Impact of disparate storage conditions on Direct Reduced Iron at Tuwairqi Steel Mills

MS THESIS

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By

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Connection with Allah Taala and the Purpose of Life

Remember that we can never be totally obedient to Him until we develop intense love for Him. Why? Because if we love our hearts more than we love Him, then we will not hesitate in the least to break His commands should we experience any difficulty to our hearts.

Consider the following example: A beautiful woman passes by. Our heart is inclined to look at her. If we love Allah intensely (more than our heart) then we will displease our heart and please Allah by not looking at her. If, on the other hand, we love our heart more, then we will go ahead and sin by casting a lustful glance at her, thereby pleasing the heart and at the same time displeasing Allah. Thus in order to stay away from sins, it is necessary that the love of Allah be more than anything else.

When I was at Tando Jam, (Sindh, Pakistan) the people at the Agriculture Department (SAU, Tando Jam) asked me: “Why is it necessary to be in the company of Allah-Walas?” The people who had questioned me were people who held M.Sc. and Ph.D. degrees, which they acquired from Germany and America. In order to answer their question, I asked them: “What purpose do your degrees in agriculture serve you here?” They replied: “We (through our knowledge) are able to transform our locally produced mangoes (which are of a lower grade) into superior quality mangoes, by engrafting the root of the locally produced mango into the root of the superior mango. We secure the joints of their roots very firmly so that the roots join fully into each other. Otherwise the characteristics of the superior mango will not enter the indigenous mango.”

I used their example, saying: “Well, according to your explanation, a simple heart (one not inculcated with Taqwa) can be transformed into a superior (Allah-Wala) heart. Like the locally produced mango, the simple heart that is devoid of the Zikr of Allah, it is engrafted into a superior heart of a Wali (friend of Allah Taala). In this way, it is transformed into superior heart. All the characteristics and qualities of the pious heart are transferred into the heedless heart. The connection between the two hearts must likewise be strong and well secured, just as you had pointed out the importance of the two mango roots which have to be well secured to each other.”

One will never attain success until he does not become a mad lover of Allah. But first you have to meet one who is already mad with the love of Allah. The lovers of Allah do not snatch away your *dunya* (your material possessions). Through their blessings you still have the dunya in your hands and in your pockets, but *dunya* will be out of your heart, and only Allah will remain in your heart. Only then will one realize that this great wealth one has acquired is more precious than all the continents. When one holds the hand of a pious person, i.e. when he surrenders himself for reformation under the guidance of a spiritual mentor i.e. a Shaikh, then it becomes easy for him to conform to the Sunnah and the Shari'ah, as well as to abstain from sins.

The purpose of our lives is to obtain piety, that is, friendship with Allah. If our currency, carpets, houses, children, business and money are snatched away at the time of death, it indicates that these things are not the aim of our life otherwise Allah would have sent all these things to the hereafter. Allah has explained the aim of our lives. Now if man becomes engrossed in material wealth, it is his responsibility. We have created you for Our worship. But you became engrossed in the world of romance running after attractive faces. You are responsible for leaving Allah's worship and wasting your life in filth.

Had I not announced the aim in the Qur'an, you could have had an excuse and said Allah did not tell you the aim. Allah says, "I did not create jinn and man except for My worship." [Surah Zariyat.] We created you for Our worship only. Therefore, only worship will go to Allah. Dear friends, only the currency of worship will go.

How does one acquire the love of Allah Ta'ala? The simplest method is to establish a link with the Ahlullah. But Alas! People today are under the misconception that Ahlullah no longer exist in this day and age. The reason for this is that Allah Ta'ala has declared in the Qur'aan Majeed [9:120]:

﴿كونو امع الصادقين﴾

"And be in the companionship of the Truthful."

This verse obviously is applicable till the Day of Judgment. If Allah Ta'ala has commanded us to be in the company of the Auliya then He will surely create pious people till the Day of Judgment. How odd it would be that on the one hand, He commands us to be in the company of the Ahlullah, while on the other hand, He does not provide and create such personalities for us? The actual object is to inculcate Taqwa (piety), to gain the pleasure of Allah Ta'ala, to shun sins and to become His truly obedient servants. This will link us to Allah Ta'ala.

Taken from the books, **Connection with Allah Taala** and **The purpose of Life**

By

Shaikh-ul-Arab wal Ajam Arifbillah Hazrat-e-Aqdas Maulana Shah
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Abstract

Global concerns over the flexibility of iron-making with scrap, quality of iron produced using blast furnace technology and increased requirement for sustainable process of iron-making have led a massive push towards direct reduced iron-making. Direct reduced iron (DRI) is a clean iron source, with a consistent chemical composition, size and shape as compared to scrap. It heavily improves the surface finish when used as an alternate to scrap or used along with scrap. DRI is a promising iron source, but it’s highly passive. It is produced from ferrous oxide by reducing the oxygen out of the material in the reduction furnace of DRI plant. The process of reduction increases the quality of DRI, but when in storage, it can easily reverse its production process as oxygen reacts with it in open air/environment and hence the quality of DRI is greatly reduced as of ferrous oxide itself.

Steelmakers prefer of having an integrated steel mill, where an electric arc furnace is also present along with the DRI facility to process in continuous operation of process plant, thereby avoiding any long storage of DRI which can impact its quality.

