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Reduction Conditions of Briquetted Solid Wastes Generated by the Integrated Iron and Steel Plant

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***Abstract*—**Iron oxides are the main input to produce iron in integrated iron and steel plants. During production of iron from iron oxides, some wastes with high iron content occur. These main wastes can be classified as basic oxygen furnace (BOF) sludge, flue dust and rolling scale. Recycling of these wastes has a great importance for both environmental effects and reduction of production costs. In this study, recycling experiments were performed on basic oxygen furnace sludge, flue dust and rolling scale which contain 53.8%, 54.3% and 70.2% iron respectively. These wastes were mixed together with coke as reducer and these mixtures are pressed to obtain cylindrical briquettes. These briquettes were pressed under various compacting forces from 1 ton to 6 tons. Also, both stoichiometric and twice the stoichiometric cokes were added to investigate effect of coke amount on reduction properties of the waste mixtures. Then, these briquettes were reduced at 1000°C and 1100°C during 30, 60, 90, 120 and 150 min in a muffle furnace. According to the results of reduction experiments, the effect of compacting force, temperature and time on reduction ratio of the wastes were determined. It is found that 1 ton compacting force, 150 min reduction time and 1100°C are the optimum conditions to obtain reduction ratio higher than 75%.

***Keywords*—**Iron oxide wastes, reduction, coke, recycling.

I. Introduction

RAPID industrialization has caused major environmental pollution problems. Iron and steel plants are an important part of industrialization because of the need for such materials in our lives largely. They are used in wide range from automobiles, ships, buildings to our daily life tools such as kitchen equipment. Due to high consumption of steel products, production of steel increases day by day. And accordingly iron ores are consumed at a high rate. Furthermore, increasing production rates generate solid wastes significantly in each processing step. Considering the amount of steel yielding from integrated plants reached to 1599 Mt in 2015, it can be imagined the huge amount of daily wastes. For these reasons many studies have been done to prevent environmental pollution and to conversion of these wastes into useful materials or raw materials. Iron oxide wastes obtained from integrated iron and steel plants are the most convenient by products that can be used as iron oxide raw material. Because iron content of these wastes are almost equal or higher than concentrated iron ores and also iron oxide exists as a separate phase [1]-[4].

There are many methods to reuse/recycle iron oxide wastes. For instance, iron slag is used as construction and asphalt making material in civil engineering applications. Moreover, iron oxide wastes are used to recover iron content for metallurgical applications. For this purpose, iron oxide wastes are converted to pellet or briquette commonly to obtain a bulk form. During this process, carbon is used as reducing agent and it is added into the bulk form homogenously. Usually, a binder is used to bring fine iron oxide and carbon particles together and to obtain a stable bulk form with a sufficient strength [5]-[8]. Then high temperature reduction processes are applied to reduce iron oxides to iron. During reduction process, the following reaction steps (1)–(4) take place in the bulk form of iron oxide wastes containing carbon [9]:

$$Fe_XO_{y(s)} + CO_{(g)} = Fe_XO_{y-1(s)} + CO_{2(g)} \tag{1}$$

Total reduction reaction is;

$$Fe_XO_{y(s)} + C_{(s)} = Fe_XO_{y-1(s)} + CO_{(g)} \tag{2}$$

When coke burns, formation of CO_2 takes place firstly;

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \tag{3}$$

After that, it reacts with C and produce CO which is the main reducer gas for iron oxides:

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \tag{4}$$

In the present study, iron oxide wastes, basic oxygen furnace (BOF) sludge, flue dust, and rolling scale which are the main wastes of an integrated iron and steel plant are used as raw materials to recover iron content and to investigate reduction behavior of iron oxide during the process.

II. Experimental Procedure

In this study, wastes obtained from the integrated iron and steel plant in Turkey was used. Chemical compositions of these wastes are shown in Table I.

All raw materials were dried in Ecocell 55 laboratory-scale oven at 110°C for 2 h to remove the moisture. While dried waste scale was ground to the size of 0.5-1 mm in a ball mill, other wastes were used as received. Then, equal amount of the wastes was weighed and mixed together in a mechanical mixer for 1 h. All iron in the wastes was assumed in the form of

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Fe_3O_4, and the amount of coke added in stoichiometric ratio was calculated on the basis of the following reaction:

$$Fe_3O_{4(s)} + 4C_{(s)} = 3Fe_{(s)} + CO_{(g)} \quad (5)$$

Chemical composition of the coke is shown in Table II.

