Kinetics of Reduction of El-Dekheila Pellets Fine Waste and Mill Scale Briquettes Using Hydrogen

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Abstract

Iron pellets are used in the production of steel at the El-Dekheila plant, West of Alexandria on the Northern coast of Egypt. A fraction of these pellets, reaching up to 10%, is lost by breakage on handling. In this paper, hydrogen reduction of briquettes consisting of waste iron pellets admixture with mill scale in different percentages was investigated. The kinetics of reduction of the pellets with different percentages of mill scale (20, 50 and 80%) was studied at different temperatures ranging from 700°C to 950°C. The results showed that maximum reduction could be reached after 20 minutes. The reduction process was found to be controlled by reaction at interface between hydrogen and solid particles. The activation energies of reduction at 20, 50 and 80% mill scale were found to be 28.78 kJ.mol^{-1}, 33.44 kJ.mol^{-1}, and 34.02 kJ.mol^{-1} respectively.

Keywords: Reduction, Mill Scale, El-Dekheila Iron Pellets Waste, Kinetics, Activation Energy

INTRODUCTION

In the iron and steel industry solid wastes are mainly produced from steel mills where large amounts of slag are produced. Also, environmental control operations associated with eliminating gaseous and liquid pollutants result in large amounts of solid wastes [1]. In this respect, iron-bearing by products such as dust, scale and sludge have been recycled or utilized [2].

Historically, mill scale was used as an oxidizer in conventional electric arc furnace in the steelmaking process. This has been replaced by oxygen lancing that resulted in higher melting and oxidation efficiencies. Some cement plants have also used minor amounts of mill scale as a raw material in the manufacture of clinker. However, this practice was abandoned as mill scale does not blend easily with other raw mix components because of its higher density [3]. On the other hand, mill scale waste management involves various activities such as collection, storage, transportation, disposal etc. These activities, even if properly controlled and proper precautionary measures adopted may have negative impact on land, water and air and consequently on human health.

Studies related to hydrogen reduction of iron ores show that the reduction mechanism depends to a great extent on the mineral composition of the ore. In this respect, Hugues et al. [4] have investigated the kinetics of reduction of Carol Lake and Kiruna ores (Sweden) in the temperature range 773–1143 K. They indicated that reduction could be interpreted by a shrinking core model. In a comprehensive work, Sun [5] investigated the kinetics of hydrogen reduction of iron ore – coal composites. He concluded that the controlling step in reduction with hydrogen is a combination of heat transfer, mass transfer and carbon gasification; although no values for activation energies were reported. Fruehan et al. [6] on studying hydrogen reduction of various types of Swedish ores indicated that the controlling step differed according to the fineness of the material used shifting from a chemically controlled to a diffusion controlled mechanism upon increasing the particle size. On the other hand, the reduction of pure hematite powder by hydrogen was studied by Wagner et al. [7] who followed the phase changes associated with increased reduction time in the temperature range 550 – 900°C. They concluded that the reaction was controlled by gaseous phase diffusion owing to the porous nature of the raw material used. They obtained relatively low values of activation energies for the hematite – magnetite – wüstite transformations (about 14 kJ.mol^{-1} in both cases). A different result was obtained by Long bottom and Kolbeinsen [8] using a sophisticated analog model. They investigated the reduction mechanism and concluded that while hematite is progressively reduced to magnetite then to wüstite, the limiting step of reduction is the final conversion to metallic iron.

Similar studies have also been performed on various iron ores using carbon monoxide as reducing agent. Prakasch [9] followed up the variation of reduction extent with temperature. He concluded that although empirical models and kinetic equations have theoretical significance and can be employed in elucidating the reaction mechanisms of iron ore, they may not be directly applicable to fluxed ore-coal composite pellets. On the other hand, Gudenau et al. [10] detailed the morphological aspect of iron ore reduction using hydrogen and carbon monoxide as separate reducing agents.

Recently, the reduction of iron ore pellets by H_2 – CO mixtures was investigated by Nyankson and Kolbeinsen [11] who deduced that the initial stage of the reduction process is interfacial chemical reaction controlled while the later stage is diffusion controlled. Also, Kazemi [12] found out that the apparent rates of reaction vary linearly with the H_2 and CO contents of the gas.

As far as Egyptian ores are concerned, the first study aiming at investigating their reduction kinetics was attempted by Sayed et al. [13] who investigated the reduction of iron ore powder with hydrogen in a static bed and followed up the reducibility as function of hydrogen flow rate and

temperature. Later, El-Hussiny et al. [14] studied the reduction of El-Baharia iron ore briquettes by hydrogen in the temperature range 700 to 950ºCand concluded that the extent of reduction highly depended on the hydrogen flow rate and temperature. They also found that the reduction of El-Baharia iron ore briquettes was diffusion controlled with activation energy of 36.12 kJ.mol^{-1}. They underwent a similar study on the same ore, in the form of pellets and obtained a different value for the activation energy namely 60.55 kJ.mol^{-1} [15]. On the other hand, Gaballah et al. [16] studied the reduction of mill scale by hydrogen and concluded that the reaction was diffusion controlled with an apparent activation energy 61.5 kJ.mol^{-1}.

Similar investigations were carried out to elucidate the reduction aspects of iron ore pellets using coke breeze as reducing agent. Hashem et al. [17] concluded that the reduction kinetics of ore briquettes using embedded coke breeze was best described by first order kinetics at temperatures below 1050ºC while the mechanism shifted to diffusion controlled reaction at higher temperatures. The same methodology was followed by other authors who researched the reduction of other Egyptian ores by embedded coke breeze [18, 19].

In the present work, hot rolling mill scale, mixed with El-Dekheila waste pellets was used to produce briquettes for potential use in the steel making process. After sintering, these briquettes were reduced by hydrogen and the reaction kinetics disclosed.

It is worth mentioning that a previous study was attempted by El-Hussiny and Shalabi [20] in which mill scale was added to blast furnace flue dust followed by briquetting and reduction with coke breeze. The reaction was found to be controlled by diffusion through the reduced layer with activation energies ranging from 131 to 148 kJ.mol^{-1} depending on the level of mill scale addition.

