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Redducibility Mill Scale Industrial Waste Via Coke Breeze at 850-950°C

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Abstract:
Mill scale is a very attractive industrial waste due to its elevated iron content (about = 69.33% Fe) besides being suiTab. for direct recycling to the blast furnace via sintering plant. In this paper the characteristics of raw materials and the briquettes produced from this mill scale were studied by different methods of analyses. The produced briquettes were reduced with different amounts of coke breeze at varying temperatures, and the reduction kinetics was determined. The activation energy of this reaction ≈ 61.5 kJ/mole for reduction of mill scale with coke breeze in the form of briquettes with 2% molasses where the chemical reaction interface model is applicable.

Keywords: Mill scale, Briquetting, Drop damage resistance, Cold crushing strength - reduction kinetic, Reduction by coke breeze.

1. Introduction
The management of wastes generated by integrated steel works has become an important issue due to ever-tightening environmental regulations Ladin et al. [1] indicated that the re-utilization of these wastes cost additional $20/t steel to the manufacture. Ladin et al. [1] illustrated that the reduction by the carbothermic process should carried out at the optimum time and C fix/Fe total ratio = 0.35 or the stoichiometric ratio should be about 1.4. Also it was found the model of reaction was that of Ginstling – Brounshtein and the energy of activation = 48 kJ/mole.
Bryk and Lu [2] studied the reduction behavior of commercial magnetite concentrate and carbon mixture in the temperature of 900-1300°C. They concluded that the reaction kinetics was affected by furnace temperature, heat transfer, particle size of coal, coal: ore ratio and the type of reducing agent.
Chinmaya and Sandesh [3] carried out the reduction process on blended mill scale powder in an inert atmosphere at 950°C in a tubular furnace for 3 hours using three different routes: reduction by C, reduction by H₂ and reduction by C+H₂ respectively. In all cases the inert atmosphere was maintained by a continuous supply of nitrogen (N₂). The results show a yield 78.14% of pure Fe in the first case and 84.89% and 83.77% of iron in the second and third cases respectively.
Fahri et al. [4] carried out the experiments on pelletized mill scale and solid

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reductants mixtures into the rotary kiln at temperatures 1050°C, 1100°C and 1150°C; they used different reductants type (anthracite and metallurgical coke) and different amounts of reductants (150% and 200% stoichiometric carbon) at different duration times during the reaction. The results were characterized using chemical analyses methods, XRD (X-ray Diffraction) and EPMA (Electron Probe Micro Analyzer) techniques. The high metallization degree was determined as 97.4% at 1150°C with anthracite applied as 200% of the stoichiometric required amount during the experiments.

Takahashi et al. [5] studied reaction rates for the reduction of iron oxide, the gasification of coke and the thermal decomposition of the binder in oxidized iron-scrap briquettes containing pulverized coke under the conditions of increasing and fixed temperatures in the nitrogen atmosphere. They indicated that the weight decrease in the reduction reaction of the briquette in the temperature range of 1270 to 1500 K. and the results showed high reaction rate at higher temperature and the retardation of reaction rate at later stage of reaction.

Ünal [6] studied the production of sponge iron by direct reduction of oxides and the effect of reductants on metallization and they concluded that (i) direct reduction using both solid and gas reductants caused higher metallization compared to using only solid reductants, (ii) as the reduction time and ratio of fixed C/Fe total increased % reduction of ore increased. The aim of this paper is to study the reduction of mill scale by coke breeze to produce iron powder.

2. Materials and experimental

2.1. Materials

The rolling mill scale used in this work was provided by a mill of the Egyptian iron and steel Co. The sample was submitted to chemical and X-ray analysis. The chemical analysis of mill scale is illustrated in Tab. I.