In order to evaluate the possibility of using it some months after its production at another corner in the world, a study was under taken to see the trend of the composition degradation of iron. For this, a DRI manufacturing facility was selected in Karachi, Pakistan.

The DRI was sampled from the manufacturing facility after production according to the international practice of sampling and the representative sample of DRI was tested to find the chemical composition and sieve sizes of the DRI samples at the time of sampling. Later the lot of samples was split in two halves, out of which half of the test samples were stored it to its existing open storage yard separately from the other piles of DRI in that yard. Apart from this, a new closed storage yard was also designed, where the remaining half of the DRI

samples were kept in DRI bags under shed, to find a possible way to extend the storage time of DRI with same or near to production quality.

DRI samples were put to chemical and sieve testing each week and the results were recorded. Over the length of six months in storage, the DRI in open storage had degraded heavily as the literature reviewed had also indicated. But, the DRI in close storage was able to resist any massive composition degradation of DRI, which can be considered an achievement towards preserving DRI for longer duration for transportation. Similarly, the results of sieve analysis also had similar trends where the close storage results were better than open storage.

It was concluded that close storage had least impact on DRI as compared with open storage results. Therefore, closed storage is recommended for storing DRI to ensure it retains its original characteristics for long duration. Bags (closed storage) also sustained the quality of DRI in storage. Future research has also been recommend to evaluate more options related to the same work done.

Acknowledgement

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Dedication

…I dedicate all my academic and professional achievements to:

…my spiritual mentor **Hazrat Sufi Shah Feroz Abdullah Memon Sahab (DB)** and to my grand spiritual mentor **Shaikh-ul-Arab wal Ajam Arifbillah Hazrat-e-Aqdas Maulana Shah Hakeem Muhammad Akhtar Sahab (RA).** My spiritual mentor, you had inspired me to pursue this degree and things have been possible through your prayers only. You educated me about Islamic values when I knew nothing and to act upon them is my duty, but thankfully through your teachings, you have pointed me to the right direction.

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Declaration

I hereby declare that none of the material in this thesis/research work has been submitted in support for another degree or qualification from another institute, organization or university of learning.

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Nomenclature
List of *Abbreviations* and Glossary of Terms [1][1]

For the purposes of this document, the terms and definitions given in ISO 11323 and the following apply.

- **DRI:** Direct Reduced Iron
- **BOF:** Basic Oxygen Furnace
- **Sponge Iron:** Refers to DRI
- **EAF:** Electric Arc Furnace
- **HBI:** Hot briquetted iron
- **SMS:** Steel Melting Shop
- **Lot**: discrete and defined quantity of DRI or HBI for which quality characteristics are to be assessed.
- **Increment:** quantity of DRI or HBI collected in a single operation of a sampling device
- **Sample:** relatively small quantity of DRI or HBI, taken from a lot so as to be representative in respect of the quality characteristics to be assessed
- **Partial sample:** sample consisting of less than the complete number of increments needed for a gross sample
- Gross sample: sample comprising all increments, entirely representative of all quality characteristics of a lot
- **Test sample:** sample prepared to meet all specific conditions for a test
- **Test portion:** part of a test sample that is actually and entirely subjected to specific test
- **Stratified sampling:** sampling of a lot carried out by taking increments from systematically specified positions and in appropriate proportions from identified parts

called strata. NOTE: Examples of strata, based on time, mass or space, include production periods (e.g. 5 min), production masses (e.g. 1 000 t), holds in vessels, wagons in a train, or containers.

- **Systematic sampling:** selection of increments at regular intervals from a lot
- **Mass-basis sampling:** sampling carried out so that increments are taken at equal mass intervals, increments being, as near as possible, of uniform mass
- **Time-basis sampling:** sampling carried out so that increments are taken from free-falling streams, or from conveyors, at uniform time intervals, the mass of each increment being proportional to the mass flow rate at the instant of taking the increment
- **Proportional sample division:** division of samples or increments such that the mass of each retained divided portion is a fixed proportion of the mass being divided
- **Constant-mass division**: division of samples or increments such that the retained divided portions are of almost uniform mass, irrespective of variations in mass of the samples or increments being divided
- **Split use of sample:** separate use of parts of a sample, as test samples for separate determinations of quality characteristics
- **Multiple use of sample:** use of a sample in its entirety for the determination of one quality characteristic, followed by the use of the same sample in its entirety for the determination of one or more other quality characteristics
- **Nominal top size of DRI:** smallest aperture size, within the range of the R20 Series (in ISO 565, square opening), such that no more than 5 % by mass of the DRI is retained on the sieve

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Chapter 1. Introduction

Introduction

Iron and steel sector is one of the most key elements in industrial growth of today. In countries like USA, Europe and China, steel production is mostly routed via the basic oxygen furnace (BOF) due to the availability of coal as a cheap resource of fuel to the steel makers. Whereas in countries where natural gas is cheap, like Middle East and Latin America, steel produced is mostly done using direct reduced iron technology with integrated DRI plant coupled with electric arc furnace [2]. [2] Figure 1 Direct Reduction Process is shown below. Figure 1 Direct Reduction Process is shown below.

