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Study of Iron Ignition Phenomenon in Libyan Iron and Steel Company During Handling and Storage

دراسة ظاهرة اشتعال الحديد في الشركة الليبية للحديد والصلب أثناء المناولة والتخزين

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Abstract

The oxidation of iron has been associated with problems especially during handling, shipping, and storing. Among these problems are fires resulting from re-oxidation of previously reduced iron in direct reduction factories.

The oxidation of the direct reduction of iron (DRI) is an exothermic reaction, which usually proceeds to a violent fire in the direct reduction (DR) plant. Fire destroys equipment and lives leaving an economic emotional disaster. [3]. The purpose of this research paper is to identify and study the causes of this problem and give some recommendations to overcome it.

The results of this research indicate that fires are directly related to the oxidation of Directly Reduced Iron, DRI. It has been found that the major part of the problem was the stability of the FeO phase. Imposing a set of operating conditions will change the situation and prevent the occurrence of fire in the product discharge and also help prevent further oxidation of DRI.

Key words: **ignition**, **iron**, **oxidation**, **steel**, **pellet**, **sponge**,

الملخص

ارتبطت أكسدة الحديد بمشاكل خاصة أثناء المناولة والشحن والتخزين. ومن هذه المشاكل الحرائق الناتجة عن إعادة أكسدة الحديد المختزل سابقاً في مصانع الاختزال المباشر، اكسدة الحديد المنتج من الاختزال المباشر هي تفاعلات طاردة للحرارة. والتي عادة ما تؤدي الي حريق عنيف في مصنع الاختزال المباشر. تدمر الحرائق المعدات والارواح تاركة كوارث بشرية واقتصادية. والغرض من هذا البحث هو تحديد ودراسة أسباب هذه المشكلة وتقديم بعض التوصيات للتغلب عليها.

تشير نتائج هذا البحث إلى أن الحرائق ترتبط بشكل مباشر بأكسدة الحديد المختزل المباشر، FeO لقد وجد أن الجزء الأكبر من المشكلة كان استقرار مرحلة سيؤدي فرض مجموعة من ظروف التشغيل إلى تغيير الوضع ومنع حدوث حريق في تفريغ المنتج ويساعد أيضًا في منع المزيد من أكسدة الاختزال المباشر.

الكلمات المفتاحية: اشتعال، حديد، أكسدة، فولاذ، اسفنج.

Introduction

DRI with its sponge-like structure is chemically reactive and easily oxidized [6]. It is produced based on the cracking of a natural gas which is mostly methane using stream and carbon dioxide to form hydrogen and carbon monoxide, and utilizes natural gas in making sponge iron, DRI is convenient process to produce iron due to the its availability in local market.

Natural gas removes oxygen from iron oxide pellets without changing the state or the volume of the pellets [1]. H_2 and CO react with iron oxide to produce iron, carbon dioxide and water vapor.

Oxidation occurs when hot DRI reacts with oxygen in air or moisture to form iron oxides such as FeO_3 and Fe_3O_4. The other forms of DRI oxidations attributed to corrosion, the Corrosion occurs when DRI products are quenched in fresh or salt, these products react with oxygen to form rust, Fe_2O_3-Fe (OH) $_3$-H_2O. [4] The corrosion reactions will continue as long as water is present since the water evaporates at about 100°C. its apparent that the corrosion reactions have a low temperature limit even though the reactions are exothermic [6]

Previous investigations have been conducted to track sources of fire occurred in Misurata Iron and steel factory. These investigations have shown that the problem

usually occurred during the discharge of sponge iron from furnaces, in the product screens, and also in the dedusting units.

The DRI is usually carried out according to the following equations: [1]

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3\,H_2 + Heat \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

$$H_2 + \tfrac{1}{2}\,O_2 \rightarrow H_2O + Heat \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.2)$$

$$2Fe + 3CO_2 \rightarrow Fe_2O_3 + 3\,CO + Heat \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.3)$$

$$CO + \tfrac{1}{2}\,O_2 \rightarrow C_2O + Heat \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.4)$$

Kinetics and Mechanism of Oxidation

The temperature is a main cause in the oxidation of sponge iron. At temperatures below 175 ^{0} C no significant oxidation will occur. This was attributed to the concept that at this temperature range, the oxides formed are likely to be alpha-Fe_2O_3 over laying the gama-Fe_20_3 whereas above 175 ^{0} C, Fe_3O_4 if formed in place of alpha- Fe_2O_3. [1,5], Fig 3.1 shows the Fe-O system.