MATERIAL AND METHODS

Characterization of Raw Materials

Rolling mill scale was kindly provided by the Egyptian Iron and Steel Company (Helwan, Cairo) while El-Dekheila pellets waste fine was collected from El-Dekheila steel Company (El-Dekheila, Alexandria). The chemical composition of mill scale and El-Dekheila waste was determined using X–ray fluorescence spectrometry and is shown in Table (1).

X-ray analyses of both mill scale and El-Dekheila pellets waste are shown in Fig (1). Mill scale consists of a mixture of iron oxides (wüstite, magnetite, and hematite) besides quartz while the main phase present in El-Dekheila waste fines is hematite.

Table 1: Chemical analysis of raw materials

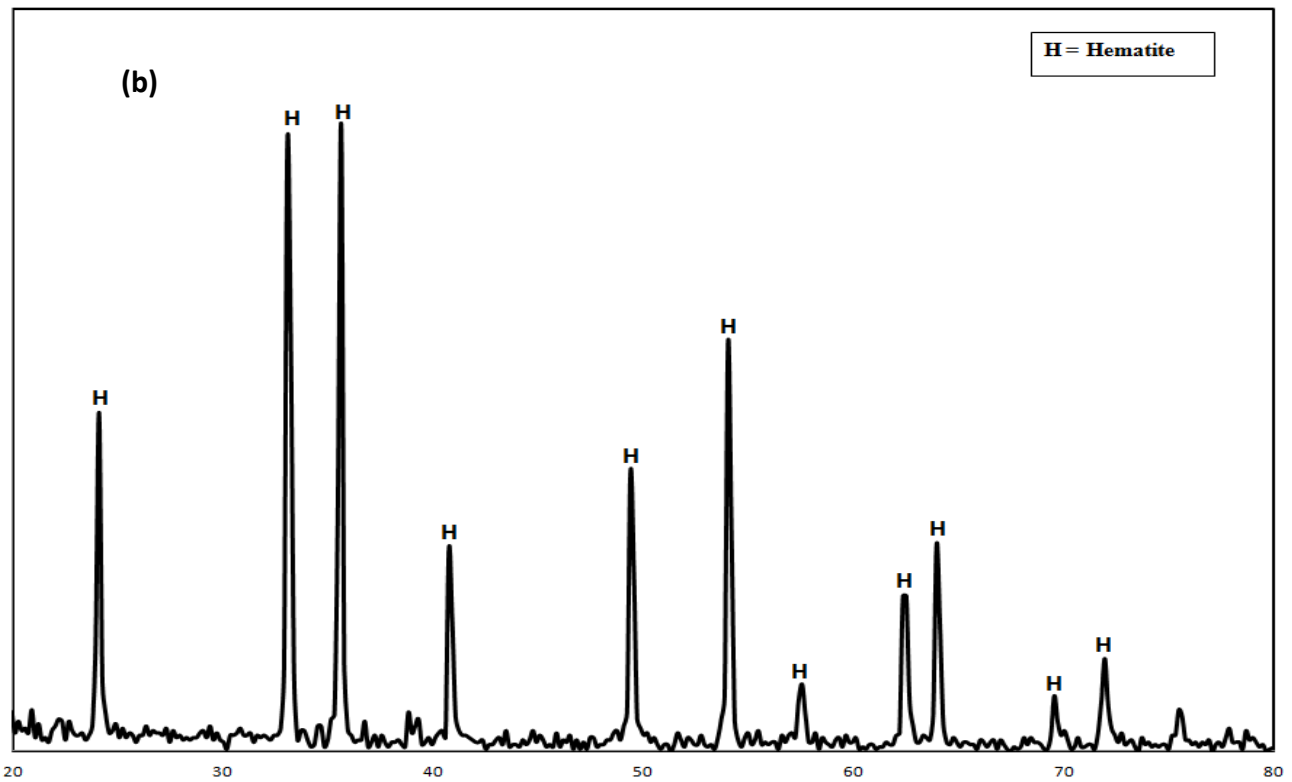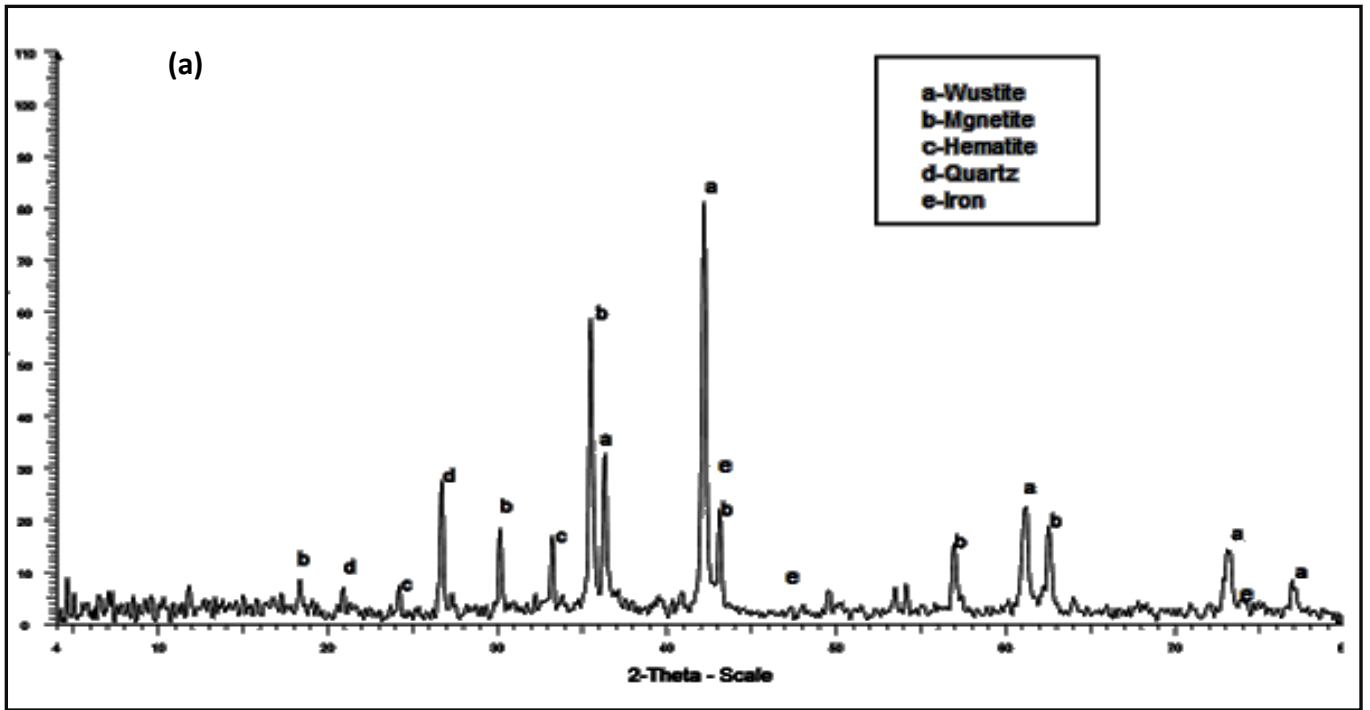| Constituent, Wt. (%)	Mill Scale	El-Dekheila Iron Pellets Waste Fines
Fe_{metal}	1.74	-
Fe_2O_3	70	95
Fe_3O_4	17.26	-
FeO	7.83	-
S	0.33	-
P	0.22	-
MnO	0.66	-
SiO_2	1.92	1.5
C	0.04	-
CaO	-	0.7