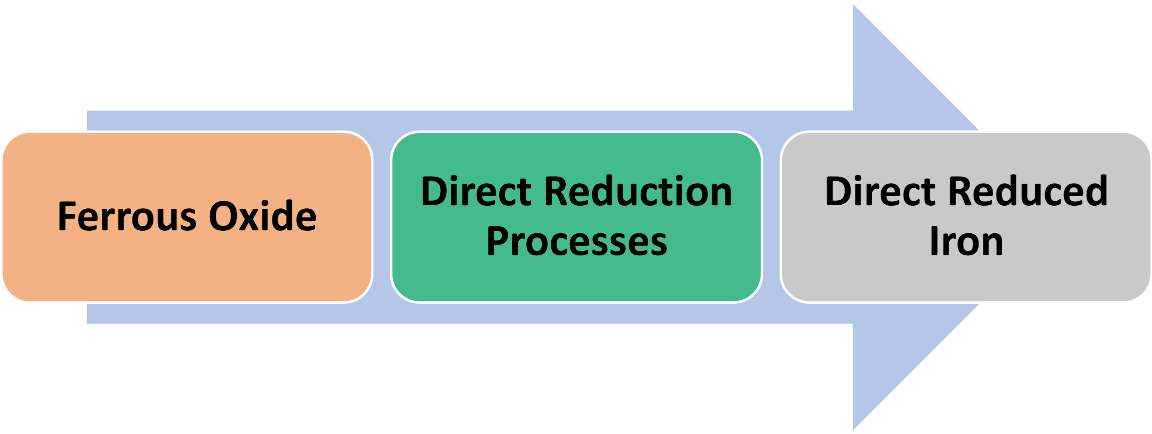


Figure 1 Direct Reduction Process

Problem Description

The production of direct reduced iron (DRI) is based on reducing the raw material Iron Oxide (Ferrous Iron) in the presence of reducing gas. DRI along with pig iron and ferrous scrap is used as a source for low-residual iron in steel production using electric arc furnace (EAF). The main technologies by which DRI is produced are MIDREX and Hyl, but lately there has been emergence of new processes by varying feedstock, reducing agents and fuel sources.

Weather conditions, long storage durations and unnecessary movements etc. all have been found to pose negative effect on DRI as the product deteriorates over the length of time as detailed in Figure 2 Reversing of Direct Reduction Process due to long storage.

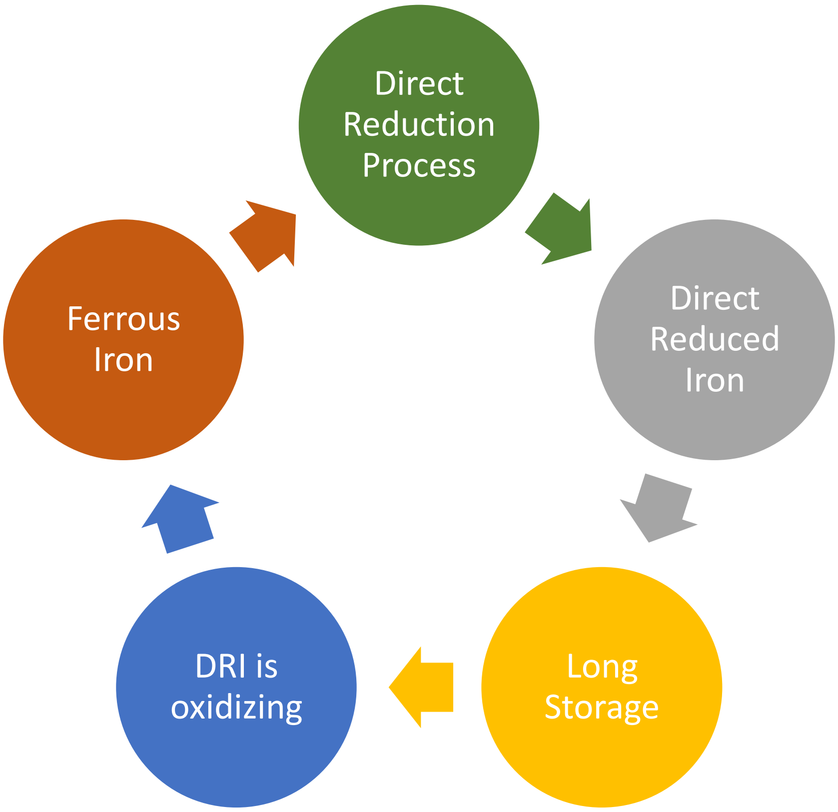


Figure 2 Reversing of Direct Reduction Process due to long storage.

In order to cater for this issue, this research aims to evaluate the effect of storage conditions over DRI. DRI normally remains in storage yards before going for further processing in general, but here in our case DRI remains in storage for long periods in particular. Hence, if DRI loses its original characteristics, its size and shape then its further processing in EAF may not yield the desired results as compared to DRI, which was not left in storage for long duration.

In most of the cases, DRI is produced in batches and stored in a dedicated storage yard in open air. Its sale value is very less than the purchase value of scrap which adds misery to the manufacturer. So, the proper management of storage becomes prime priority so that it may retain its original properties for long duration.

Alteration to its novel properties not only make it less valuable than a scrap material but also delimits its further processing as a result causing a major loss to the organization. This problem is more severe in Pakistan due to the non-availability of adequate natural gas at economical price to the organization and hence the rate of DRI even exceeds from that of the scrap material which delimits its usage as raw material. So, evaluation for better storage option was done. A step wise approach was followed to figure out the best possible solution to this problem.