**Tab. I Chemical analyses of mill scale.**

<table>
<thead>
<tr>
<th>Weight %</th>
<th>Constituent</th>
</tr>
</thead>
<tbody>
<tr>
<td>69.33</td>
<td>Fe total</td>
</tr>
<tr>
<td>1.74</td>
<td>Fe metal</td>
</tr>
<tr>
<td>7.00</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>17.26</td>
<td>Fe$_3$O$_4$</td>
</tr>
<tr>
<td>7.83</td>
<td>FeO</td>
</tr>
<tr>
<td>0.33</td>
<td>S</td>
</tr>
<tr>
<td>0.22</td>
<td>P</td>
</tr>
<tr>
<td>0.66</td>
<td>MnO</td>
</tr>
<tr>
<td>1.92</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>0.04</td>
<td>C</td>
</tr>
</tbody>
</table>

The X-ray analysis is illustrated in Fig. 1. From which it is clear that mill scale mainly consists of Wustite, magnetite, iron, hematite and quartz.
2.2 Coke Breeze

The chemical composition of coke breeze used contains 90.6 % fixed carbon, 1.16% volatile matter, 8.24% ash, and 0.75% humidity. About 96.5% of the coke breeze fines used in this work have size in range -0.25 + 0.125 mm.

3. Experimental Procedures
3.1 Preparation of Samples

The preparation of samples for the briquetting process was carried out by mixing of mill scale with different stoichiometric ratios of carbon to convert all FeO & Fe₂O₃ to Fe according to the following equations:

\[
\begin{align*}
&\text{FeO} + C \rightarrow \text{Fe} + \text{CO} \\
&\text{Fe}_2\text{O}_3 + 3C \rightarrow 2\text{Fe} + 3\text{CO}
\end{align*}
\]

10 grams of the mixture of mill scale with different stoichiometric coke breeze with 2% molasses binder was pressed in the mould (12 mm diameter and a height 22 mm using MEGA.KSC-10 hydraulic press).

The stoichiometric amount of coke

\[
(Z) = \frac{100 \times X}{Y}
\]

Where X = Stoichiometric amount of carbon.
Y = Percentage of carbon in coke.

The produced briquettes were subjected to mechanical tests (Drop damage resistance test) [7,8] and compressive strength tests (Annual Book of ASTM Standards).

3.2 Reduction Procedures

The reduction of mill scale with carbon was performed in thermogravimetric apparatus in nitrogen atmosphere. This scheme is similar to that used by El Hussiny and Shalabi [9,10] (Fig. 2). The reduction procedure is similar to that described in that paper.
The percentage of reduction was calculated according to the following equations:

\[
\text{Percent of reduction} = \frac{(W_0 - W_t) \times 100 \times 16}{\text{Oxygen(m)} \times 28}
\]

Where:  
- \(W_0\) the initial mass of sample after removal of moisture.  
- \(W_t\) mass of sample after each time, \(t\)  
- Oxygen (m) indicates the mass of oxygen percent in mill scale sample  
- Concentrate in form \(\text{FeO} \& \text{Fe}_2\text{O}_3\).

4. Results and Discussion

Figs. 3 and 4 show the relation between the change of pressure load at constant amount of molasses (2%) on the drop number (drop damage resistance) and cold crushing strength (CS) of the briquette which contain one stoichiometric amount of coke breeze. It is clear that as the compacting pressure load is increased both the drop damage resistance and crushing strength increased. This is due to the fact that an increase in pressure load increases the compaction of briquette and subsequently the Vander Waals forces [11,12]. Also the increase of briquetting pressure leads to progressive crushing of the macro pores [13].
4.1. Effect of Stoichiometric Amount of Coke Breeze Added on The Mechanical Properties of The Briquette

Figs. 5 and 6 illustrate the effect of stoichiometric amount of fine coke breeze added to mill scale on the mechanical properties of the briquette pressed at constant load (173.5 MPa) and amount of molasses added 2%. From these two figures it is evident that as the amount of coke breeze increased both drop damage resistance and cold crushing strength increased.

Fig. 5. Effect of stoichiometric amount of coke breeze added on drop damage resistance of briquettes.

Fig. 6. Effect of stoichiometric amount of coke breeze added on crushing strength.
4.2. Effect of Stoichiometric Amount of Coke Breeze on The Degree of Reduction

Fig. 7 shows the effect of amount of coke stoichiometry on the reduction percentage of mill scale at temperature 900°C. It is clear that as the stoichiometry amount of coke increased the reduction of mill scale increased. It is also clear that as the time increased the reduction increased.