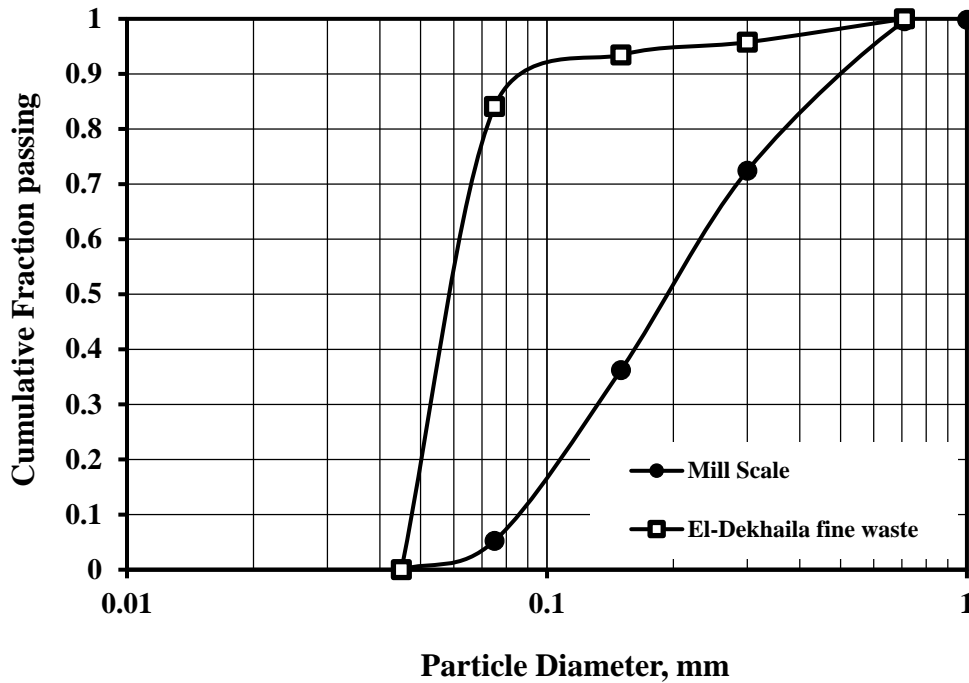**Figure 1:** XRD pattern of raw materials: (a) Mill scale, (b) El-Dekheila waste pellets fines

Figure 2: Screen analysis of raw materials

Screen analysis of the two raw materials used in this study revealed that fine pellets were much finer than mill scale as evidenced from Fig (2). The median particle sizes (D_{50}) were 0.19 mm and 0.055 mm for mill scale and pellet fine waste respectively.

Finally, the powder densities of the two materials were determined using the pycnometer method in accordance with ISO 1183 – 1 [21]. The values obtained were comparable: 5.21 and 5.18 $g.cm^{-3}$ for mill scale and waste fines respectively.

Experimental Methods

Mill scale (M) and El-Dekheila pellets waste fine (E) were mixed together with different percentages varying from 0% to 100% mill scale in presence of 2.5% wt. molasses and 3% wt. water as binders. Cylindrical briquette specimens were molded using MEGA.KSC-10hydraulic press. Both drop number and crushing strength were determined after three days to ensure complete drying of samples. This technique has been previously used in similar contexts [14, 16]. The briquette specimens were subsequently sintered at 1150°C for 2 hours. Three specimens were tested per sample and the average reading recorded.

A thermo-balance was used to reduce the fired briquettes using hydrogen. Nitrogen was introduced at a rate of 0.5 $L.min^{-1}$ at the start and at the end of reduction to purge any traces of air. The weight of sample was continuously recorded every 3 minutes and the weight loss was considered to be due to oxygen removal. The extent of reduction α was determined using the following equation:

Extent of reduction $\alpha = \dfrac{(W_0 - W)}{\text{Mass of Oxygen}}$ (1)

Where:

W_0 =Initial mass of sample after removal of moisture (g).

W = Mass of sample after time t (g).

The mass of oxygen indicates the mass of oxygen percent initially in the sample in the form of FeO, Fe_2O_3, and Fe_3O_4.

A similar technique has been used and described by El-Hussiny and Shalabi [20].

