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Utilization of Low Grade Coal for Direct Reduction of Mill Scale to obtain Sponge Iron: Effect of Reduction Time and Particle Size

Rahul Sen^a, Satender Dehiya^a, Upender Pandel^a, M. K. Banerjee^b^aDepartment of Metallurgical and Materials Engineering, MNIT Jaipur, 302017, India^bMinistry of Steel, Chair Professor

Abstract

Demand of today is to optimize the available resources and reutilize the waste materials. Mill scale is waste cum byproduct obtained during hot rolling operation of steels. In Rajasthan there are hundreds of hot rolling mills producing tons of mill scale everyday and in Nagaur, Rajasthan there are huge reserves of low grade coal. In this paper an attempt has been made to utilize the low grade coal for direct reduction of mill scale in laboratory to obtain sponge iron. The paper comprises the study on effects of variation in particle size (60-100, 170-200 and <325 ASTM sieve size) and time (30, 60, 90 minutes) on reduction behaviour of mill scale in a fixed reducing atmosphere (900 °C), taken lime (10% of weight of mill scale) as catalyst. Further reduced samples were characterized by using EDX, SEM (Scanning Electron Microscope) and XRD (X-Ray Diffraction). It has been identified that the maximum reduction of mill scale (81.64%) is found in the sample reduced for 90 minutes with particle size ranging between 60-100 (ASTM sieve size)

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Keywords: Mill scale, coal, sponge iron

1. Introduction

Rolling mill scale is solid by product obtained from steel making industries. It is an oxide layer formed by flaky small particles of thickness generally less than 2.0 mm. It constitutes iron, its oxides (hematite, magnetite, wusite etc.), traces of non ferrous elements and alkaline compounds. Mill scale is contaminated with lubricants and greases from the equipment associated with rolling operations. It generally ends up in landfills or in some proportion used in road and building contraction. Mill scale disrupts the useful land where it has been dumped, decreases the fertility of soil and its sludge badly contaminates the water bodies. Reduction of mill scale to sponge iron is a new way to take advantage of a waste or cheap byproduct of steelmaking industry. During the process of direct reduction entire amount of oxygen present in the iron oxide is removed by suitable reductant to give high degree of metallization. Direct reduced iron often called as Sponge Iron (solid porous iron lumps with many voids). Sponge iron can be re-used to the electric furnace as metallic charge in steel making or as a raw

material in the production of iron-base powder metallurgy parts. In addition, sponge iron can be utilized as raw material to hydrogen roasting department, as coolant in basic oxygen furnace or in production of welding electrodes [1-7]

1.1. Classification of DRI processes

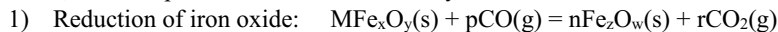
Depending upon the type of reductant utilized, sponge iron or DRI can be produced from iron bearing raw material by two different processes: Coal based and Gas based reduction processes shown in table 1 [8, 9]

Table 1. Types of reduction processes to produce DRI or sponge iron

Reductant	Type of Reduction process
Coal based	1) Rotary kiln processes (SL/RN, Krupp-CODIR, DRC, ACCAR, TDR etc.), 2) Retort process (Kinglor Meteor), 3) Rotary hearth processes (Inmetco, Fastmet)
Gas based	1) Shaft processes (MIDREX, HYL process, Purofer), 2) Fluidized processes (FIOR/FINMET, Circofer)

1.2. Reduction kinetics

In production of sponge iron by reduction of iron oxide, the most commonly used reducing agent are carbon monoxide, hydrogen and mixtures of these two gases. In gas based reduction process (e.g. Shaft Process) CO and/or H₂ works as reducing agent to give metallic iron from iron oxides and in coal based reduction (e.g. Rotary Kiln process), at reducing temperature, carbon in coal and the CO produced works as reducing agent. When the reduction is carried out by solid carbon or carbon monoxide, the final process of reduction is always written as:



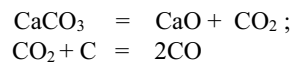
The necessary CO is provided directly or by the Boudouard reaction, given below:



Solid state direct reduction processes generally operate within narrow temperature range of 800-1100°C, in order to prevent the formation of any semi solid phases. [3, 9-12]

1.2.1. Effect of calcium carbonate on degree of reduction of mill scale

Calcium carbonate (Lime stone powder) mixed with coal powder which works as catalyst and helps in scavenging sulphur. CaCO₃ decomposes to CaO and CO₂. CaO acts as a catalyst, the gasification reaction gets accelerated. [13]