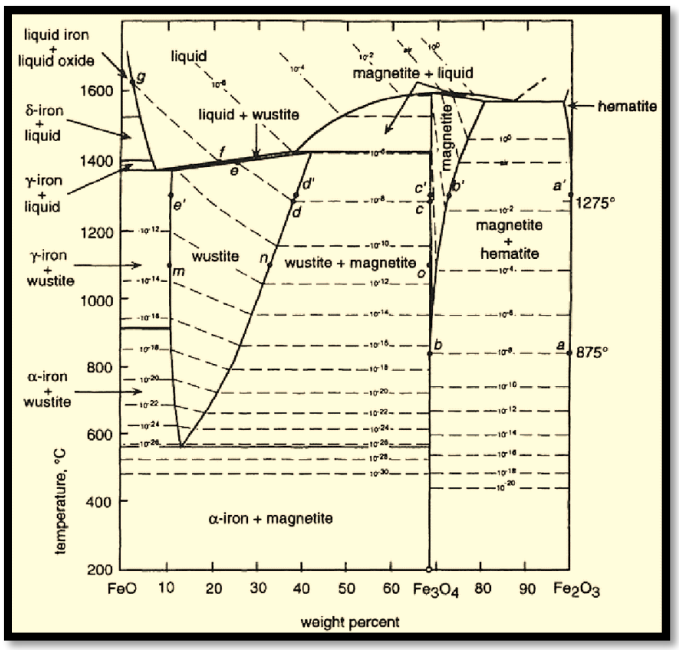

Fig 3.1 The phase diagram of the binary iron – oxygen system

Experimental Procedure

Material

A sample of a considerable amount of directly reduced iron pellets was taken directly from the convey belt of the product. Module II furnace, Misrata Iron and Steel factory.

The used ore was imported from Brazil. The chemical composition and physical properties are in Table 2.1. in Table 2.2 respectively. The average degree of metallization of DRI pellets was 91.03% and the average carbon content was 1.74%

Table 4.1 Chemical Composition of imported ore.

Chemical Composition	Percentage%
Fe	**68.090**
$Si0_2$	**1.13**
$A1_2O_3$	**0.590**
P	**0.019**
S	**0.002**
CaO	**0.710**
Mg	**0.230**

Table 4.2 Physical Properties of the Brazilian ore

Property	value
Bulk density	2.12 g/cm3
Porosity	30.5 %
Moisture	2.0%
Compressive Strength	310 kg/cm2

The sample is then sized into an average of 10-12mm in diameter and pellets are kept in a dry-sealed container oxidizing agent.

The oxidizing gas

The oxidizing gas was normal air at the seashore. The average ambient temperature was 32°C. The average moisture content was 36.5%

Inert Material

Nitrogen gas of 99% purity supplied from the Iron and steel factory was used as inert gas.

Apparatus

A reducibility testing system was converted to an oxidation system and was used in the oxidation experiments carried out at the Central Laboratory of the Iron and Steel factory. Figure 4.1. and Fig. 4.2 Show the reducibility testing system and schematic diagram of the experiment respectively.

Fig. 4.1 A Reducibility testing system

A-Furnace.
B-Alumina balls.
C- Stainless steel wire basket.
D- Thermal couple.
E- Screen.
F-Temp. measurement.
G- Temp. control panel.
H- Flow rate and pressure control.
I- Sensitive balance.
J- Nitrogen gas cylinder.
K- Air compressor.

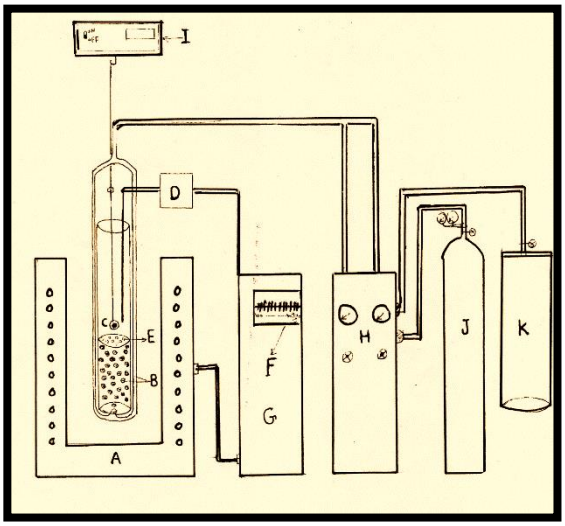

Fig.4.2 Illustration of the experiment

The Experiment:

The sample of each experiment consists of just one pellet of DRI accurately weighted, placed in a basket of stainless-steel wire and hung in the balance.