RESULTS AND DISCUSSIONS

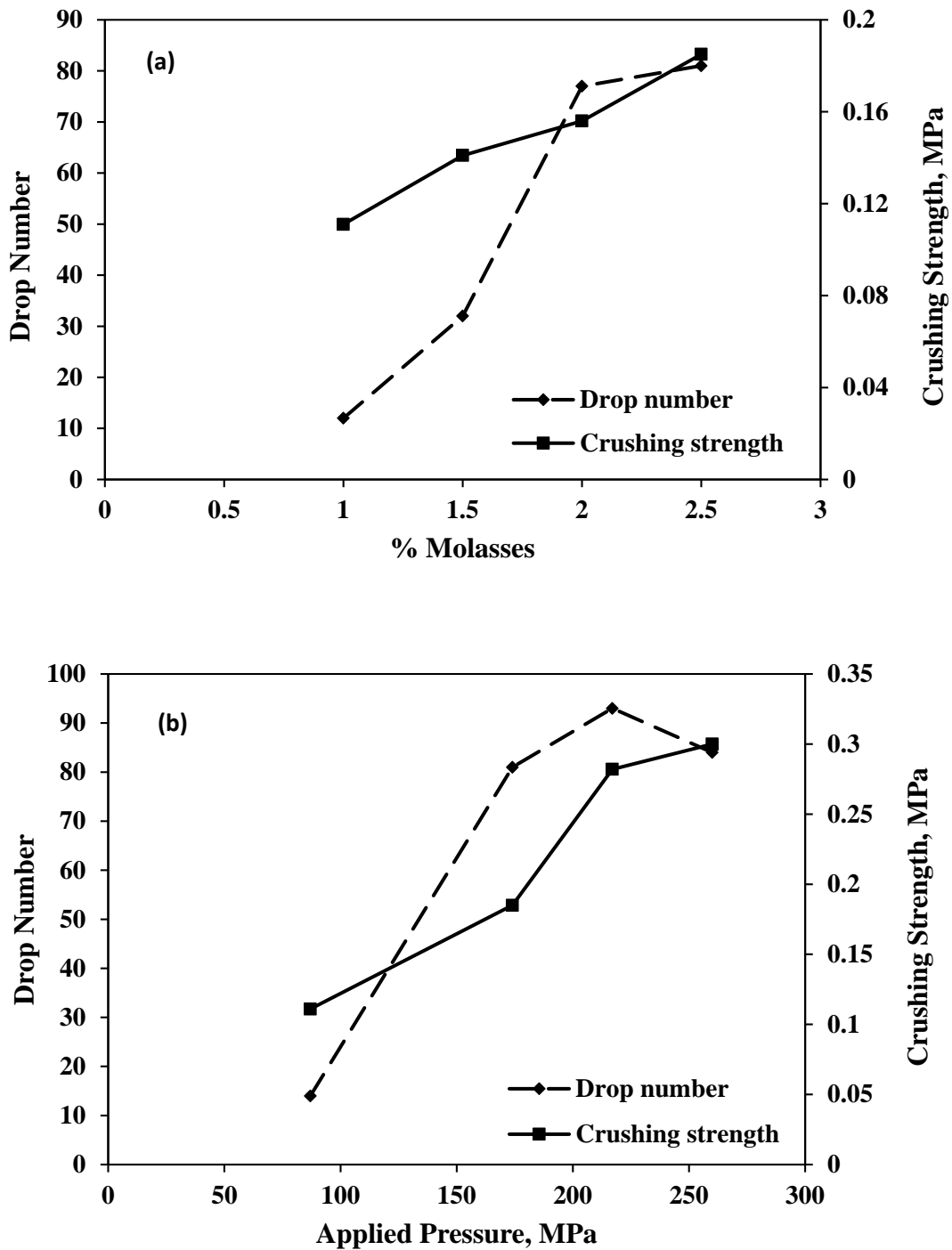**Effect of Molasses Percentage on Drop Nº and Crushing Strength**

Fig (3a) illustrates the effect of molasses percentage on both drop number and crushing strength of dried specimens of pellets fines pressed at about 217 MPa. As expected both properties increased by increasing molasses percentage and steadied at 2.5% molasses. This molasses concentration was accordingly used throughout the work. Molasses rather bituminous coal has been chosen for its cheapness and local availability [22, 23].

Effect of Forming Pressure on Drop Nº and Crushing Strength

Fig (3b) illustrates the effect of forming pressure on both drop number and crushing strength using 2.5% molasses. On increasing the applied pressure, the compaction of briquette increased leading to increased Vander Waals forces. The

highest forming pressure corresponding to the highest drop number obtained was found to be about 217 MPa, a value close to that obtained by El-Hussiny et al. [14] on testing similar specimens of another Egyptian ore (El-Baharia from the Western desert).

Figure 3: Effect of both molasses percentage and forming pressure on drop N° and crushing strength of dried samples

## Effect of Percentage Mill Scale on Drop N° and Crushing Strength

On adding mill scale to pellets fine waste using 2.5% binder and at a forming pressure of about 217 MPa, it was observed that the drop number increased to its maximum value of 100 at 20% mill scale and remained constant at that value. On the other hand, the effect of adding mill scale to fine waste powder on crushing strength of dried briquettes was insignificant, its values ranging from 0.3 to 0.32 MPa for addition levels from 0 to 100%.

Effect of Percentage Mill Scale and H_2 Flow Rate on Reduction at Temperature 950°C

Fig (4a) shows the variation of the extent of reduction of the sintered briquettes for different percentages of mill scale addition and different soaking times at 950°C. In all experiments the hydrogen flow rate was fixed at 1.5 L.min^{-1}. The curves indicate that 20 minutes are sufficient to reach a maximum reduction approaching 100%. It also shows that too low and too high a mill scale level tends to delay the reduction process with the best results achieved in the 20–50% mill scale region. Below 20% and above 50% mill scale, there is a tendency for the curves to shift to lower conversion for all times investigated. This is presumably due to the large particle size of mill scale particles compared to that of waste fines which tends to increase the porosity of the mix in the 20–50% mill scale range.