1.3. Coal

Coal is solid natural fuel obtained from earth crust comprises fixed carbon, moisture, volatile mixture and ash. According to heating value and fixed carbon percent coal classified into three major types, shown in table 2 [10, 14]

Table 2. Type of coal with their heating value and fixed carbon content

Coal	Fixed carbon (%)	Calorific value (KJ/Kg)
Anthracite	86-98	35890
Bituminous	40-85	24000-36000
Lignite	Less than 40	Approximately 700

2. Raw material

There were three raw materials used in the reduction of mill scale. The raw materials were easily available in local area, quite cheap in cost, so the overall production of the iron powder or sponge iron was cost effective. The source of raw material with their price index is shown in table 3. [10, 15, 16]

Table 3. Raw material used in experiment with their price index and source.

Sr. No.	Raw material	Price (INR/Kg)	Source
1.	Mill scale	5 to 7	SARADA Enterprises, a hot rolling mill in Jaipur
2.	Low grade coal	1.5 to 4	Matasukh coalmines, Nagaur district, Rajasthan
3.	Lime stone	10 to 15	Local market, Jaipur

2.1. Proximate analysis of coal

In this study mill scale is reduced by low grade coal in presence of lime (taken 10% of weight of coal). Proximate analysis of coal used in this study was done by Indian School of Mines, Dhanbad and also verified with the data mentioned on Rajasthan State Mines and Minerals Ltd., shown in table 4.

Table 4. Proximate Analysis of coal used in the experiment

Parameter	Lignite coal (wt%)
Fixed carbon	26.68
Ash	9
Volatile matter	25.26
Other components	39.06

2.2. Stoichiometric ratio of mill scale and coal

The amount of fixed carbon necessary to fully reduce the iron oxide within the mill scale was designated as the stoichiometrically required amount. It was calculated by studying the main peaks of XRD of unreduced sample of mill scale. Since coal was having 26.68 % fixed carbon and act as reducing agent, the corresponding value of coal required per sample of mill scale was calculated. From calculation and best results, 1:1 ratio of mill scale and coal + lime was taken. In the study, mill scale = 25 gram, coal = 22.5 and lime 2.5 gram was taken per sample for reduction in alumina crucible.

3. Experimental procedure

3.1. Material cleaning

Mill scale was washed with water to remove oils, grease and other impurities present in it.

3.2. Sample preparation

Mill Scale, lime stone and low grade coal were crushed by roll crusher and finally ground to fine particles in by hammer and hand rolling, later then passed through various sieves by using sieve shaker. In the study, all raw materials (mill scale, coal and lime stone) of particle size 60-100, 170-200 and < 325 ASTM sieve size.

3.3. Arrangement of mill scale and coal in crucible

Mill scale was placed centrally (provide maximum surface area for direct reduction) in the vertical column of 23 mm in diameter and mixture of coal with lime (10 wt% of mill scale) was put around the column in mill scale in the alumina crucible as shown in figure 1 (a) and (b). The samples were well covered/insulated by glass wool and silica lead cover to prevent oxidation.

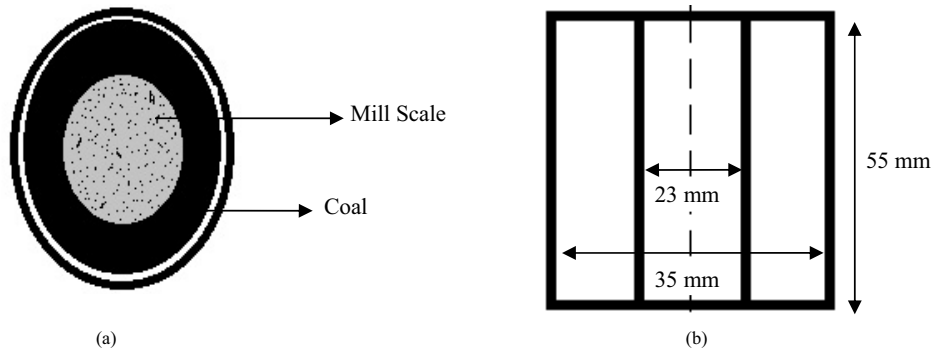


Fig. 1. Arrangement of mill scale and coal in the alumina crucible (a) top view and (b) side view

3.4. Reduction in muffle furnace

The reduction was carried out in laboratory scale muffle furnace at 900°C. The study carried out for different range of particles (60-100, 170-200 & 325 ASTM sieve size) and were collected after a predetermined period of time (30, 60, 90 minutes) after the charge of the reactants.

3.5. Material separation

When samples get cooled, they were magnetically separated to look for iron power. A strong magnet was used to solve the purpose.

