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Correlation of nickel extraction with iron reduction in oxidic nickel ore by a thermogravimetric method

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Abstract

The reduction roasting of chromite overburden with $CO/CO_2/N_2$ gas mixture in the temperature range 700–750°C has been shown to result in the formation of metallic nickel and different lower valence states of iron, viz: magnetite, wustite and metallic iron. The reduced calcine was cooled to room temperature under an inert atmosphere and leached with ammonia-ammonium carbonate solution to bring the metallic nickel into soluble form. This paper reports the results from estimation, by thermogravimetric (TG) and chemical methods, of the percentage iron reduced to lower oxide stages such as magnetite and wustite in the calcine under different experimental conditions. Further, the percentage extraction of nickel is correlated with iron reduction.

Keywords: Chrome ore; Chromite overburden; Iron reduction; Laterites; Nickel extraction; Thermogravimetry

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1. Introduction

In commercial practice, the extraction of nickel from oxidic sources like laterites involves the reduction of the ore with CO gas ($CO/CO + CO_2) = 0.5$–0.6) at temperatures of 700–750°C for 45–60 min, cooling of the calcine and leaching of the cooled calcine with ammoniacal solution under aeration [1, 2]. During the reduction roasting of the ore, the reduction of the iron has to be restricted to the magnetite stage only. Further reduction of iron to wustite and metallic stages results in greater consumption of reagents during the leaching operation of the calcine, poor settling characteristics of leach slurry and loss of nickel by adsorption in the hydrated iron oxide phase. However,

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in all commercial nickel reduction plants the iron reduction proceeds up to wustite with around 10 percent to the metallisation stage [3]. Ray and co-workers in a study on iron ore reduction by CO gas [4] have said that, since the reduction of Fe_2O_3 to metallic iron is a multistage process, one would expect distinct peaks of lower oxides of iron (Fe_3O_4, FeO, Fe) of which there can be two at a time, according to phase rule. Thus the available equilibrium data show a three-step plot. The reduction of $Fe_2O_3 \rightarrow Fe_3O_4$ requires negligible P_{CO}, whereas the subsequent steps, viz. $Fe_3O_4 \rightarrow FeO$ and $FeO \rightarrow Fe$ require increasing amounts of P_{CO}. Therefore, the equilibrium P_{CO_2} is lower. Several investigators have reported determination of ferrous iron, ferric iron and metallic iron from mixtures by standard chemical methods [5, 6] as well as through estimation of residual oxygen in reduced iron ores [7, 8].

During mining of chrome ore in the Sukinda region of Orissa State about ten tonnes of overburden are generated per tonne of ore. Around 1.5 million tonnes of overburden have already been stockpiled over the years. The generation of overburden per annum is about 0.3 million tonnes [9]. Considering the low grade of nickel laterites and the required investment for its mining, the chromite overburden can be a suitable source for extraction of nickel and cobalt. Therefore, an extensive study [10] has been made in this laboratory to develop a reduction roasting process for the extraction of nickel from the chromite overburden using a multiple hearth furnace (MHF). As a part of the above programme, detailed laboratory reduction roasting investigations were also carried out for optimisation of process parameters [11, 12].

The reduction roasting of chromite overburden with CO is to reduce the nickel oxide completely and the iron oxides partly. The aim is to produce magnetite at low temperatures with the minimum concentration of reductant (p_{CO}) in a reasonable time. The equilibrium diagram for CO reduction of iron oxides is shown in Fig. 1 and the dotted lines in the diagram shows the working region of the present investigation. From this figure it is clear that, at temperatures between 700–750°C and with the CO concentration range of 0.33 to 0.57, the iron oxide reduction proceeds to magnetite and wustite stages only.

The objective of the present investigation was to develop a method for the estimation of different lower valence states of iron present in the reduced calcine by thermogravimetric and chemical methods and correlation of the data for estimation of nickel recovery.

2. Experimental

2.1. Raw materials

Chromite overburden from Sukinda mines of Orissa, India used in this study contains Ni–0.9%, Fe–31.7%, Cr–7.23%, Al–1.36%, Mg–2.61%, Si–7.23% and LOI–6%.