On the other hand, Fig (4b) shows the effect of varying the hydrogen flow rate on the extent of reduction of briquette samples containing 50% mill scale formed at a pressure of 217 MPa and sintered for 2 hours at 1150°C then reduced at 950°C. The percent reduction increased with increasing hydrogen flow rate from 1 to 1.5 L.min^{-1}. Above 1.5 L.min^{-1} the reduction process slowed down as evidenced by the relative position of the curves in the figure. This is presumably due to rapid diffusion of hydrogen across the briquettes at flow rates exceeding 1.5 L.min^{-1} which does not allow for enough interaction with different oxides. This suggests that the slowest controlling step of reduction is probably direct reaction at interface rather than diffusion of hydrogen across the product layer. That is why a hydrogen flow rate of 1.5 L.min^{-1} was adopted throughout this work.
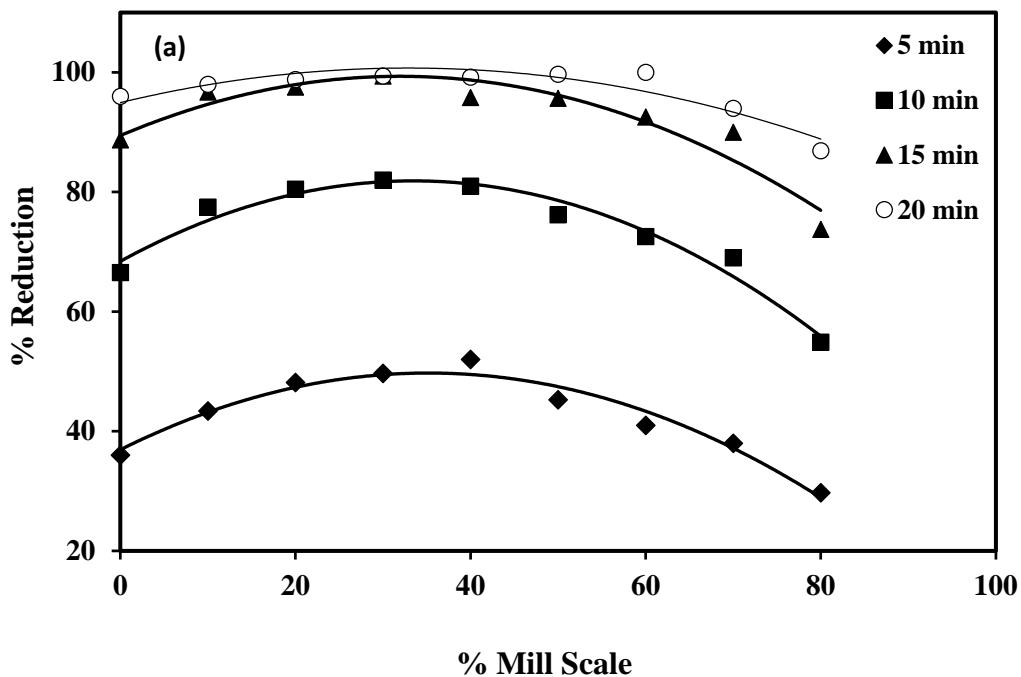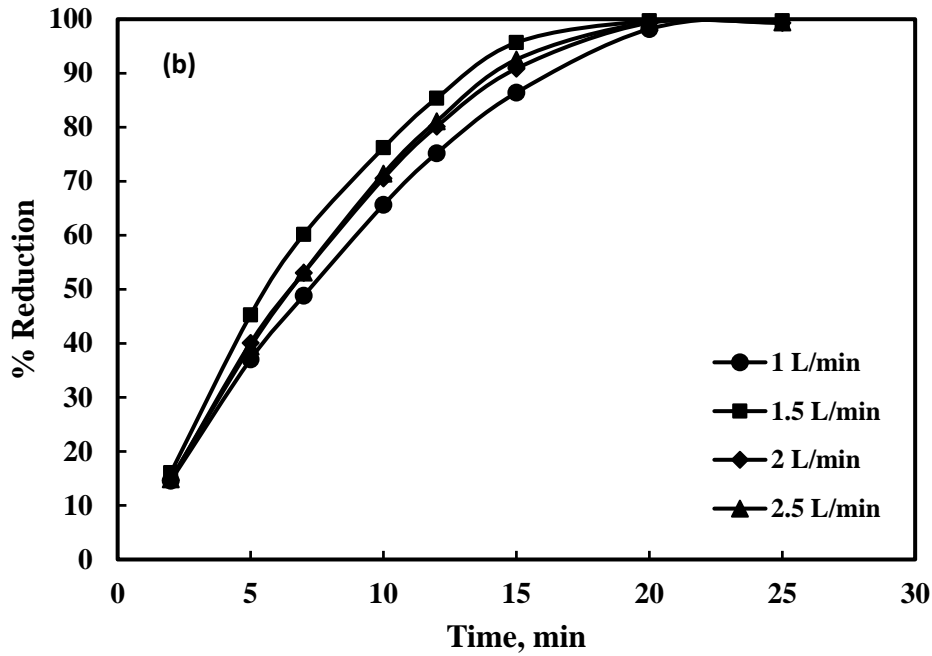
Figure 4: Effect of both mill scale addition and hydrogen flow rate on percent reduction at 950°C

To assess that interpretation, the bulk density of sintered pellets was calculated for unreduced briquettes, Fig (5) illustrates the variation of porosity following addition of mill scale. The porosity of briquettes can be calculated using the following equation:

$$\rho_B = \rho_T.(1 - p) \tag{2}$$

Where ρ_B = bulk density of the briquettes (g.cm^{-3})

ρ_T = true (Powder) density of mill scale and waste (g.cm^{-3})

The powder density was taken as 5.2 g.cm^{-3} without serious error since the individual densities are very close (5.21g.cm^{-3} for mill scale, and 5.18 g.cm^{-3} for waste fines).