Objective of Research

The key objective of this study was to figure-out the optimal storage configuration to be adopted which will consider its properties during storage with respect to time. So, this is achieved by the following objectives:

1. Examine the effect of storage on composition on DRI
2. Examine the effect of storage on sieve size of DRI
3. Identify which storage is best option for storing DRI
4. Propose a solution for this case study to store DRI in a condition which has least effect on its characteristics/properties.
5. Find critical properties which degrade more during the storage phase.

Organization for the Case-Study

The DRI manufacturing plant Figure 3 Direct Reduced Iron manufacturing plant located in Karachi Pakistan, a joint-venture investment by World’s No.1 Steelmaker POSCO, Korea and Al-Tuwairqi Holding, KSA [3].[3] It is a MIDREX MEGAMOD plant having a production capacity to produce over 1.28 MTPY of DRI. It is located in Karachi, Pakistan [4]. [4]

Figure 3 Direct Reduced Iron manufacturing plant located in Karachi Pakistan [50]

Plant Facts

Following are the plant facts for TSML as officially quoted by MIDREX, USA [5]. [5]

Table 1 Direct Reduced Plant Information [6] [6]

Plant	Location	Design Capacity (Mt/y)	Shaft Furnace Modules	Product	Start-up
Tuwairqi Steel Mills	Karachi, Pakistan	1.28	1	HDRI/CDRI	2013

Thesis Layout

Whole thesis is assigned in a proper layout consisting of introduction with the rationale of project with the defined aims and objectives to sort out the problem. Then after that review of literature of DRI along with certain issues related to its storage has been kept forward to see its status in the present industry and whole country. To achieve the assigned aims and objectives, a proper set of experimental protocols are followed. So, we tried to give direction to our pre designed approach. By following the protocols we nurtured the results which are discussed under result and discussion heading. After carrying out this study, a conclusion with its best future prospect has also been suggested which may require further study.

Chapter 2. Review of Literature

Direct Reduced Iron

The origin of steel can be traced back to 5000 year from today [7].[7] Grobler along with his coworkers (1999) suggested electric arc furnace (EAF) as best alternate option which can be set up in small scale with low capital investment. It had various advantages like it uses scrap as raw material as compared to iron ore. It has continuous casting and near net shape casting (NNSC) feature which add preference to its use. With the passage of time, its production capacity increased and made itself almost the ideal alternate for high quality steelmaking. It helped steelmakers to approach differently to generate high quality, low-residual scrap, which is the main source of metallic used in EAF steelmaking.

Since the late nineties, the increasing demand of DRI made it the best alternate for scrap as feedstock in EAF. The gradual rise in its demand was due to favorable options of EAF and ‘mini-mill’ set-up of steelmaking compared to blast furnace/ basic oxygen converter, which are comparatively less flexible [8]. [8]

Melting of DRI in furnace as a partial replacement to steel scrap as input charge of materials can produce high quality steel. For all such reasons the DRI production has been widely acknowledged globally and new plants are being constructed to fulfill the requirement of steel makers.

Considering the fuel sources of DRI as detailed later in the report, the DRI cannot be produced everywhere in the world and there is a big need to store it for transportation to other steelmakers worldwide.

Definition

Grobler et. al (1999) mentioned that the term ‘reduced iron’ which is manufactured from chemical change through which ferrous oxide (iron ore) undergoes when it is subjected to high temperatures in a furnace in the presence of reducing gases. Whereas, the term ‘direct reduction’ points to the processes which produce metallic iron by reducing iron oxide by keeping the temperature of iron below its melting point. The output or product of such solid state manufacturing processes is called DRI [7].

Process

The MIDREX process (Figure 4 Principle of MIDREX® Direct reduction process [9]) can accommodate iron ore charge in the form of pellets, iron oxide lump and/or pellet lump combination into highly metallized reduced iron. [50] The iron produced is in the form of hot DRI also known as HDRI or cold DRI also known as CDRI. CDRI/HDRI are ideal raw materials to be used as feed material in electric arc furnace. Steel made using CDRI/HDRI is of high quality.