2.2. Equipment

Roasting experiments were carried out by keeping the stainless steel reactor with the sample in a muffle furnace maintained at ± 5°C. A chromel–alumel thermocouple was connected to the temperature-controlling device of the furnace.

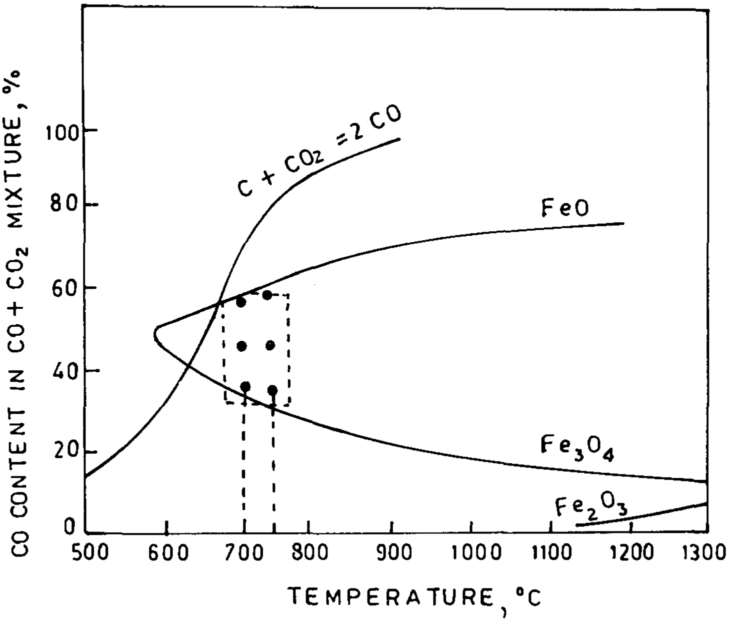

Fig. 1. Equilibrium curves for the reduction of iron oxide by carbon monoxide.

A Netzsch simultaneous STA 409 thermal analyser was used for the weight gain measurements of the reduced ore.

2.3. Experimental procedure

Reduction roasting experiments on laboratory scale were carried out by taking 10 g of the ore (ca 100 mesh) in a boat kept in a sealed reactor for a fixed temperature for a fixed time. The reactor had provisions for gas inlet and outlet and thermocouples for temperature measurements. The reducing gas was generated by passing air (30 l h^{-1}) over a bed of charcoal at appropriate temperatures. After completion of each roasting experiment at different gas compositions, the reactor was cooled to room temperature by passing purified nitrogen gas. Around 0.5 g of calcine was taken for estimation of different iron phases and about 3 g for nickel extraction by ammoniacal solution. Ferrous iron was estimated by the standard method [13].

3. Results and discussion

Initially the ore was heated to a temperature of 800 °C to remove free and inherent moisture and to convert the oxides of iron to haematite. The conversion of haematite was tested by taking a thermogram. Standardisation of TG method for determination of percentage magnetite and wustite phases was tried on chromite overburden samples reduced at 600°C with 10% CO gas and at 800°C with 40% CO gas to magnetite and

