

## The effective parameters on thermal recovery and reduction of iron oxides in EAF slag

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### Abstract

Steelmaking slag of Mobarakeh Steel Company (MSC) has a high iron content which makes it unsuitable for conventional slag recovery; as in cement industries. On the other hand, EAF slag in this company is almost free of zinc because of using more than 90 percent DRI in the charge. Therefore, removal or recovery of iron from the slag can be a suitable solution to slag recovery in this company. In this research work, cold bonded briquette was made from mixtures of milled slag and coke breeze. The effect of binder content on the strength of the briquettes was studied. The reduction of iron oxides was also investigated by heating up the briquettes in a muffle furnace. The results indicated that using 4wt% sodium silicate as binder leads to reasonable compression strength of about 1500kg although the strength could be increased to as high as 2000kg by using 6wt% binder. Up to 40% reduction, the reducing rate was almost high; then it decreased and reached a minimum value at 70% reduction. Using extra carbon than the reaction stoichiometry didn't have significant effect on the reduction. Temperatures above 1000°C up to 1200°C had also a small positive effect on the reduction rate. When reduction was performed at 1000°C, for 180min, semi-reduced material (70% reduced) could be obtained, which can be used (cold or hot) in BOF or other steelmaking processes.

*Keywords:* EAF slag, Briquette, Recovery, Reduction.

### 1. Introduction

An integrated steel plant generates approximately 420 kg of solid waste per ton of steel, consisting mainly of slag, dust and sludge. Slag is actually a secondary resource of metals, rather than an end-waste which is utilized as a resource material in many areas. The conventional method for disposal of slag is dumping<sup>1)</sup>. Thanks to the intensive research work during the last 30 years, about 65% of the steel slag is used in qualified fields of application, but the remaining 35% is still dumped<sup>2)</sup>. However, it is possible to use the dumped slag in different fields of application such as cement production, road construction and civil engineering, fertilizer production<sup>3,4)</sup>, landfill daily cover, soil reclamation and water refinement and production of metallic iron and iron concentrate<sup>1)</sup> (Fig. 1).

Steelmaking slag comprises about 10–15 wt % of the steel output<sup>1)</sup>. It means that each year more than 100,000,000 tons of steel slag is produced in the world. Chemical compositions of various steelmaking slags are summarized in Table 1.

Steelmaking slag typically contains 20–25% iron.

which is normally in the form of iron oxide such as magnetite ( $\text{Fe}_3\text{O}_4$ ) or other complex oxides with CaO or  $\text{SiO}_2$ <sup>2)</sup>. Iron can be separated from slag by applying mineral processing technology and subsequently recycled as feed materials for the blast furnace. Due to high basic oxides (MgO, CaO) in the slag, it can be used as a part of flux used in iron and steelmaking processes<sup>1,2)</sup>.

The magnetic separation method can be used for separating metallic iron and iron minerals from steel slag<sup>5)</sup>.

As mentioned above, steel slag is usually subjected to metal recovery prior to its application outside the iron and steel making process. The methods for slag processing are different, depending on the cooling method, chemical and mineralogical composition of steel slag, and its application. In general, steel slag processing includes crushing, grinding, screening and magnetic separation, and sometimes removal of phosphorous<sup>2)</sup>.

In order to liberate metallic iron and iron-bearing minerals from steel slag, size reduction is necessary. By autogenous grinding, magnetic separation and screening, 8% metallic iron, 4–7% iron concentrate and 85% ironless slag can be obtained. The metals in iron and steel slag are tightly bound to the slag matrix and not readily leached, and there are few environmental concerns regarding their application.

However, by applying mineral processing technologies such as crushing, grinding, classification and magnetic