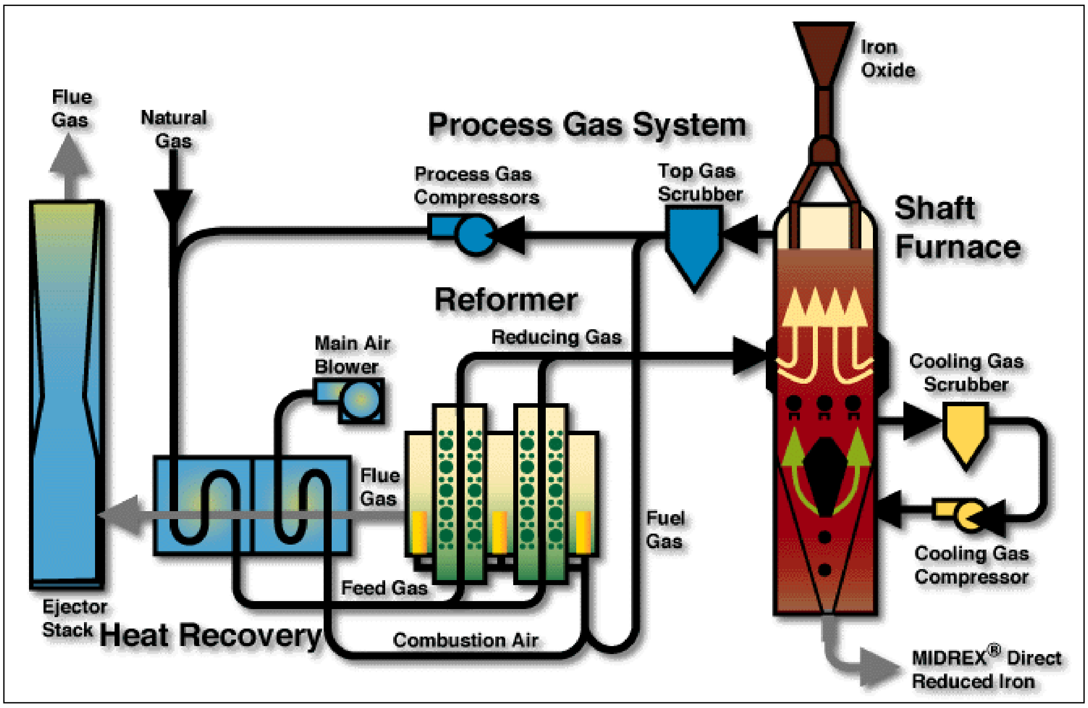


Figure 4 Principle of MIDREX® Direct reduction process [9][9]

Most naturally occurring iron oxide has the chemical composition of hematite, Fe_2O_3, which has 30% percent of oxygen in terms of weight. *Figure 5. Outline of overall reduction* *reactions in* MIDREX® Shaft Furnace [11]. The oxygen in iron ore is chemically bonded and it is removed using high temperature solid state reduction reactions with carbon monoxide (CO) and hydrogen (H2) to produce metallic iron (Fe). The CO and H_2 containing gas is called the reducing gas. The reduction reactions occur inside the MIDREX® Shaft Furnace. Carbon dioxide (CO_2) and water vapor (H_2O) are byproducts produced by the iron oxide reduction reactions. [50]

The overall reduction reactions are:

$$Fe_2O_3 + 3H_2 \text{ ---------------> } 2Fe + 3H_2O$$

$$Fe_2O_3 + 3CO \text{ ---------------> } 2Fe + 3CO_2$$

The degree of metallization is a quantitative means of determining the amount of oxygen removed from the raw material which is iron oxide during the reduction reactions.

Degree of Metallization, % = {(% Metallic Fe)/(% Total Fe)} x 100

The plant production capacity is based on a degree of metallization of 92 to 94 percent, which in most plants has been found to optimize the overall steelmaking plant economics [10].[10]

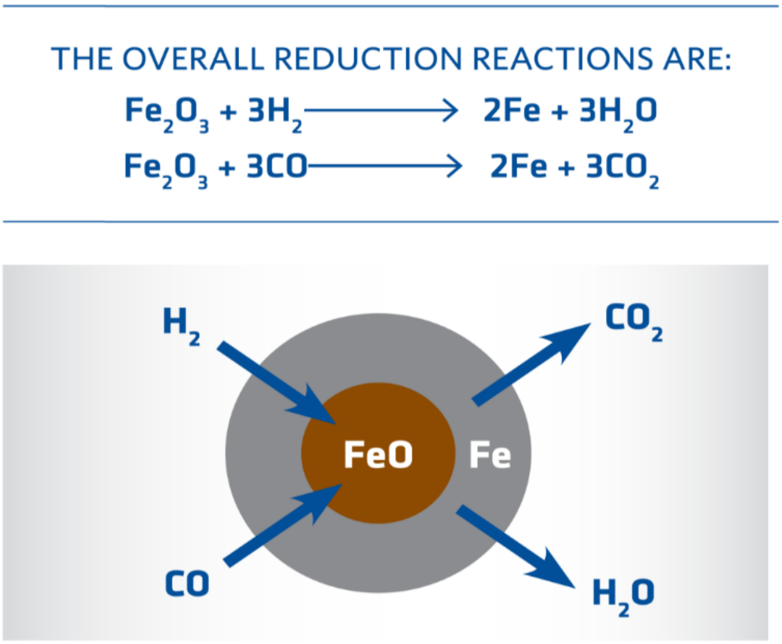


Figure 5. *Outline of overall reduction reactions in* MIDREX® Shaft Furnace [11].[11]

Types of Direct Reduction Process [12] [12]

Direct reduction process can be divided in to two categories:

1. Coal-Based Process
2. Gas-Based Process

Coal-Based Process

The process which uses lump of iron ore of rich grade along with reducing agent of non-coking coal. During this process, rotary kiln (usually horizontally inclined) which rotates at a constant and predetermined speed is where the reduction reactions take place. At all zones of the kiln, temperature of 800-1050 ^{0}C range is maintained constantly. Inside the kiln, ore is reduced while it flows down due to gravitational force. The products hot reduced iron and the coal which is semi-burnt both are cooled in a cylindrical cooler (using water as cooling agent) after the product is discharged from the kiln to a temperature of 100-200 ^{0}C. The reduced iron is separated from other impurities by use of magnetic separators after the reduced iron is discharged from the cooler. After that, DRI is passed through sieve screens of two sizes, i.e. –3 mm and +3 mm. DRI of +3 mm fraction directly goes for usage, whereas DRI of -3 mm fraction is either used directly or it is briquetted by use of binders like molasses along with hydrated lime.