TABLE I
CHEMICAL COMPOSITIONS OF WASTES

Components (%)	BOF Sludge	Scale	Flue Dust
Fe	53.8	70.2	54.3
SiO_2	1.67	1.88	1.72
CaO	9.80	0.94	8.93
Al_2O_3	0.12	0.39	0.15
MgO	0.01	0.01	0.01
Mn	0.62	0.92	0.59
S	2.08	0.06	1.96
K_2O	0.10	0.01	0.11
Na_2O	0.01	0.01	0.01
P	-	0.05	-
Zn	0.99	0.01	0.91
Cu	0.18	0.04	0.16
As	0.02	0.01	0.02
Pb	0.10	0.01	0.09
TiO_2	0.03	0.03	0.03
CaO/SiO_2	5.86	0.50	5.19

TABLE II
CHEMICAL COMPOSITION OF COKE

	C	Volatile Matter	Ash	Moisture
%	80.24	3.2	16	0.56

In order to investigate the effect of coke amount on reduction behavior of iron oxide wastes, two groups of mixtures contained different coke amount were prepared: stoichiometric ratio and twice the stoichiometric ratio.

Weighed waste and coke powder were mixed in a mixer. To be able to obtain a compact and strength briquettes, 5% molasses of total weight of a mixture was added. After homogenization, the mixtures were put into a cylindrical shape mold with 10 mm in diameter. The mixtures were compressed under various pressures from 1 ton to 6 tons to investigate effect of compacting force on strength and reduction behavior of iron oxide waste-coke briquettes.

A muffle type furnace was used in the reduction experiments. Firstly, the furnace was heated to reduction temperatures (1000°C and 1100°C) and then the cylindrical iron oxide waste-coke briquettes were put into the furnace. The samples were hold in the furnace for 30, 60, 90, 120, 150 min at each reduction temperature.

After completion of the reduction time, iron oxide waste-coke briquettes were immediately removed from the furnace and put into a desiccator to cool them to room temperature. Then, each reduced samples were weighed to determine weight loss during reduction. Depends on weight losses, reduction ratios of samples were calculated according to the following formula [9]:

$$\text{Reduction ratio, \%} = \frac{\text{Removed oxygen from iron oxide}}{\text{Initial oxygen in iron oxide}} x100$$

In the calculation of the reduction ratios, besides the weight loss resulting from the removal of oxygen, weight losses because of volatile matter, moisture, and carbon in the coke were also taken into account.

III. RESULTS AND DISCUSSION

A. Effect of Compaction on Reduction Ratio

The iron oxide briquettes which contain stoichiometric coke were compressed under forces from 1 ton to 6 tons to investigate the effect of compacting force on reduction behavior of samples. The relationship between reduction ratio and compacting force is shown in Fig. 1.

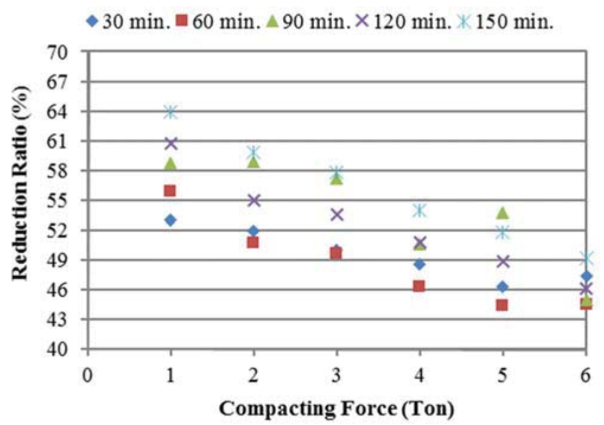

Fig 1 Effect of compacting force on reduction ratio of iron oxide waste-coke briquettes at 1000°C

It is seen from Fig. 1 that higher reduction ratios were obtained at lower compacting forces for 1000°C reduction temperature. Reduction ratios show similar trend for each time period. It is clear from the figure that reduction ratio decreases with increasing compacting force. For 150 min reduction time, while 64% reduction ratio is obtained for 1 ton compacting force, reduction ratio decreases to 49% when force is raised to 6 tons. When compacting force is increased solid particles close to each other more and is compressed. So, pore volume for gas diffusion is decreased. This situation partially prevents to diffuse of CO gas into the sample to reduce iron oxide. Besides that, it prevents removing of reaction product, CO_2, from the sample. Because of these reasons, reduction ratios of the samples decrease with increasing compacting force.

B. Effect of Coke Amount on Reduction Ratio

To investigate effect of coke amount on reduction behavior of iron oxide waste-coke briquettes, experiments were performed in constant compacting force, 1 ton, and at constant temperature, 1000°C. Reduction ratio results of the experiments which were performed with samples containing stoichiometric coke and twice the stoichiometric coke are shown in Fig. 2.