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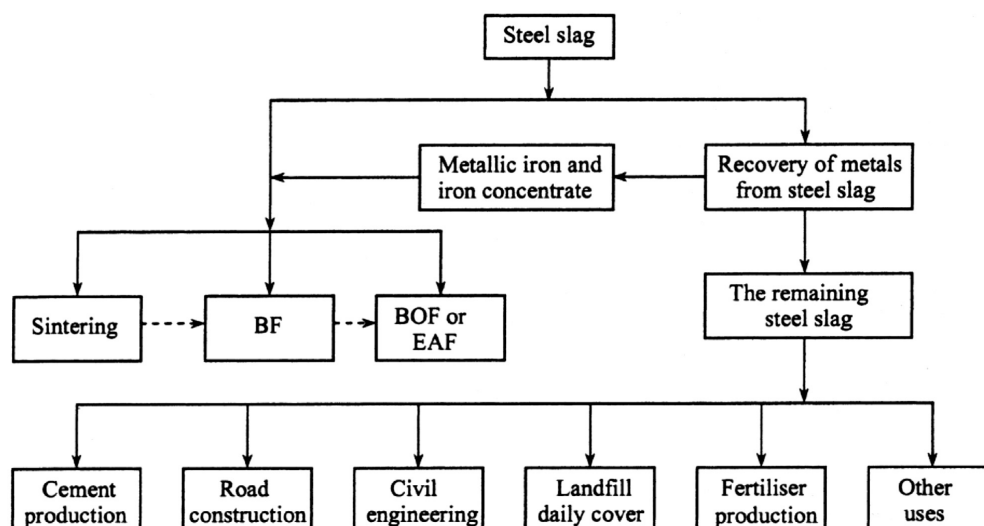
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Fig. 1. Utilization of steel slag <sup>1)</sup>.Table 1. Chemical composition of steel slag (wt %) <sup>2)</sup>.

Country	Slag	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	SiO <sub>2</sub>	MgO	MnO	CaO	Fe total
Europe	BOF slag low MgO content	<3	<2	18–12	<3	<5	55–45	20–14
	BOF slag high MgO content	<3	<2	15–12	8–5	<5	50–42	20–15
	EAF slag low MgO content	7–4	<1.5	17–12	8–4	<6	40–30	28–18
	EAF slag high MgO content	7–4	<1.5	15–10	15–8	<6	35–25	29–20
Japan	BOF slag (converter)	1.5	NR	13.8	6.4	5.3	44.3	17.5
	EAF slag (electric furnace oxidation)	7.0	NR	19.0	6.0	6.0	38.0	15.2
China	BOF slag	2.8–0.9	0.9	15–9	-2.5 10	6–1.5	48–34	27–17
USA	BOF slag	2	3–1	15–10	10–5	10–5	50–40	30–15

NR=no report.

separation, it is possible to produce iron concentrate (Fe>55%) from steel slag. Carbothermic reduction of slag and sludge to produce semi reduced iron has also been reported <sup>6)</sup>.

## 2. Experimental procedure

EAF slag from Mobarakeh Steel Company (MSC) and fine coke were used in this experiment as raw materials. Analysis of the slag (Table 2) showed that it contains 27.7%FeO and 7.3% Fe<sub>2</sub>O<sub>3</sub>.

The slag was crushed, ground and screened to 325 meshes. Grounded slag was mixed with fine coke and sodium silicate as binder, and pressed into briquettes. Briquette making was carried out at 150 kg/cm<sup>2</sup> pressure using a cylindrical die.

Cold-bonded Briquettes were reduced under isothermal conditions in a muffle electric furnace. Reduction was carried out at different temperatures (1000–1200°C) with time intervals of 20, 60, 120 and 180 minutes. Also, the effect of extra carbon than reaction

stoichiometry (reaction 1, 2) was considered and briquettes with 0, 30 and 100 wt% excess carbon (fine coke) were made. Chemical analysis was carried

out of reduced briquettes to determine un-reduced FeO content. The weight changes of the samples ( $\Delta m$ ) was also used to calculate degree of reduction according to equation (1):

$$R = 16 \Delta m / 28m_o \quad (1)$$

Where:

R= degree of reduction

$\Delta m$ = weight loss during reduction

$m_o$  = weight of the oxygen in iron oxide of the sample (could be worked out from chemical analysis of slag).

The Arrhenius equation ( $K = A e^{-E/RT}$ ) was used for the activation energy calculation; where, K = Rate Constant, A= Arrhenius Constant, E= Activation Energy, R= Gas Constant, T= Temperature.

Table 2. Chemical composition of EAF slag of MSC (wt.%).

FeO	Fe <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	MnO	P <sub>2</sub> O <sub>5</sub>
27.7	7.3	29.2	19.1	10	3.9	2.2	0.6

### 3. Results and discussion

Fig. 2 shows the change of briquette strength with binder dosage. As seen, compression strength of the briquette increases with increasing the binders content, and it reaches a constant value of 2000 kg at 8 wt% binder. Since compression strength of 1500 kg is adequate for most industrial reduction processes, 4 wt% binder were used to prepare samples for reduction tests.

