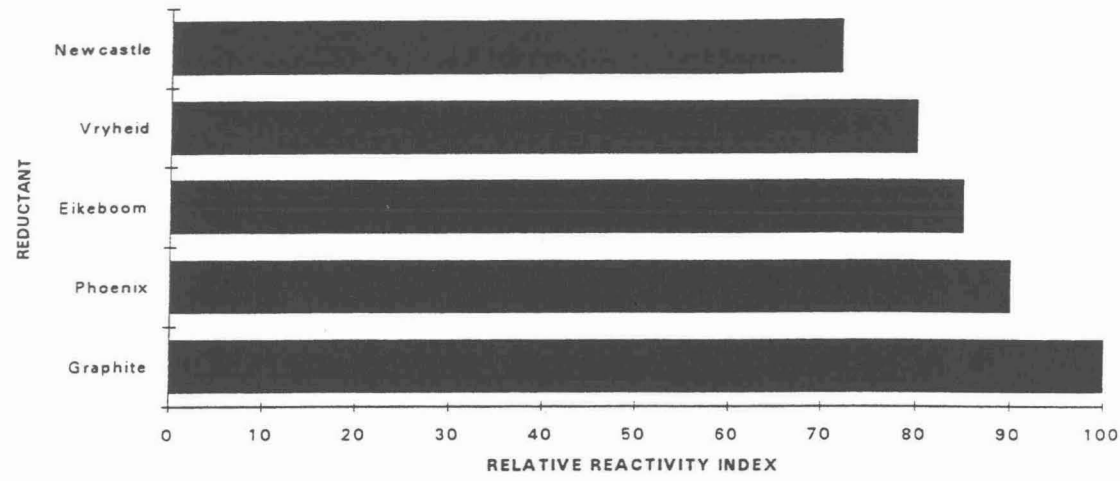

Figure 7: Reactivity Rating of Reductants

The results are also displayed in the form of Reduction versus metallisation curves in Figure 8, after Barnes [5], which shows the chromium, iron and total metallisation obtained for the reactivity and reproducibility tests. The results confirm earlier findings [4] that the final degree of metallisation obtained at a given temperature is a function of the amount of carbon.

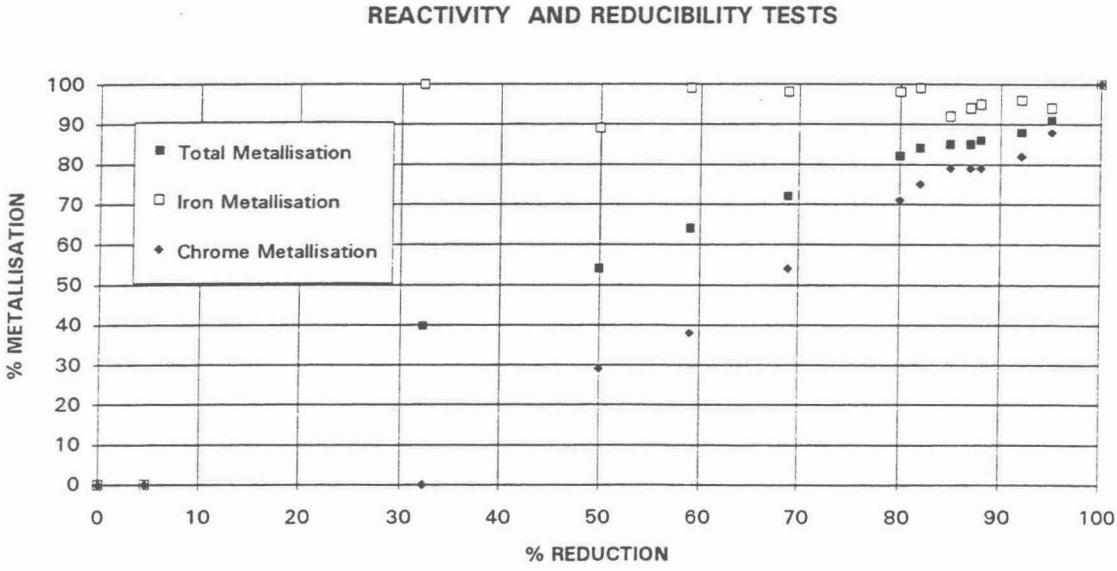

Figure 8: Metallisation versus Reduction Correlation

Reducibility

Only three additional ores were available for this series of tests. The first was a Zimbabwean chromite ore which had a high Cr/Fe ratio and was expected to show a lower reducibility than the Henry Gould ore. The second ore was designated WCM (from Western Chrome Mines) for which samples of both lump ore and screened fines were provided. These are run-of mine MG-1 ores, while the Lefco Concentrate from Crocodile River Mine is a gravity concentrate of UG-2 ore. Three runs on the Zimbabwean ore and one run on WCM lumpy ore have been conducted. Further experiments are being done. Table IV summarizes the available results. A reducibility rating is displayed in Figure 9. The basis for this rating is that iron oxide exhibits 100% reduction (and metallisation) at 1300°C while pure chromium oxide under CO gas remains unreduced at this temperature [6].

TABLE IV : Summary of Reducibility Tests

Description	Cr Metallisation	Fe Metallisation	Total Metallisation	% Reduction TGA
Henry Gould	79	94	86	87
Zimbabwean Ore	68	100	74	68
WCM Lumpy	84	94	88	96

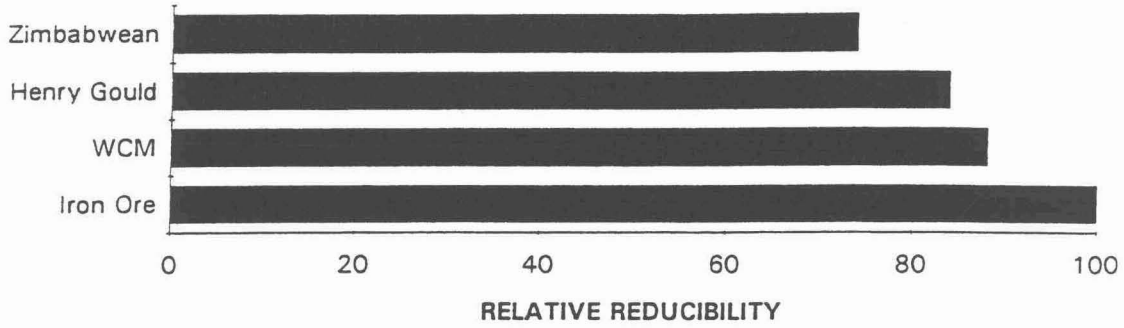

Figure 9: Relative Reducibilty Rating

CONCLUSIONS

Although the TGA technique is able to produce a wealth of data applicable to kinetic studies, it should be used with extreme care and must be interpreted with metallization data obtained by chemical analysis. A simpler test in which a pre-weighed sample of reductant and ore is subjected to a fixed temperature for a set time under an inert atmosphere, re-weighed and chemically analysed to determine the metallisation could be adequate for standard procedures. The TGA is limited in terms of equating mass-loss to reduction in the case of the coal samples containing large amounts of volatile matter. On the other hand the mass loss data provided by TGA along with metallization and microscopic data provides all that is necessary to predict, model and simulate the kinetics of the processes taking place in the reduction reactions. The test parameters chosen proved sufficiently discriminating to enable chromites and reductants to be ranked. The reductant reactivity tests are continuing as a priority, and attempts will be made at explaining the behaviour observed.

ACKNOWLEDGEMENTS

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