The figure indicates the presence of a maximum porosity region between 10 and 50% mill scale. This facilitates the diffusion of hydrogen inside the sintered mass thus increasing the extent of reduction.
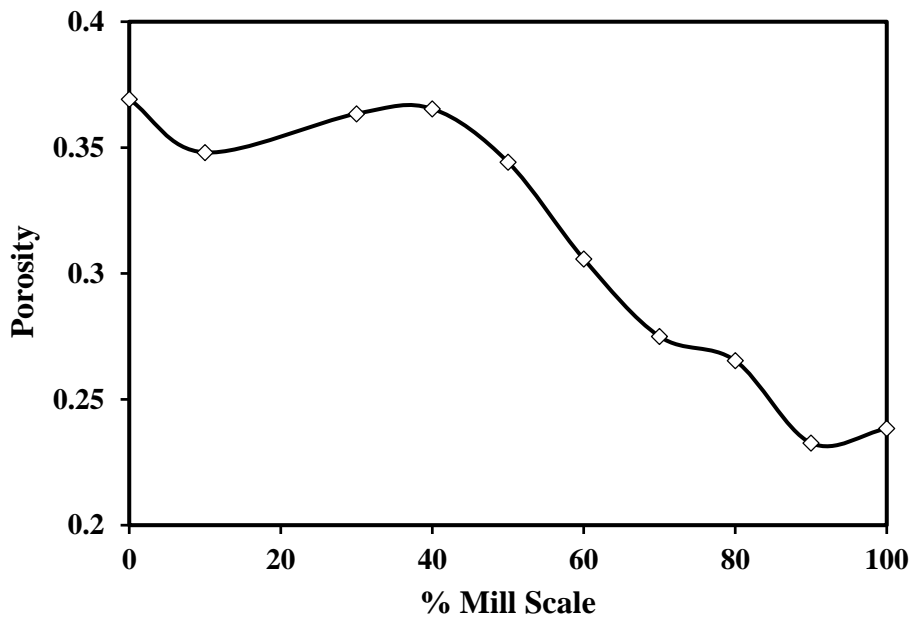

Figure 5: Variation of porosity of briquettes with mill addition

Figs (6 a, b) show the SEM micrographs of two samples: They correspond to specimens containing 30% and 90% mill scale respectively. While the first micrograph reveals the presence of porous regions, the second one shows less porosity associated with a higher level of sintering. These figures corroborate the previous findings that increasing the mill scale level over 50% enhances sintering producing low porosity briquettes that decrease the extent of reduction by impeding hydrogen diffusion.
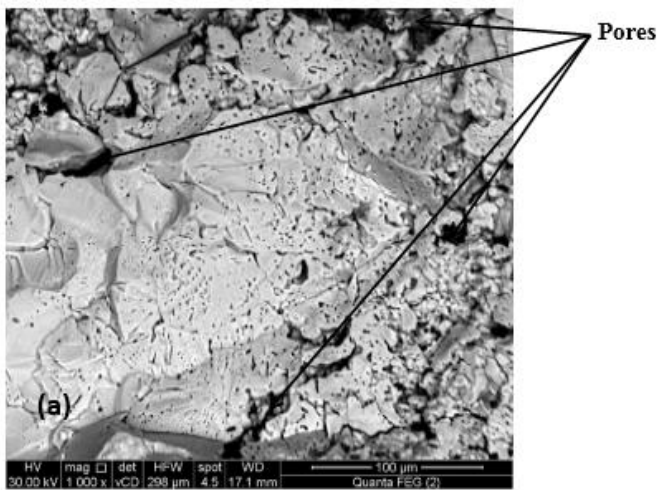

(a)
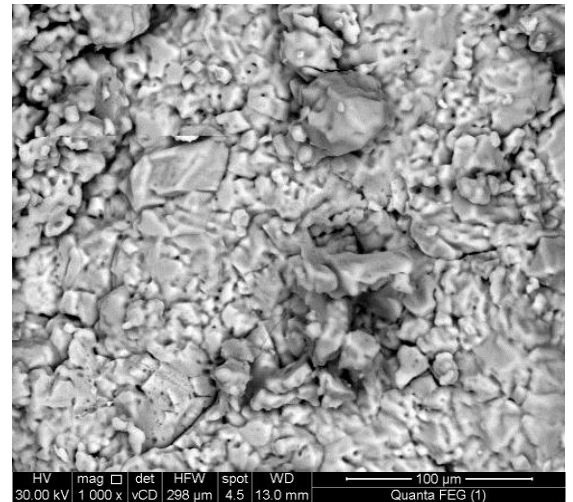
(b)

Figure 6: SEM micrograph for sample: (a) containing 30% mill scale at 1150°C for 2 hours, and (b) containing 90% mill scale at 1150°C for 2 hours

Kinetics of Reduction of Briquettes by Hydrogen

The kinetics of reduction of sintered briquettes using hydrogen was studied over the temperature range 700 – 950°C for samples containing 20%, 50% and 80% mill scale.

Fig (7) illustrates the variation of percent reduction of sintered briquettes containing 20% mill scale with time when reduced at a hydrogen flow rate of 1.5 L.min^{-1}. Similar curves displaying the reduction behavior at higher mill scale additions (50 and 80%) were also obtained but were not included to avoid redundancy.
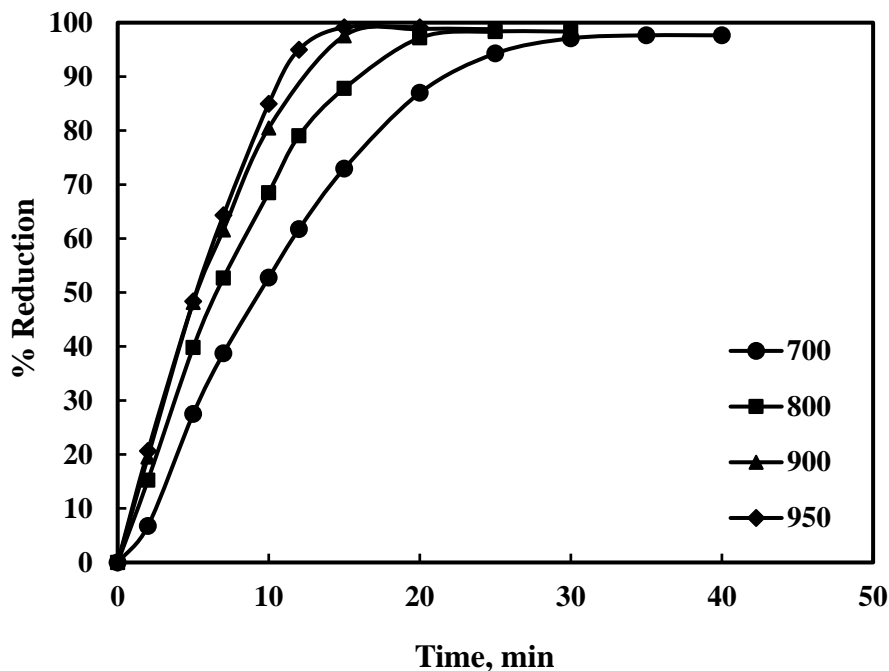
Figure 7: Effect of temperatures on the reduction of a briquette containing 20% mill scale

