

STUDIES ON REACTIVITY TOWARDS CARBON DIOXIDE AND MOSSBAUER SPECTROSCOPIC ANALYSIS OF FERRO-COKE SAMPLES

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Introduction

FERRO-coke^{1,2} (i.e., coke produced by addition of ferruginous materials to coals) is believed to economise coke consumption, and also to enhance the productivity of the blast furnace. Realising this, studies were undertaken in the past at the Central Fuel Research Institute on the aspects relating to the production of ferro coke briquettes³ (from lignite available in India) with the ultimate objective of using them in low shaft furnaces. Investigations⁴ were also conducted on the quality of coke produced by the addition of different amounts of iron-bearing materials to various types of coals, both on the laboratory and pilot plant scales. Simultaneously, basic studies⁵ on the action of iron-oxide in ferro-cokes were also carried out. Results on the reactivity of ferro-cokes⁶ as well as iron impregnated cokes⁷ have also been reported. The present investigation was undertaken with a view to finding out the reasons for the increase in the reactivity by carrying out Mossbauer studies on the ferro-cokes.

Experimental

(a) *Preparation of ferro-coke.*—A high volatile Raniganj coal crushed to -0.2 mm size was used in the study. The procedure⁸ described by Bose *et al* was adopted for preparing iron-oxide. Different ferro-coke samples were prepared by carbonising the crushed coal and iron-oxide (-0.2 mm) mixtures (iron-oxide varying from 3–17%) at 900°C in a silica retort using a tube furnace.

(b) *Reactivity test.*—The reactivity (R_{CO_2}) of the coke towards carbon dioxide was determined by the Indian Standard method⁹.

(c) *Mossbauer studies.*—Mossbauer spectrometer (MBS-35) along with multichannel analyser MCA-

38A was employed for identifying the various phases of iron in the coke samples. The Mossbauers source was 5 mci Co-57 in Cu and Pd-matrices. The data were recorded on a teleprinter. The Mossbauer unit was standardised with pure samples of metallic iron and sodium nitroprusside. Powdered coke samples were taken between two thin plates of beryllium. Care was taken to ensure that approximately 5–10 mg/cm² of iron present in the coke was available in the specimen for test. All experiments were conducted at $23^{\circ}\pm 1^{\circ}\text{C}$.

Results and Discussion

Reactivity results.—Table I gives the properties of the coal used in the experiments. A high volatile coal was chosen, because earlier studies⁴ had indicated improvement in coke strength when ferro-coke was prepared from such samples.

The results of the proximate analyses of the ferro-cokes prepared are presented in Table II.

As expected, with the increase in the quantities of iron-oxide in the blends, there is a progressive increase in the ash content of the coke samples. The corresponding reactivity values are also shown in the table. The reactivity of the samples is seen to be more or less steady upto 7% addition of iron-oxide but, thereafter, a steep rise is registered with a peak value around 12% iron-oxide. Further addition upto 17% lowers the reactivity value.

Mossbauer results

The samples prepared by adding 0–3% iron-oxide did not show a good Mossbauer spectrum. The spectrum of the ferro-coke having 5% iron-oxide indicates that iron is mostly present in ferrous and ferric state and a part only as metallic iron (Fe^0). The spectrum containing 7% iron-oxide mixed in the blend shows the presence of α -iron and Fe^{3+} state of iron. Further, the isomer shift of the order of 1.01 mm/sec is also observed, which clearly indicates the presence of Fe^{2+} species in the sample.

Figures 1, 2 and 3 depict the Mossbauer spectra of metallic iron (Fe^0), 12% iron oxide mixed coke and 15% iron oxide mixed coke respectively. Though apparently the curves seem to be identical, they

TABLE I
Properties of coal

Particulars	Air dried basis %				Dry mineral matter free basis%		
	Moisture	Ash	Volatile matter	Fixed carbon	Volatile matter	Carbon	Hydrogen
Seetalpur Colliery, Sanctoria Seam	1.6	11.6	35.6	51.2	40.2	84.0	5.5

TABLE II
Properties of ferro coke samples

Coke prepared from	Properties of coke				
	Air dried basis %				R_{CO_2} Reactivity towards carbondioxide
	Moisture	Ash	Volatile matter	Fixed carbon	
1. Seetalpur coal	0.8	18.4	1.1	79.7	123
2. do. + 3% Fe-oxide	1.4	21.6	1.5	75.5	129
3. do. + 5% Fe-oxide	2.1	24.4	1.7	71.8	116
4. do. + 7% Fe-oxide	2.5	26.6	1.1	69.8	122
5. do. + 10% Fe-oxide	4.2	30.6	1.5	63.7	167
6. do. + 12% Fe-oxide	5.0	35.6	1.9	57.5	188
7. do. + 15% Fe-oxide	169
8. do. + 17% Fe-oxide	122

have salient distinguishing features. Figure 2 shows that mostly the iron is in the form of metallic iron (Fe^0), however, in this case a broadening of the line width is also noticed at channel number 593 and 631 and also a slightly observable peak at 613, suggesting the presence of some interstitial solid solution of carbon in iron. In the case of 15% iron-oxide mixed coke (Fig. 3), the presence of interstitial solid solution of carbon in iron is clearly observed, as is frequently noticed in steel samples. It may be pointed out that this is perhaps in the form of cementite⁹, i.e., Fe_3C and this is characterised by the extra peaks at channel numbers 613 and 642 which are distinctly identifiable. Nevertheless, the occurrence of metallic iron (Fe^0) is predominant as the other peaks are superimposed on the peaks of the spectrum of iron (Fe^0), (Fig. 1). Further work is in progress in this direction.

From the above, it may be concluded that when the iron oxide in the coke is reduced to iron (Fe^0) higher value of reactivity is recorded, and, perhaps the reaction⁶ $CO_2 + C = 2CO$ is catalysed. This catalytic action is retarded when the presence of iron oxide exceeds 12%. Thermogravimetric studies by Cypres¹⁰ *et al.*, have also emphasised the importance of the structure of iron oxide in coal-iron oxide pyrolysis reactions.

Conclusions

The reactivity of carbon (towards CO_2) of ferro cokes produced by the 'pyrolysis of iron-oxide coal mixtures, changes with the percentage of iron-oxide in the blend. Upto about 7% iron oxide addition the reactivity values seem to be more or less steady, it records a steep rise around 12% addition, and registers lower values on further addition. The

change in the values around the point of inflexion, as reflected by Mossbauer studies on the ferro-coke samples, is attributed to the state of iron present in the coke; mostly the iron is in the form of metallic iron (Fe^0) at this stage.

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