The furnace was heated to the required temperature using the temperature control in the control panel while applying a flow of nitrogen gas. When the required temperature was reached, the system was hold at that temperature for 10 minutes, so that the heat got distributed evenly on the body of the sample, afterward, the nitrogen flow turned off and the air flow turned on.

Balance readings were registered every ten minutes for two hours. Oxidation experiments were carried out first at a certain temperature and varied the oxidizing gas flow rate. The minimum flow rate of oxidizing gas was found to be 8 L/minute hence in the subsequent experiments the oxidizing gas flow rate was set to 10 L/minute.

Oxidation experiments were carried out at different temperatures starting at 25℃, 50℃, 1OO℃, 150℃ and then of 1OO℃ interval up to 8OO℃. In each experiment, the change in weight (ΔW) and time were recorded in a time interval of ten minutes for two hours.

After two hours air was turned off and turned on the nitrogen gas for cooling. Once the sample reached room temperature, nitrogen gas was turned off and the sample was carefully collected and put in a desiccator or in a sealed plastic bag for further processing such as x-ray metallography etc. for each experiment, the change in weight vs time was calculated and plotted also curves of oxidation % vs time were produced for each experiment.

Five samples were used in this experiment with different percent in the chemical composition and different temperatures at the same reaction time. Table 4.1shows the chemical composition of the samples which used at different temperatures. Table 4.2 illustrates the temperatures applied at 120 minutes for each sample alone.

table 4.1 the chemical composition of the samples (%)

SAMPLE	Fe	Mn	P	SiO2	TiO2	Al2O3	CaO	MgO	S	Cr
O1	72.62	.064	.033	.923	.316	.318	1.61	.816	.002	.017
O2	73.62	.017	.055	1.695	.059	.724	0.886	.360	.002	.010
O3	73.43	.075	.045	.865	.267	.299	1.739	.905	.002	.015
O4	73.42	.067	.026	.876	.234	.355	1.98	1.02	.002	.012
O5	72.95	.064	.036	.950	.295	.333	1.79	.880	.002	.013

Table 4.2 Temperatures applied at 120 minutes for the samples

Sample	Temperature (C°)	Time (minutes)
1	200	120
2	300	120
3	500	120
4	700	120
5	800	120

Results and Discussion

Oxidation experiment was carried out on DRI pellets from Module II of the direct reduction plant in the Central Laboratory. The reduction gas temperature was 780℃. The average metallization degree of pellets was 91.03% and the average carbon content was 1.74%. Oxidation experiments were performed at different temperatures using dry air as oxidizing agent.

The oxidation process was studied and correlated with the structure of the sponge iron. The course of oxidation was followed by a weight-gain as a function of time technique. The Oxidation Curves were plotted in Fig 5.1. As oxidation temperature increased to 200°C, an abrupt increase in the oxidation extent was observed (49% oxidation after 20 minutes). There are different oxidation stages which can be clearly distinguished from the graph.

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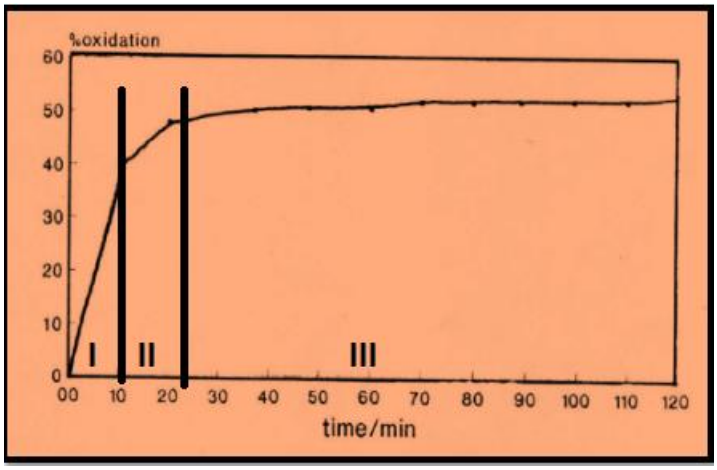


Fig 5.1 Oxidation % and time at 200℃ and 1 atm

The initial stage is characterized by very high rate of oxidation stage (I). The middle stage (II) has an intermediate rate and the latter stage (III) is marked by very small rate of oxidation.

Measurements to eliminate the effect of oxidizing gas flow were done holding all variables constant while changing the oxidizing gas flow at temperature of (25℃). Increasing the oxidizing gas flow rate increased oxidation rate. A flow rate of less than 8L/min. did not affect the oxidation rate. In the subsequent experiments the oxidizing gas flow was set to 10 L/minute.