The process parameters of the reduction experiments were reaction temperature, time and excess carbon percent than stoichiometry value (EC%). Reduction experiments of the composite pellets were carried out at 1000, 1100 and 1200°C with different fine coke consumptions.

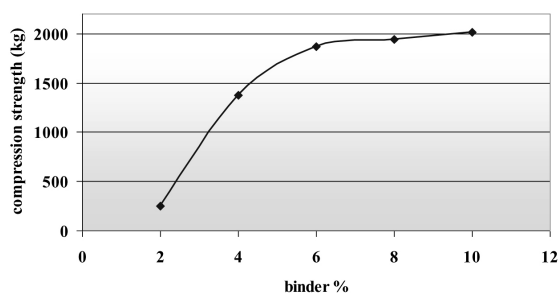


Fig. 2. Effect of binder dosage on the briquette compression strength.

Figs. 3 and 4 show the effect of temperature, time and EC% on the FeO % and degree of reduction, respectively. As seen in Fig. 4, the amount of reduction increases, for any EC ratio as the temperature increases. Also, longer reduction time is required at lower temperatures in order to reach the same reduction degree. The Effect of time on the reduction degree is higher than that of temperature. For all conditions, in order to reach a high degree of reduction (above 50%), the reduction time should be higher than 120 min.

Other researchers reported that reduction of iron oxides occurs either by carbon or by carbon monoxide, where indirect reduction with CO requires higher temperature; since the carbon gasification reaction is highly endothermic <sup>8,9)</sup>. However, the results indicate that temperature in the range of 1000-1200 °C does not have a great effect on the reduction rate. Using excess carbon also does not have a significant effect on reduction. As can be seen in Fig. 5, the rate of reduction is relatively high at the first 40% of reduction. In fact, the first 40% of reduction takes place at 60 min while the next 20% reduction requires 120 min time. This situation is usually the case when reduction proceeds with diffusion. As was noted, reduction experiments were carried out at 30 and 100% EC. Fig. 5 clearly indicates that increasing this ratio causes a little increase in the degree of reduction.

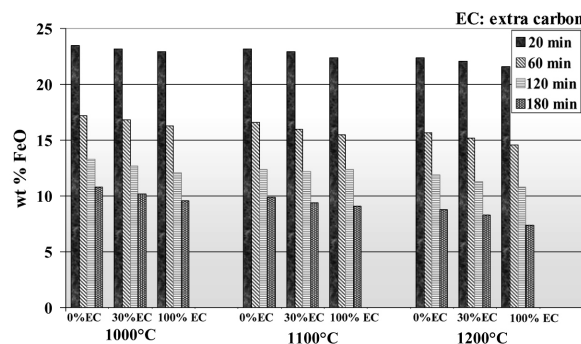


Fig. 3. FeO% of cold bonded briquettes containing different EC% reduced at time and temperature.

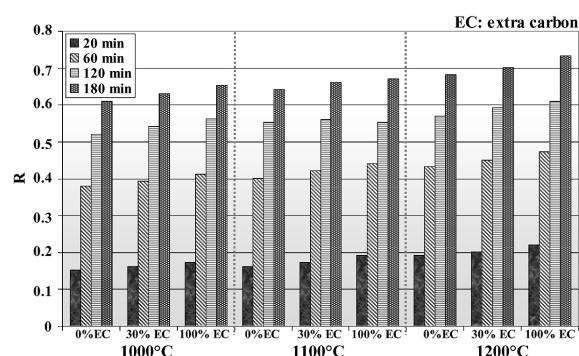


Fig. 4. Degree of reduction of cold bonded briquettes containing different EC%.

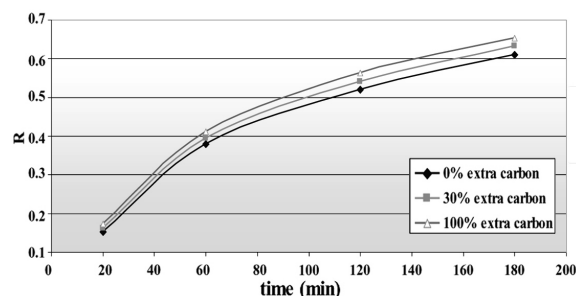


Fig. 5. Effect of EC % on the degree of reduction with increasing time at 1000°C.