- $C + O_2 \rightarrow C O_2$
- $CO_2 + O_2 \rightarrow 2CO$
- $Fe_2O_3 + CO \rightarrow Fe_3O_4 + CO_2$
- $Fe_3O_4 + CO \rightarrow FeO + CO_2$
- $FeO + CO \rightarrow Fe + CO_2$

Raw Material for this process

Iron ore and Coal

The iron ore used as a raw material should have

1. High resistance for physical and thermal degrading.
2. Excellent reducibility
3. Should have constituents as mentioned in Table 2 Key constituents of Iron ore.

Table 2 Key constituents of Iron ore

Description	Value
Moisture	8 % max
Total iron	27 - 30 %
Ash	23 -25 %
Fixed carbon	+ 40 %

Chemical Composition (in %)

Following is the chemical composition as detailed in Table 3 Chemical Composition of Iron ore which is mostly found in iron ore.

Table 3 Chemical Composition of Iron ore

Description	**Value**
Total iron	65 - 67 %
SiO_2 + Al_2O_3	2 - 3 %
CaO + MgO	0.5 - 1 %
Sulphur	0.02 % max.

Physical Composition

Following is the chemical composition as detailed in Table 4 Physical Composition of Iron Ore which is mostly found in iron ore.

Table 4 Physical Composition of Iron Ore

Description	Value
Size	5 - 20 mm
Shatter index	+ 95 %
Tumbler index	+ 88 %
Abrasion index	+ 5 % max
Reducibility index	+ 94 %
Thermal degradation index	-5%

The coal which will be used

1. Should be very reactive.

2. Have high fusion temperature with less amount of ash as residue.

3. Should have typical chemical and Physical characteristics as mentioned in Table 5 Chemical Characteristics of Coal and
4. Table 6 Physical Characteristics of Coal.

Table 5 Chemical Characteristics of Coal

Description	Value
Size	0 - 20 %
Ash softening point	1250 ^{0}C
Calorific value	5200 k. cal molelce
Reactivity	2.2 CO / gm. . deg

Table 6 Physical Characteristics of Coal

Description	Value
Size	0 - 20 %
L.O.I	45 %
Insoluble	5 - 7 %
Size	0.5 - 4 mm

Composition of DRI

Table 7 Composition of Direct Reduced Iron produced from Coal process

Description	Value
Total iron	91 - 93 %
Metallic iron	80 - 84 %
Metallization	90 - 92 %
Carbon	0.25 %
Sulphur	0.02 - 0.03 %
Phosphorous	0.035 - 0.05 %
Gangue	3 - 4 %

Gas-Based Process

Natural gas is utilized as the reducing agent in this process. It is reformed to enrich with H_2 and CO mixture and this reformed gas preheated in gas-based process. In this process, a retort aligned vertical is used instead of a rotary kiln which was used in coal based DRI production process. The charge of iron ore which is reduced in shaft furnace moved down by gravitational force and gases travel up. As there's zero possibility of contamination in gas-based reduction process of iron therefore magnetic separators are not required. The product is either cooled directly or it is briquetted to get hot briquetted iron (HBI) in hot condition.

Raw Material for this process

Iron ore and natural gas Physical and Chemical Composition of iron ore pellets

Table 8 Physical properties of iron ore pellets

Description	Value
Size	12 - 16 mm
Avg. Cold cr. Strength	200
Bulk density	2.2 t / m3

Table 9 Chemical Properties of iron ore pellets

Description	Value
Total iron	65 - 67 %

$SiO_2 + Al_2 O_3$	2 - 3 %
CaO + MgO	1 - 2 %
Sulphur	0.025 %

Table 10 Chemical constituents of natural gas after reformation

Description	Value
Nitrogen CO + H_2	90 % or above
CO_2	0.1 - 5 %
CH_4	85 – 93 %
C_2H_6	3 – 8 %
C_3H_8	1 – 4 %

Composition of DRI produced from Gaseous Process

Table 11 Composition of DRI produced from Gaseous process

Description	Value
Total iron	92-95 %
Metallic iron	81 - 85 %
Metallization	85 - 93 %
Carbon	1.2 - 2.5 %
Sulphur	0.003 % max
Phosphorous	0.035 - 0.05 %
Gangue	6 - 8 %

Factors affecting the rate of reduction

1. Temperature of reduction.
2. Time of reduction.
3. Particle size of iron ore.
4. Pellet size.
5. Presence of catalyst.
6. Reactivity of solid carbon.
7. Chemical nature of oxide.
8. Fe_2O_3/C.