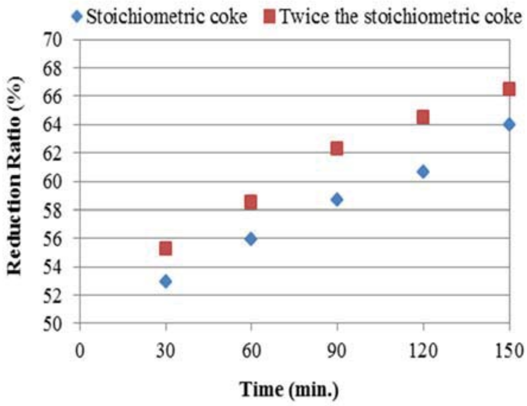

Fig. 2 Effect of coke amount on reduction ratio at 1000°C

It is seen from Fig. 2 that reduction ratio of samples containing twice the stoichiometric coke is higher than samples containing only stoichiometric coke during reduction time of 150 min at 1000°C. Reduction ratio is 53% in 30 min and it reaches up to 64% in 150 min when stoichiometric coke is used. In the case of twice the stoichiometric coke, reduction ratio is approximately 55% in 30 min, and at the end of the reduction it reaches to 66.5%. It means that, not only time and temperature but also amount of coke in iron oxide briquettes affects the reduction ratio. However, increase in the reduction ratio depending on the increase in the amount of coke is not at high levels.

C. Effect of Temperature on Reduction Ratio

Reduction temperatures of 1000°C and 1100°C were chosen to observe effect of temperature on reduction behavior of iron oxide wastes. Reduction ratio results at these temperatures are shown in Fig. 3. The samples which were produced with compacting force of 1 ton were used in these experiments.

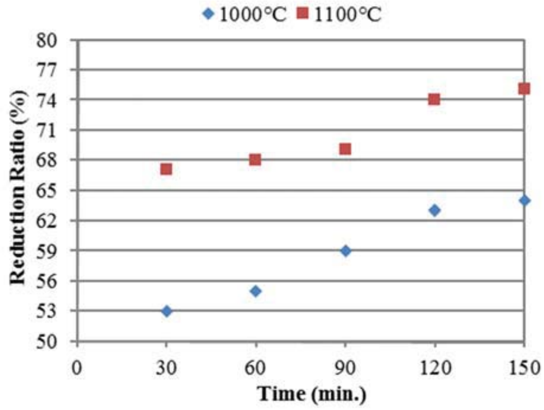

Fig. 3 Relationship between temperature and reduction ratio

It is clear from Fig. 3 that the temperature has a significant effect on reduction ratio. While reduction ratio is 53% in 30 min at 1000°C, it increases to 67% at 1100°C at the same reduction time. At the end of the reduction process, reduction ratios reach to 64% and 75% for 1000°C and 1100°C, respectively. The effect of temperature on reduction behavior is higher than the other parameters such as coke amount, and compacting force.

The samples reduced at 1100°C were investigated with optical microscope. Formation of iron and partly reduced regions can be seen in Fig. 4. The images show that iron formation developed and partly reduced regions diminished as the time passed.

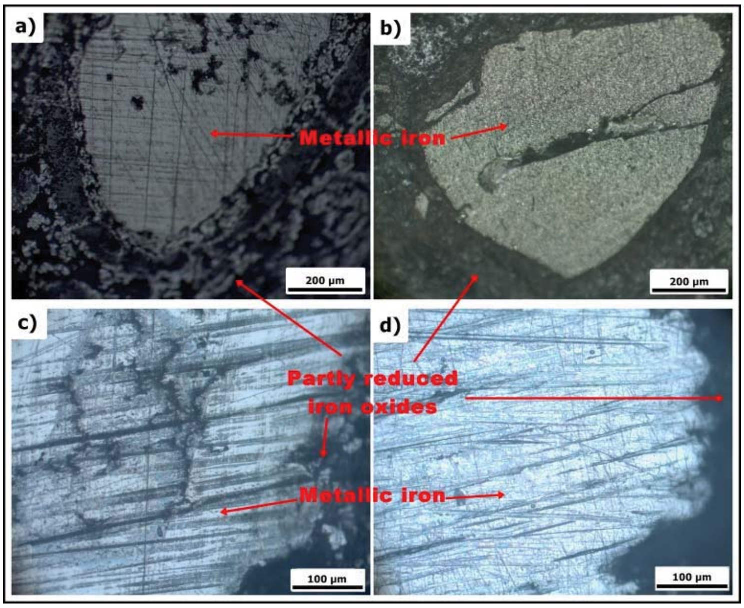

Fig. 4 Optical microscope images of reduced samples at 1100°C (a) and (c) 30 min, (b) and (d) 150 min

IV. Conclusion

Following results are concluded from reduction behavior experiments of iron oxide wastes which are generated from the integrated iron and steel plant:

1. Reduction ratios of iron oxide waste-coke briquettes were affected by compacting force significantly. It was observed that while compacting force increased from 1 to 6 tons, reduction ratio decrease from 64% to 49% for 150 min reduction time.
2. Addition of coke in twice the stoichiometric coke amount into the briquettes increased reduction ratios slightly.
3. The temperatures of 1000°C and 1100°C are chosen for an economic reduction process. Although a significant reduction ratio obtained at 1000°C, it was below the desired reduction ratio. Increment of temperature from 1000°C to 1100°C, reduction ratio of the sample increased from 64% to 76% at the end of 150 min. Besides, longer reduction time increases reduction ratio considerably.
4. According to the results, the optimum reduction conditions can be obtained using 1 ton compacting force, reduction time of 150 min, and reduction temperature of 1100°C.

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