In all three cases, the model that best fitted experimental data was that of reaction at interface according to the following equation for cylindrical bodies [24].

$$k.t = 1 - (1 - \alpha)^{0.5}$$

(3)

Where

t = time (min)

k = reaction rate constant (min⁻¹)

R = fraction reduced

Fig (8) displays the relation between $f(R) = 1 - (1 - \alpha)^{0.5}$ and time at different reduction temperatures for the briquette containing 20% mill scale. The plot yielded sets of straight lines at all temperatures investigated, the minimum determination coefficient obtained being $R^2 = 0.995$. The slope of the straight lines obtained was calculated to deduce the reaction rate constant (k). Similar straight lines were obtained for the other two levels of mill scale addition investigated.
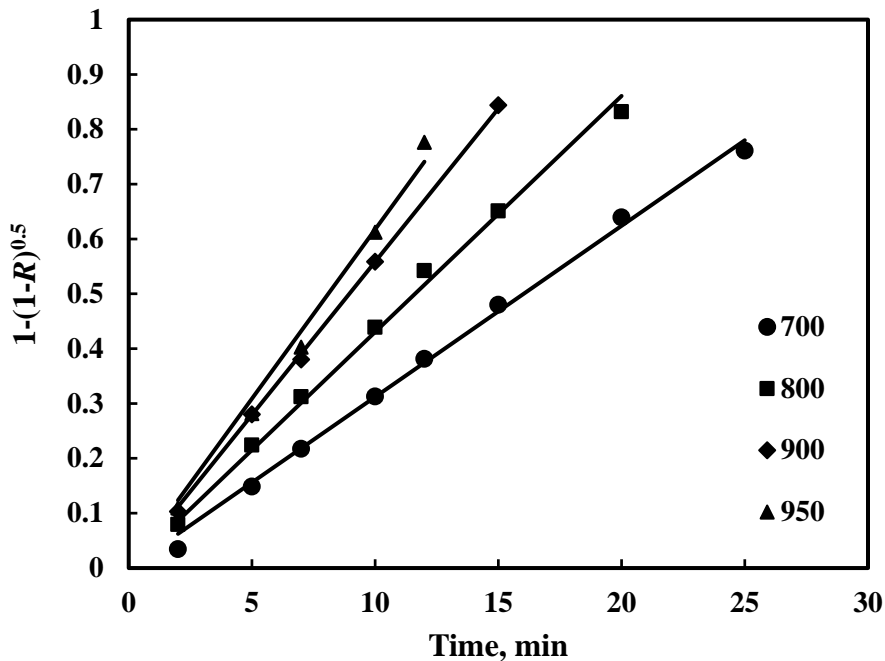

Figure 8: Chemical reaction at interface controlling plots (20% mill scale)

Arrhenius plots illustrated in Fig (9) show that straight lines were obtained on plotting (ln k) against (1/T) for the three level of mill scale addition. From the slope which equals to E/R, the results showed that the activation energy of 20%, 50% and 80% mill scale were 27.16 kJ.mol⁻¹, 33.44 kJ.mol⁻¹ and 34.02 kJ.mol⁻¹ respectively suggesting a slight increase in activation energy following increased mill scale addition.

Actually, the values of reaction rate constants (k) represent the reciprocals of the time required for complete reaction (τ) [25]. These values are reported in Table (2).

The values of (τ) in this table confirm that increasing the mill scale content causes the rate of reduction to decrease.