4. Results and discussion

4.1. Chemical analysis test

Chemical analysis of the mill scale samples done before and after the reduction process to know the extent of reduction of iron oxide into iron. Chemical analysis test (done at National Test House Jaipur) show that mill scale before reduction contains **63.71 %** of iron by mass. Value of iron content in different mill scale samples reduced for different timings at 900 °C shown in table 5. It shows that with increase in reduction time iron content increases for all given sieve size and with decrease in size of particles, percentage of iron in sample decreases.

Table 5. Chemical analysis test results of mill scale samples reduced at 900 °C for different holding time

Sr. No.	Particle size (ASTM sieve size)	Time (minutes)	Iron content (% by mass)
1.		30	77.81
2.	60-100	60	78.75
3.		90	81.64
4.		30	72.27
5.	170-200	60	74.64
6.		90	80.99
7.		30	74.96
8.	<325	60	76.65
9.		90	78.94

4.2. XRD analysis

Analysis by X-ray diffraction of unreduced mill scale (Fig. 2) shows the presence of hematite (Fe₂O₃), magnetite (Fe₃O₄) and wustite (FeO) phases. It was observed that highest intensity peak was of iron and some other peaks of lower intensity of iron oxides. Sample of mill scale size 60-100ASTM sieve size, reduced at 900°C for 90 minutes (Figure 3) confirmed the gradual reduction of iron oxide phases and formation of metallic iron phase. There were some variation in intensity of different peaks but pure iron phase had been detected.

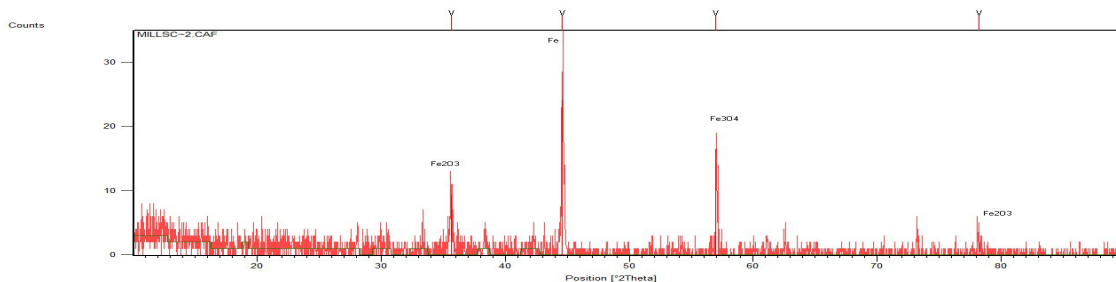


Fig. 2. X-RD plot showing different peaks representing various phases of iron oxides in a unreduced mill scale sample of 60-100 ASTM sieve size

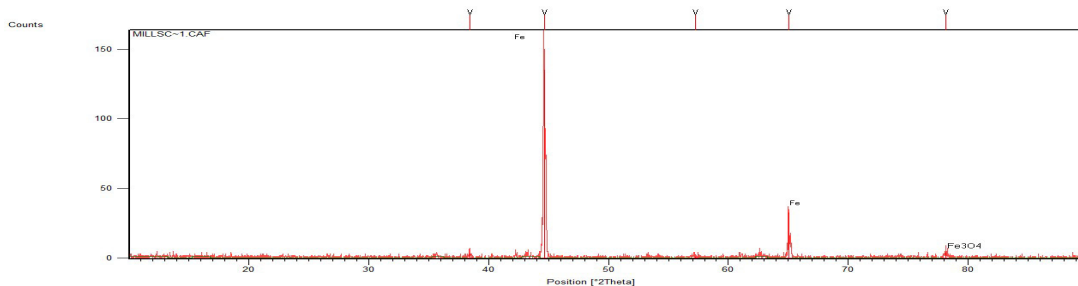


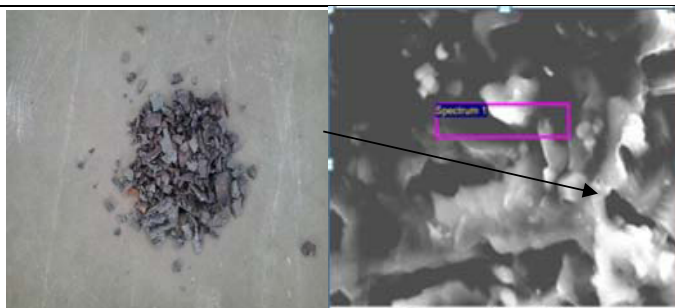
Fig. 3. X-RD plot showing different peaks representing various phases of iron, decrease in iron oxide peaks in a sample of mill scale of 60-100 ASTM sieve size, reduced at 900°C for 90 minutes

4.3. Energy-dispersive X-ray spectroscopy (EDS or EDX)

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on the investigation of an interaction of some source of X-ray excitation and a sample. The EDX analysis of unreduced mill scale shown in figure 4.3 and Elemental analysis is shown in table 6.