The experiments were repeated in the temperature range of 25℃ to 800℃, the duration of each experiment was 120 minutes. Time and weight change were recorded every 10 minutes, the results are shown Fig. 5.2 at temperature range 25℃-170℃ did not indicate any signs of oxidation.

The curves of oxidation obtained at (200-500°C) had the same trend and same stages. The different stages of oxidation curves throughout the temperature range (200°C -700°C) were tested against different equations to illustrate the mechanism of oxidation at various stages. The initial stages of oxidation were tested against an asymptotic equation.

$$W1 = k_1(1 - e - k_2 t) \quad \text{..... (5.1)}$$

Where:

W - is the oxidation percent

k_1 & k_2 are constants. (Growth or decay rate)

t– is the time (min)

The high rate of oxidation in the initial stage (short time) means that the pore diffusion constrained by a gradual decrease in the pore diameter owing to the oxide film blocking the pores in the sponge iron. It can be attributed to the greater reactivity of iron at higher oxidation temperatures which allowed for vigorous reaction of oxygen on sponge iron surface and high rate of oxide growth occurs near the external surface with the pores near the surface being rapidly closed.[7]

On the other hand, at low oxidation temperature the less reactive iron phase allowed for fair oxidation to occur on the surface leaving open pores which let oxygen to penetrate deeply inside the sample giving rise to a higher rate of oxidation.

The experimental data for the intermediate stage of oxidation as shown in figure 5.2 which shows the oxidation% vs time at variable oxidation temperature.

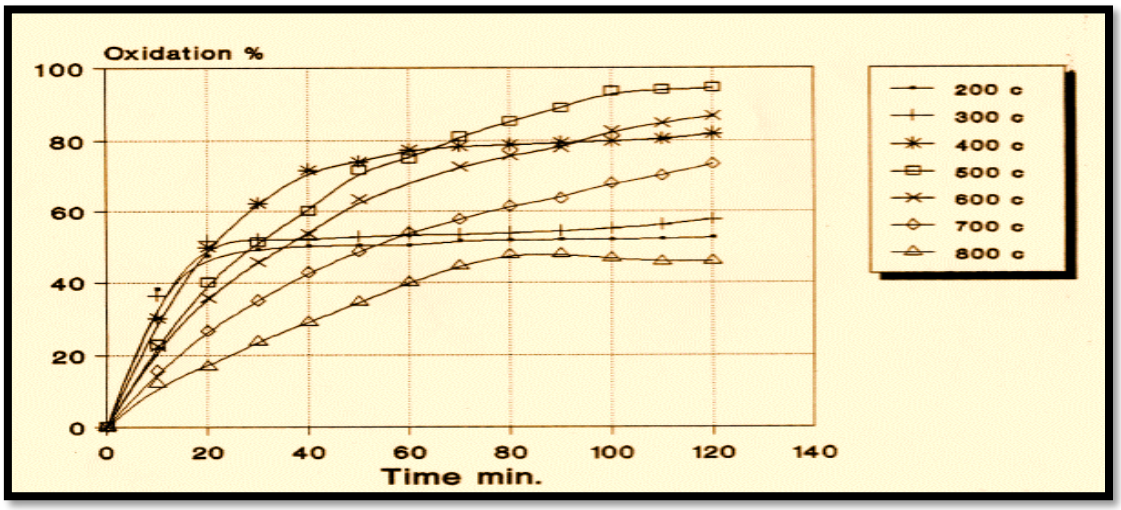


Fig.5.2 shows the oxidation% vs time at variable oxidation temperature

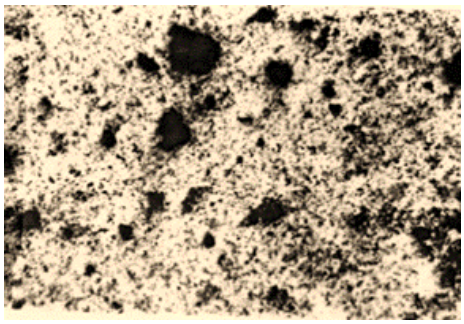
$W_2 = k_3 + k_4 t$..... (5.2)

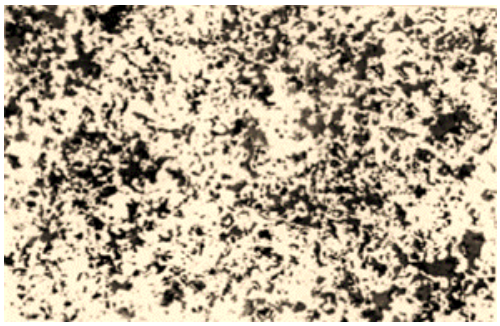
Oxidation process at intermediate stage followed a parabolic expression. This means that solid state diffusion (ionic diffusion) became the rate controlling mechanism. At this stage of oxidation, the pores were lined by thick oxide film and the pores at external surface of the sponge iron sample (pellet) were blocked by the oxide film formation leading to a decrease in the oxygen diffusion through this film.