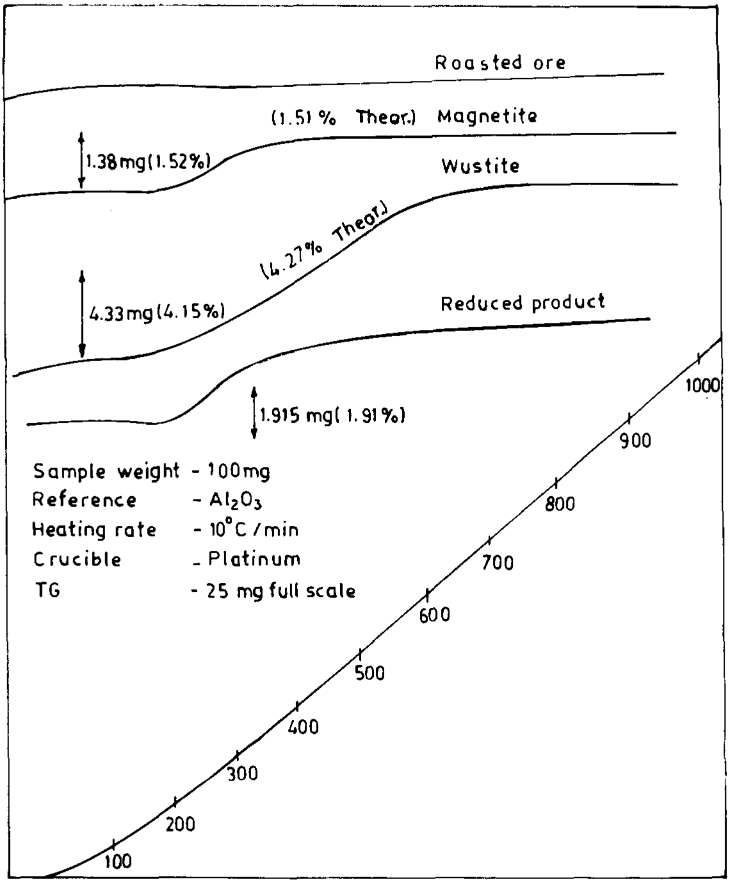

Fig. 2. TG curves for reoxidation of reduced ore.

wustite respectively. This was verified by the chemical method also [13]. The results of the weight gained by reoxidation of the reduced ore containing magnetite and wustite to haematite are shown in Fig. 2.

It can be seen that the calculated values of weight gain (1.52%) for magnetite to haematite and 4.15% for wustite to haematite are in good agreement with the corresponding theoretical values of weight gain indicating that the reduction of iron has been restricted to magnetite and wustite stages only. On the other hand, reduction of ore at 750°C for 30 min roasting time with 12% CO, followed by reoxidation of calcine showed a weight gain of 1.91%. This indicates that the reduction of iron during roasting goes beyond the magnetite stage. The percentage magnetite and wustite estimated by TG method are 86.8% and 13.18%, respectively, whereas the estimated values for the corresponding phases by chemical method are 88.74% and 11.26%.

The methods for estimation of percentage magnetite and wustite based on total iron in the reduced ore by TG and chemical method are given below:

TG method

Basis : 100 g of reduced ore
Total iron present : X g
Theoretically if X g given is present as 100% magnetite, the corresponding Fe^{2+} : X/3 g
Weight gained by oxidation of X/3 g : $0.1432\,X/3 = Y$ g
Actual % weight gained on reoxidation : Z g
Excess weight gained : $(Z - Y)$ g
Weight gained by oxidation of 100% wustite (theoretical) g (W) : 0.1432 X
% wustite corresponding to $(Z - Y)$ g : $(Z - Y)/W \times 100 = P_1$ (%)
Therefore, the % magnetite will be less than 100% by P_1% : $(Y \times P_1)/100$
% wustite for $(Y \times P_1)/100$ g wt gain : $(Y \times P_1)/W = P_2(\%)$
By Itrition method
% wustite for wt gain by $P_2(\%)$: $(Y \times P_2)/W = P_3(\%)$
% wustite for wt gain by $P_3(\%)$: $(Y \times P_3)/W = P_4(\%)$

⋮

% wustite for wt gain by $P_n(\%)$: up to $P_n \leqslant 0.1$
Total % of Wustite : $\Sigma(P_1 + \cdots\cdots P_n)$

Chemical method

Basis : 100 g of reduced ore
Total iron present (Fe^{3+}) : X g
Estimated Fe^{2+} : Y g
Balance of iron as Fe^{3+} : $(X - Y)$ g
Theoretical distribution of Fe^{3+} and Fe^{2+} in 100% magnetite : 66.66% (Fe^{3+}) + 33.34% (Fe^{2+})
Grams of Fe^{2+} corresponding to $(X - Y)$ g of Fe^{3+} : $0.5\,(X - Y)$ g
Grams of Fe^{2+} as FeO (Z g) : $[Y - 0.5(X - Y)]$ g
% Wustite (W) : $Z/X \times 100$
% Magnetite (M) : 100-W g

By applying the above thermogravimetric and chemical methods, the percentage distribution of iron as magnetite and wustite (based on total iron present) in the reduced material has been calculated for various experimental roasting conditions. The results are shown in Table 1. It can be seen that the estimated values of percentage iron reduced to magnetite and wustite during reduction of nickel ore by weight gain method match well with the values obtained by chemical analysis.