![Fig. 7. Effects of time on the degree of reduction of the briquette of mill scale with different amount of coke breeze.](image)

4.3. Effects of Temperature on The Degree of Reduction with Coke Breeze

Experiments were performed in the temperature range of 800 to 850°C in nitrogen atmosphere for the briquette contain 2 stoichiometric amount of coke breeze and pressed at 173.5 MPa. Plots of the reduction percentage of mill scale by coke breeze as a function of time are shown in Fig. 8. From this Figure, it is clear that the reduction rates increased with increasing temperature. At high reduction temperatures (more than 900 and up to 950°C), with increasing temperature, the oxygen removal increased. The increase of reduction percentage with rise of temperature may be due to the increase of number of reacting moles having excess of energy which leads to the increase of reduction rate [14,15].

![Fig. 8. Effects of temperature on the degree of reduction of the briquette of mill scale with coke breeze.](image)
4.5. Kinetics of Reduction of Mill Scale by Coke Breeze

The following models have been used to interpret experimental results of Fig. 8. When chemical reaction at interface controls in cylindrical pellets, the following equation is used [16].

\[
1 - (1 - R)^{1/2} = k.t
\]

Where:  
- \( R \) is the fraction reduction
- \( k \) is the rate constant
- \( t \) is time

The results show that this model gave fair straight lines at all temperatures (as shown in Fig. 9); the slopes of these straight lines gave the constant rate for each reduction temperature.

The natural logarithms of these constants were used to calculate the activation energies (Fig. 10). From the slopes of these straight lines, it was found that the activation energy of these reactions 61.5 kJ/mole.

![Graph showing the relationship between [1-(1-R)^{1/2}] and reduction time of briquette of mill scale with coke breeze.](image1)

**Fig. 9.** Relationship between \([1-(1-R)^{1/2}]\) and reduction time of briquette of mill scale with coke breeze.

![Graph showing the relationship between Ln k and 1/T.](image2)

**Fig. 10.** Relationship between Ln k and 1/T.
4.6. X-ray Analysis of Sample Reduced by Coke Breeze at 950°C

Fig. 11 illustrate x-ray analyses of a reduced mill scale briquette contain 2 stoichiometric amount of coke breeze in nitrogen atmosphere at (950°C). From which it is clear that the reduction of mill scale reached to about 100% metallic iron and it is clear that there is some carbon stayed in the reduction sample.

![Fig. 11. X-ray analysis of sample produced at 950°C.](image)

4.7. Microscopic Analyses of the Reduced Mill Scale Briquette by Coke Breeze

Figs. 12 to 14 show that the microscopic analyses of the produced mill scale briquette by coke breeze in nitrogen atmosphere for different stoichiometric amounts of coke. When the amount of coke breeze is stoichiometric, the phases shown in the micrograph of the reduced briquette at 900°C are: Wüstite (grey), iron (white) and pores (black) the present of wüstite is due to incomplete the reaction and the present of pore due to the escape of carbon monoxide. The microscopic analysis of a reduced briquette with twice the stoichiometric amount of coke breeze at 900-950°C shows only iron (white) and pores(black).

![Fig. 12. Microscopic structure of the reduced mill scale briquette at 900°C & amount of coke breeze added equal the stoichiometric amount.](image)
Fig. 13. Microscopic structure of the reduced mill scale briquette at 900°C amount of coke breeze added equal twice the stoichiometry amount.

Fig. 14. Microscopic structure of the reduced mill scale briquette at 950°C amount of coke breeze added equal twice the stoichiometry amount.

5. Conclusions

As the pressing pressure load increased both the drop damage resistance and crushing strength of the briquette of mill scale and coke breeze increased. As the amount of coke breeze increased the quality of the mechanical properties of briquette improved.

The reduction rates increased with increasing temperature. At high reduction temperatures (more than 900 and up to 950°C), with increasing temperature, the oxygen removal increased.
The activation energy of this reaction \( \approx 61.5 \text{ kJ/mole} \) for reduction of mill scale with coke breeze in the form of briquettes with 2% molasses where chemical reaction at interface is applicable.

6. References

3. Chinmaya Joshi and Sandesh Gokanwar under Prof. N.B. Dhokey,“Recovery of metallic iron from mill scale”, Department of Metallurgy and Material Science, College of Engineering, Pune 3 october 2012.