For the stages of oxidation, a logarithmic expression of the form:

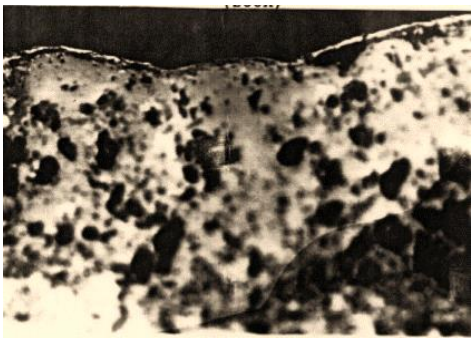
$W = k_5 + k_6 \, Ln(t)$..... (5.3)

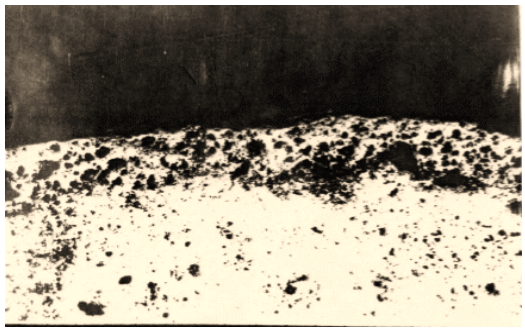
was used to test the experimental data obtained for oxidation of sponge iron sample at 200 - 800°C. The rate controlling step at the latter stages of oxidation was solid state diffusion in which cavities form at the interface between the oxide film and metallic iron thus restricting the oxide film growth. The photomicrograph of sponge iron oxidized at 700°C is done as shown below.





A– sponge iron sample with porous structure (200X) **B– Micro structure of DRI before oxidation (50X)**





C – Micro C microstructure of DRI sample oxidized at 700°Cfor 120min

D - Magnification of (50X) for the same sample

Fig.4.3 Microstructure of the tested samples

Conclusions:

Directly reduced iron produced at 780°C was subjected to oxidation studies at 25-800°C. the conclusion of this study can be summarized as follow:

1. Below 175 °C negligible oxidation occurred. At 200-500°C a significant oxidation was observed at the initial stages followed by an abrupt change in the rate of oxidation at the latter stages.

2. Above 500°C the rate of oxidation gradually decreased with time.
3. Kinetic studies showed that oxidation process can be classified into three stages. At the initial stages of oxidation process followed an asymptotic equation indicating that self-blocking pores mechanism was the rate controlling step.
4. The intermediate stages of oxidation were represented a parabolic expression showing that solid state diffusion (ionic diffusion) was a controlling mechanism.
5. In the latter stages the process of oxidation followed a logarithmic relation which indicated that solid state diffusion occurred and cavities at the interface between the oxide film and metallic iron were formed.
6. Oxidation resistance can be enhanced by several ways, among them; passivation technique, hot briquetting or even by increasing the reduction temperature.
7. The last way is restricted by formation of so-called cluster which has an adverse effect on the reduction process.
8. The reduction temperature was found to have a pronounced effect on oxidation; as the reduction temperature decreases, the reactivity of sponge iron increases hence a higher potential for oxidation than reduction at high temperature.
9. Fire occurrence was mainly due to excess fines in the sponge iron.

Recommendations: –

The fires and oxidation of sponge iron in the Direct Reduction Plant of Misrata Iron and Steel company, the following recommendations will help reduce the occurrence of fire in the product discharge:

1. Increase the reduction temperature as high as possible, this will decrease the reactivity of sponge iron by closing the pores.
2. Decreasing the dust or fines content of the product of furnace, this can be achieved by increasing the cooling gas flow in the cooling zone of the furnace as to remove dust generated by burden weight.
3. Keeping the seal gas as dry as possible or use no reacting gas such as nitrogen to reduce the chance of oxidation.
4. Keeping dust collection as clean and effective as possible, this will remove the fines generated that could not be removed in the cooling zone.

5. Modify the product discharge chute to make a smooth transfer of dust and fines instead of the existing situation where fines and dust accumulate and ignite causing fire.

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