Table 6. Elemental analysis (weight % and atomic %) of unreduced mill scale of sample size 170-200 ASTM sieve size

Element (Et)	O K	Al K	Si K	Ca K	Mn K	Fe K	Cu K	Total
Weight (wt) %	38.54	10.40	2.62	8.17	1.95	33.89	3.26	100
Atomic (At) %	63.36	9.74	2.15	5.36	0.93	15.96	1.35	100



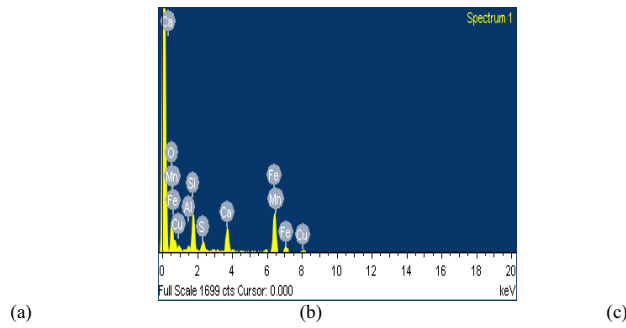


Fig. 4. SEM image and EDX showing the atomic spectrum of unreduced mill scale of sieve size 170-200 ASTM

Table 7. Elemental analysis (weight % and atomic %) of mill scale of sample size 170-200 ASTM sieve size reduced for 900 minutes.

Element	Al K	Si K	Ca K	Mn K	Fe K	Total
Weight %	0.60	0.36	1.79	12.12	85.13	100
Atomic %	1.22	0.70	2.44	12.10	83.55	100

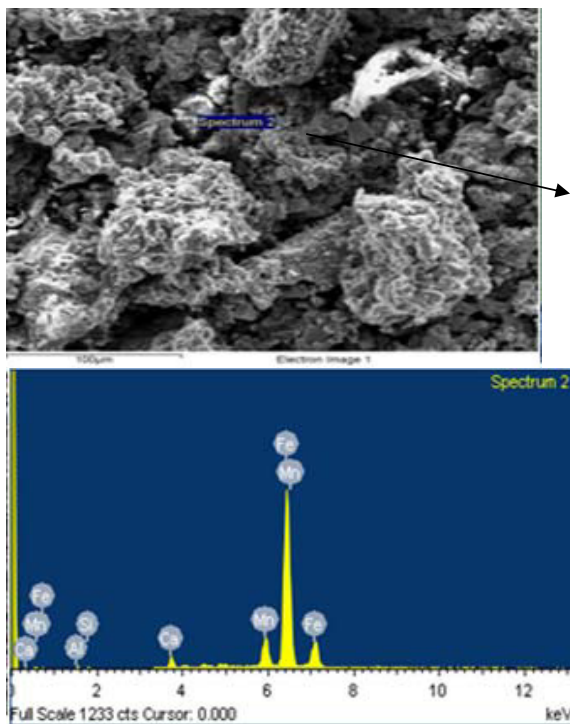


Fig. 5. Energy dispersive spectroscopy showing atomic spectrum of mill scale of particle size 170-200 ASTM sieve size, reduced at 900°C for 90 minutes

5. Conclusions

Result obtained from chemical analysis was understood as holding time in the furnace was increased, percentage of total iron in the sample got increased simultaneously. Same trends visible for all the samples of different particle size but best results were seen in mill sample reduced for 90 minutes with particle size ranging between 60-100 (ASTM sieve size). This was due to the permeability of mill scale column which was more for ASTM sieve size 60-100 than other range of sieve size. This was due to the fact that carbon and carbon monoxide (CO) can penetrate well into the scale column and enhance reducibility and as particle size gets finer there has been decrease in degree of metallization for

corresponding heating time. The XRD of unreduced and reduced mill scale sample confirmed the gradual reduction of metallic oxide to iron phase. On comparing the EDX elemental analysis of unreduced and reduced sample of mill sample confirmed the complete removal of oxygen from iron oxide and increase in percentage of iron after reduction. The most effective result of thermal treatments, performed at 900°C for different reaction time, found in sample reduced for 90 minutes of particle size range between 60-100 (ASTM sieve size), which yielded the highest iron content (81.64%) in all the treated samples.

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