Advantages of using DRI

1. Purity or the absence of non-metallic substances, increases productivity and energy consumption.
2. Uniform density and shape influences the number of back charges, productivity, energy consumption and damage to furnace walls and refractories.
3. DRI lump, pellets or briquettes from electric arc furnace can be dumped cold into a steel making furnace along with scrap, using standard bucket charges.
4. It has lower capital and operating costs.
5. It lessens the reliance on coke as a fuel source.
6. DREAF facility can be established in less than two years, as compared BOF facility which take 5-7 years [13].[13] Several DR plants have been established in less than 18 months [14]. [14]
7. Easy availability- the supply of DRI can be increased according to the demand.
8. The use of hot DRI directly transported and charged to a furnace, can reduce energy consumption by as much as 16 to 20 per cent by making use of the energy value of the DRI at temperatures greater than 600°C [15]. [15]
9. Negotiable price for DRI makes it rational than scrap with the producer which are routinely published by grade and market.
10. Blending abilities of DRI with scrap allow cheaper, low quality scrap grades to be used.
11. It acts as a coolant in the oxygen furnace and as charge material in blast furnace which in turn increase productivity and decrease coke consumption [16].[16]
12. Use of DRI is environmental friendly as it prevents the effect of hazardous contaminants such as lead or cadmium in EAF dusts.

Disadvantages of using DRI/HBI [50]

1. Due to the nature and surface area of untreated DRI, it has the inherent disadvantage to be highly reactive with moisture, leading to re-oxidation and possible exothermic auto-ignition. However, various methods of passivation has been found out and the problem has been overcome by hot briquetting.
2. Unlike blast furnace pig iron, DRI contains some siliceous gangue, which needs to be removed in the EAF, increasing the power consumption.
3. Increased refractory consumption if large amounts of pre-reduced pellets are used instead of scrap.

DRI an alternative for scrap

Mostly all EAF based melt shops are based on the principle of melting 100 % scrap which considers the usage of DRI as scrap substitute. So, 100 % scrap based melting demands different approach of its evaluation, handling and melting. Scrap density may range between 0.20 to 0.50 t/m^3 in different parts of the world [17].[17] In many new installations this leads to 4 or 5-bucket scrap charges to an EAF. Use of purchased continuously fed DRI eliminates the multiple charges and reduces tap to tap times. Many low residual products require the use of a scrap substitute such as DRI. The proper use of DRI can be defined for any plant by considering its qualities, storage, feeding, melting and slag. This knowledge can make remarkable difference between profit and loss to the steelmaker. For industrial use and processing the mined ore is usually prepared and sold to steel makers as concentrate, fines, pellets, pig iron or iron nuggets. Table 3 illustrates the production of DRI in following forms.

- **Pellets:** DRI pellets are spheres of typically 8–18 mm (0.31–0.71 in) [12].
- **Lumps**: A small mass of matter of irregular shape; an irregular or shapeless mass [13].

- **Fines:** During cold DRI production, fines are obtained through solid/gaseous reduction route**.** Typically they size ranges between 0-4 mm [18].[18]

Table 12 Different forms of Direct reduced iron (DRI).

Name	Form	Picture
Pellets	DRI pellets are spheres	
Lumps	Small mass of irregular shapes	
Fines	Sponge iron or DRI	

Most commercially supplied DRI is sold as pellets and HBI which is hot briquetted iron. Some fines or lump material may be mixed in with the pellets or briquettes. The color can range from gray to almost black. DRI that has been stored in the open will develop a rusty surface [8].

Table 13: **Physical Characteristics of DRI [19, 20]** [19] [20]

Product	Size (mm)	Apparent Density (gm./cm^3)	Bulk Density (gm./cm^3)
DRI	4 to 18	3.4 to 3.6	1.6 to 1.9

A low apparent density will lead to poor yields, increased slag FeO content and higher energy consumption. For effective melting, the pellets or briquettes must penetrate the slag layer. Non-foaming EAF slag density ranges from 2.6 to 3.5 tons/m^3 depending on FeO content and other compositional factors. If the apparent density of the DRI or HBI is less than the slag density, it will float on top of the slag.

Gravity fed fines may be sucked directly into the bag-house. Storage costs and charging times can be influenced by bulk density. The higher the bulk density the less the charging time and storage area required.

The chemical composition of the DRI determines such important factors like yield, slag weight, energy consumption, carbon and raw material feeding rates, and oxygen usage.

DRI pellets and to a much lesser extent HBI are subject to oxidation. By knowing the approximate chemical composition of the DRI at the time of use, the steelmaker can fine-tune the melting process. Table 5, illustrates the typical compositions of DRI at the time of production.

Table 14 Chemical Properties of DRI [20, 21] [20] [21]

DRI and HBI	
Fe Total	89.2 to 94 %
Fe Metallic	79 to 89 %
Metallization	83 to 95 %
Carbon	0.30 to 4.0 %
P	0.005 to 0.09 %
S	0.001 to 0.03 %
SiO_2	1 to 5 %
Al_2O_3	0.5 to 3 %
CaO	0.1 to 2.0 %
MgO	0.1 to 1.0 %
Residuals	Trace

Metallization is usually expressed as a percentage: Fe Metallic/Fe Total x 100. For example, a DRI pellet that has 86 % Fe Metallic and 92 % Fe Total would have 93 % Metallization [22]. [22]

Although a steelmaker may know the metallization it is still very important to know the percentage of "FeO" contained in the DRI or HBI. This is calculated by the following formula:

$$(\text{Fe Total} - \text{Fe Metallic}) \times 72/56 = \text{FeO}$$

Furthermore, one can calculate the amount of oxygen in the iron: FeO x 16/72 = O wt. percent. Carbon is contained in the DRI or HBI. If carbon is maintained at a 0.75 ratio to the oxygen in the FeO, the carbon will form CO in a stoichiometric balance. Equivalent carbon content is the percentage difference between carbon contained in the DRI and the carbon needed to reduce the oxygen in the FeO. If it is negative, then the steelmaker must add carbon to the bath to reduce the FeO in the DRI. If it is positive, then the steelmaker may need to blow oxygen to remove the excess carbon from the steel bath.