Since the slowest reduction corresponds to the mix containing 80% mill scale, Fig (10) was obtained to illustrate the XRD pattern of that mix after 20 minutes at reduction temperatures of 700 and 950°C. It is clear that the reaction is almost completed at 950°C as the main phase was metallic iron with minor wüstite inclusions while the reduction was far from completion at 700°C where various iron oxides can be observed including the highest oxidation state oxide, hematite. These results are in line with the calculated reaction times in Table (2).
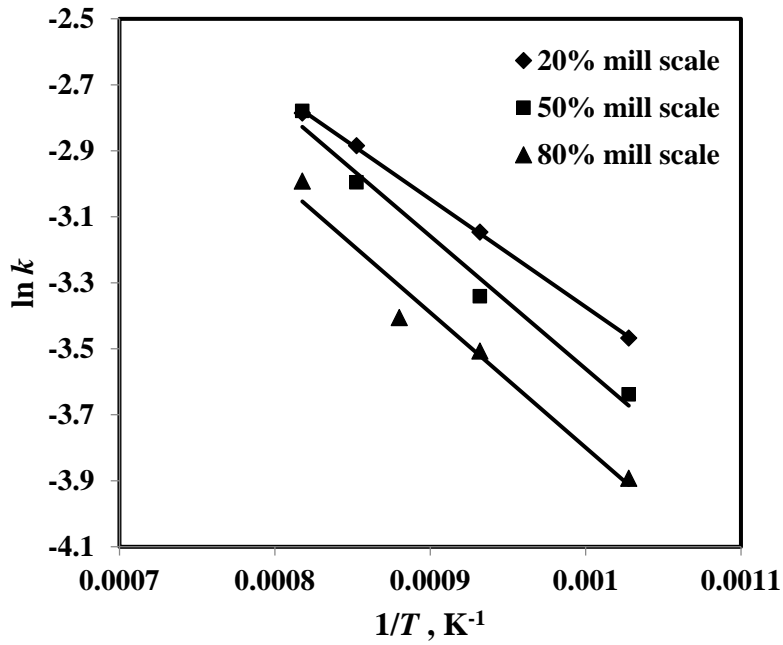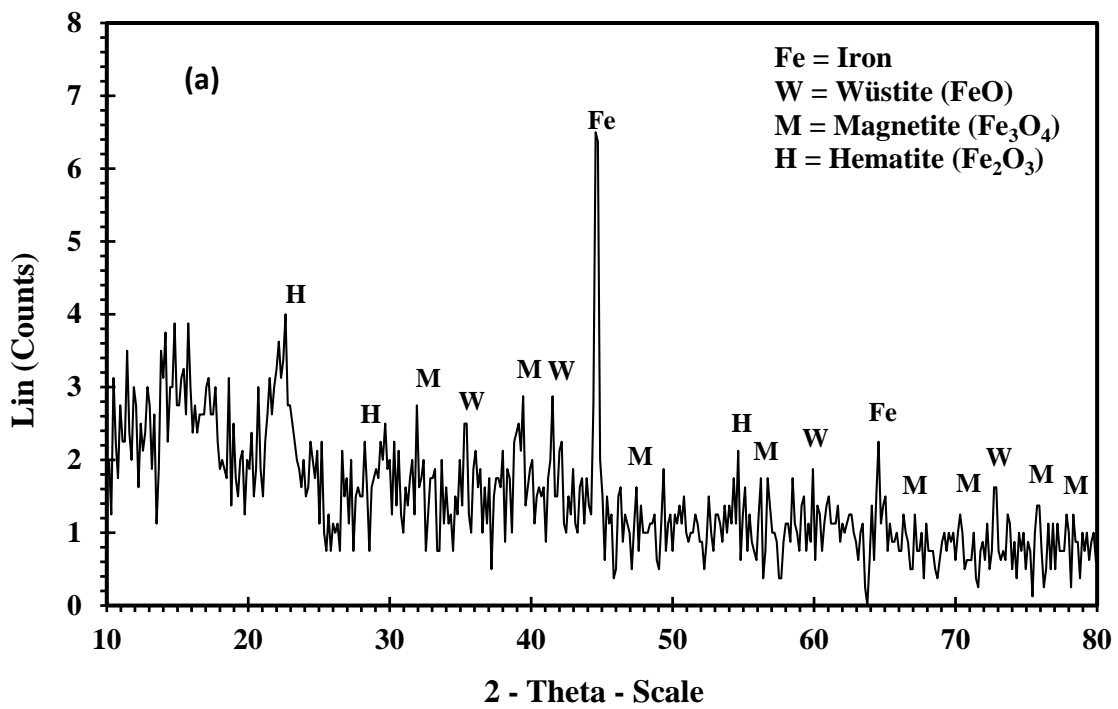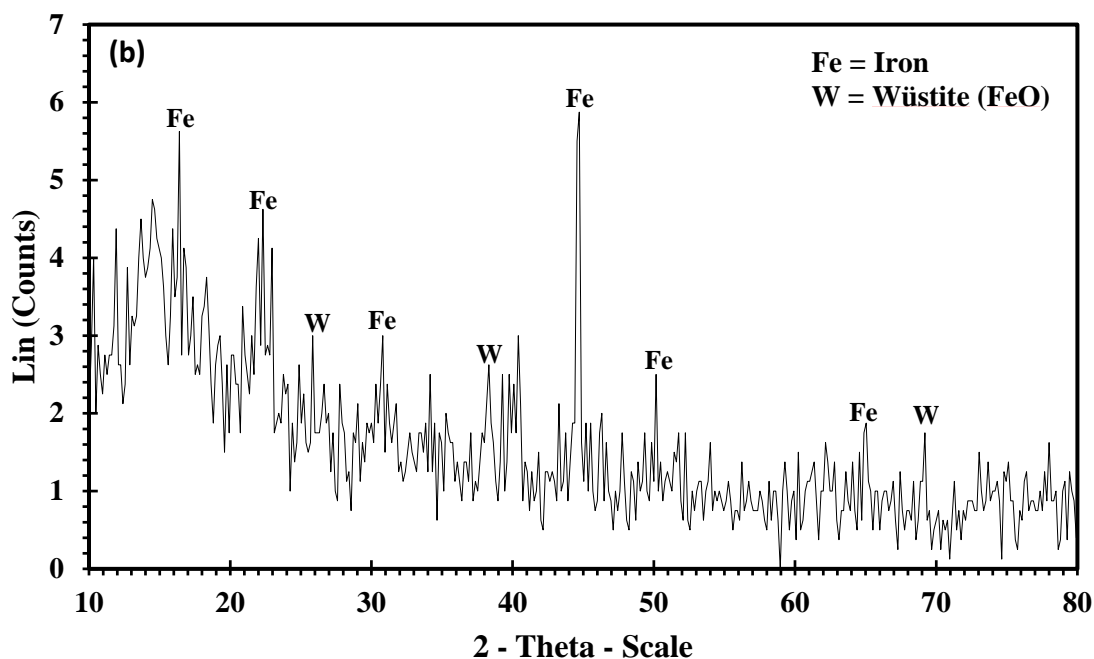
Figure 9: Arrhenius plots for reduction reaction

Table 2: Calculated time required for complete reduction (τ min)

% Mill Scale	700ºC	800ºC	900ºC	950ºC
20	32.0	23.3	17.9	16.2
50	38	28.2	20.0	16.1
80	49	33.3	30.1	19.9

Figure 10: XRD chart for samples containing 80% mill scale fired for 20 min at: (a) 700°C, and (b) 950°C

CONCLUSION

Fine pellet waste collected from El-Dekheila Steel Company was mixed with mill scale in levels ranging from 0 to 100% and briquettes were formed using 2.5% molasses binder and a forming pressure of 217 MPa. The samples obtained were then sintered at 1150°C and subjected to reduction using hydrogen in a thermo-balance at a flow rate of 1.5 L.min^{-1}. The following conclusions could be drawn:

a) A reduction time of 20 minutes at 950°C is sufficient to practically achieve full reduction at all levels of mill scale addition.

b) The percentage of mill scale addition that corresponds to maximum reduction ranges from 20 to 50% mill scale.

c) The reduction process of briquettes by hydrogen is controlled by reaction at interface with values of activation energies slightly decreasing with increased mill scale addition.

d) The time required for complete reduction at all temperatures investigated increases with increased mill scale addition.

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