#### Kinetics of DR process:

Reaction kinetics of iron ore reduction deals with the rate at which iron oxide is converted to metallic iron by removal of oxygen. The rate at which the ore is reduced influences the production rate, which ultimately determines the economic, feasibility, and competitiveness of the process technology involved. The reduction of iron oxide to metallic iron proceeds through various kinetic steps one of which is the slowest step, which controls the overall reaction rate. Different mathematical model equations are proposed to represent different rate controlling steps, which are given below:

**Equation**

$$1 - (1-R)^{1/3} = kt$$

$$-\ln(1-R) = kt$$

$$[1 - (1-R)^{1/3}]^2 = kt$$

$$1 - 2/3R - (1-R)^{2/3} = kt$$

$$k'[1 - 2/3R - (1-R)^{2/3}] + D/r_0[1 - (1-R)^{1/3}] = kt$$

**Controlling step**

Chemically controlled

Chemically controlled

Diffusion Controlled

Diffusion Controlled

Mixed Controlled

The results of the isothermal reduction of slag for different time, temperature and EC% are shown in Fig. 4. In order to ascertain the appropriate kinetic equation, these results were checked against standard reduced time plots. Reduced time plots of experimental data are then superimposed on them in order to determine which theoretical plot fits the experimental data. Fig. 6 shows the theoretical plots for five kinetic laws and experimental points from the reduction data presented in Fig. 4. It is found that the following model would change linearly with time,

$$1 - 2/3R - (1-R)^{2/3} = kt \quad (2)$$

This model shows that the reduction process was diffusion control. Fig. 7 shows the Arrhenius plot. Slope of the graph gives the value of activation energy which was calculated from Arrhenius Equation:  $K = Ae^{-E/RT}$ . The activation energy of the process was calculated as 96.52 kJ/mole. In a number of other research involving the iron oxide-carbon system, kinetic data obtained were found to fit the Ginstling-Brounshtein model ( $1 - 2/3R - (1-R)^{2/3} = kt$ )<sup>7,8</sup>. The activation energy values they calculated seem to be lower than those found in this study. Utilization of slag in present work in comparison to iron oxides with higher purity is a reason for this.

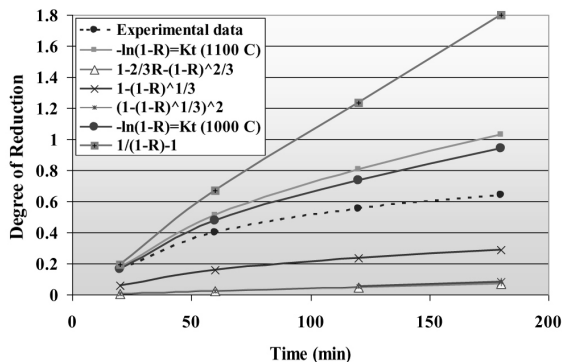


Fig. 6. Experimental data compared with five different kinetic mechanisms.

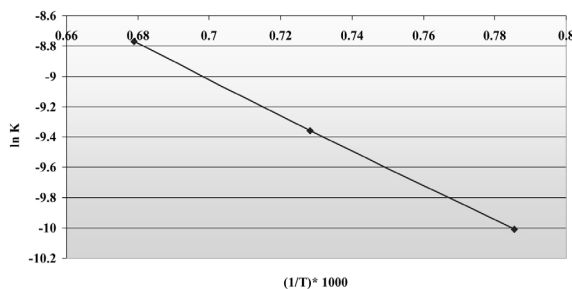


Fig. 7. Arrhenius plot  $\ln(K)$  vs  $1/T \times 10^3$ .

**4. Conclusion**

- Cold bonded briquette can be produced from the crushed steelmaking slag, using sodium silicate as a binder. With addition of 4 wt% binder, compression strength of about 1500 kg can be obtained. The strength reaches a maximum of about 2000 kg when 8 wt% (or more) binder is used.
- Excess carbon above the stoichiometric value doesn't have a significant effect on the rate of reduction at the experimental conditions.
- Temperature in the range of 1000 – 1200 °C has a little effect on the rate of reduction, being higher at higher temperatures.
- The reduction process could be divided in to two stages. The reduction rate at the first stage (up to 40 % reduction) is relatively higher than that in the second stage. However, at 1200 °C a reduction degree of 70 % can be achieved after 180 min.

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