Finally, the percentage extraction of nickel obtained by ammonia-ammonium carbonate leaching of the reduced calcine was plotted against percentage wustite (Fig. 3). The data were fitted to a regression analysis [14] between 1/% W and 1/% Ni

Table 1
Comparison of distribution of iron as magnetite and wustite phases by chemical and oxidation method

Temperature: 700°C; $CO/(CO+CO_2)=0.33$									
Expt. No.	Time/min	Total Fe/%	Wt gained by reoxidation (Total Fe basis)/%	Ferrous iron (Total Fe basis)/%		Wustite/%		Magnetite/%	
				Chem	Oxdn	Chem	Oxdn	Chem	Oxdn
K 105	65	34.20	4.65	34.50	32.44	–	–	100.00	97.33
K 104	90	34.34	4.72	39.59	37.98	8.40	6.95	91.60	93.05
K 102	120	34.20	5.18	37.37	36.10	5.70	4.28	94.30	95.72
K 103	150	34.25	4.87	37.15	37.30	4.31	5.80	95.69	94.20
Temperature: 750°C; $CO/(CO+CO_2)=0.46$									
K 99	90	49.00	7.65	57.36	56.00	23.02	21.08	76.98	76.92
K 100	90	33.51	7.23	51.89	50.50	25.75	27.80	74.25	72.20
Temperature: 750°C; $CO/(CO+CO_2)=0.57$									
K 94	30	34.21	7.63	53.82	54.00	30.73	29.89	69.27	70.11
K 91	60	34.20	9.57	66.19	66.80	49.26	50.25	50.74	49.75
K 8	90	51.66	10.48	70.57	69.50	55.86	54.26	44.14	45.74

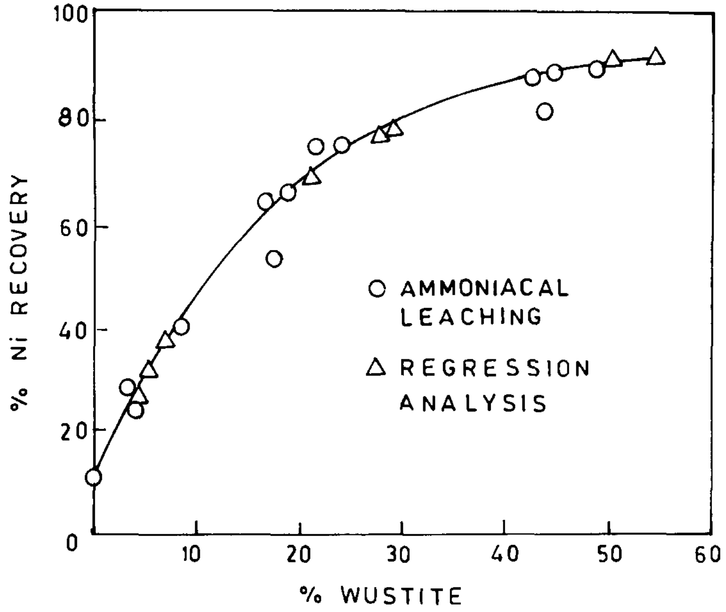

Fig. 3.

to get a linear relationship between % W (wustite) and % Ni with regression of 0.9983; the relationship is given by

$$\%\,\text{Ni extraction} = \frac{\%\,\text{W}}{0.0085 \times \%\,\text{W} + 0.1275}\ (\text{for values W} > 0)$$

Using the above equation, the percentage nickel extraction values were calculated for the whole series of experimental data shown in Table 1 using the percentage wustite values. The results obtained are shown in Fig. 3 and the percentage nickel extraction data match well with the values of chemical leaching method. It is clear from Fig. 3 that for more than 90% extraction of nickel about 50% of iron should be reduced to wustite.

Conclusions

Reoxidation of the reduced calcine could be used as tool for the estimation of percentage distribution of iron as magnetite and wustite in reduced chromite overburden.

The percentage nickel extraction calculated from the values of wustite match well with those of chemical leaching.

To achieve more than 90% extraction of nickel, about 50% of iron should be reduced to the wustite phase.

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