Generally, a positive equivalent carbon leads to a reduction in electrical energy consumption with the blowing of oxygen while a negative equivalent carbon can cause bath decarburization. In most plants where bulk oxygen is available, a positive equivalent carbon is desired. The carbon content of the DRI or HBI is dependent on the supplier's process parameters. The FeO content is likewise affected by the supplier's process parameters but shipping, storage techniques and shelf time can also affect the value. Adjustment of the DRI or HBI manufacturing process will affect costs and productivity so the supplier and customer must come to both a technical and economic agreement regarding the carbon and FeO or metallization content of the pellets or briquettes.

Steelmaker with DRI or HBI in raw material inventory should check chemistry when the material is received and thereafter on a monthly basis. No ore deposit consists entirely of a single ore mineral. The ore is always mixed with unwanted or valueless rocks and minerals that are collectively known as gangue [23].[23] Gangue content must be measured and reported since this affects slag composition and energy consumption. Even though the total iron, carbon and gangue quantities will not change, the material can continue to oxidize during storage.

Storage of DRI

Pyrophoric property of DRI makes it prone to re-oxidation which requires careful handling. It is done by coating and cooling before being transported in ships, rails and highways. So, it becomes mandatory to follow certain guidelines or follow certain necessary preventive measures during handling, storage and transportation of sponge iron. Certain guidelines according to Indian standards are found to be very basic regarding storing DRI in a storage pile and storage bin [24]. [24]

In Storage Pile

Following guidelines should be followed for storage of DRI in a storage pile for longer duration (25).[25]

- The temperature of DRI iron should always be maintained below 65°C. Individual heap temperatures should be closely monitored at least once a day by inserting thermocouple probes with temperature gauges as close to the center of the heap as possible.
- Material should be kept in a dry state avoiding direct contact with water at all times.
- Storage at all points should preferably be under cover (providing adequate ventilation) to protect from rain. The storage building should be designed in such a way that water

entry from the sides is avoided. Sidewalls may not be required, if direct contact with water can be avoided but for complete protection, these may be necessary.

- The storage area should be paved and levelled for a quick access, so that material can be isolated in case of accidental re-oxidation resulting in ignition. A minimum of outward slope (at least one in fifty) is required to allow water to drain out in case water accidentally enters the building.
- Separation walls should be installed to divide the product in lots of about 2 000 t to avoid the possibility of re-oxidation and spontaneous combustion of the entire lot in the eventuality of a hot material finding its way into the pile. Ideally, the heap size should be maintained as small as practicable (say 100 t) with the largest possible extent of spreading (heap height 1.5 m, Max).

Storage in a Bin

The following points should be followed while storing the DRI in a storage bin:

- DRI should be loaded dry and it should be below a temperature of 65°C. The bin temperature should be monitored regularly (at least once every day).
- Efforts should be made to avoid fines generation during loading into the bin and in order to prevent any material segregation and stagnation. Discharge should be smooth and even.
- Water intake to the bin should be avoided.
- The bin should be divided into segments to permit discharge from any compartment in case of eventual re-oxidation by accidental intake of hot material.
- Facilities for nitrogen/CO_2 purging should be available in case the bin temperature shows an increasing tendency.

HBI has a much more dense structure and lower surface area to volume ratio as compared to pellets. It will cause 70 % lower metallization loss as compared to DRI pellets over the same time period and it becomes negligible 0.6m below the surface [26].[26]

Upon receipt at the steelmaking plant, the DRI or HBI should be kept dry by spreading a tarp on top of the material. The storage pile should minimize the surface area to volume ratio. The storage area should have a level bottom with good drainage. Due to the possibility of oxygen depletion in confined spaces, personnel should always check the atmosphere before entering a storage silo containing DRI or HBI. Minimal handling should be done to prevent the production of more fines [27].[27]

The most commonly used iron-bearing minerals contain iron compounds [28] [28] as detailed in following Table 15 Iron Mineral compounds:

Table 15 Iron Mineral compounds

Description	Value
hematite Fe_2O_3	70% Fe
magnetite, Fe_3O_4	72.4% Fe

Where there are of much less importance which are detailed in following Table 16 Iron Mineral compounds:

Table 16 Iron Mineral compounds

Description	Value
limonite, $2Fe_2O_3 \cdot 3H_2O$	60% Fe
siderite, $FeCO_3$	48.3%Fe
pyrite, FeS_2	46.6% Fe

These iron percentages are in their pure states. In ores, the Fe content is lowered according to the amount of impurities present. Overall, the quality of iron ore is mainly judged based on the Fe content. More specifically, ores with Fe contents above 65% are regarded as high-grade ores; 62–64% medium- (or average) grade ores and those below 58% Fe are considered as low-grade ores [29-32]. [29] [30] [31] [32]

So, the key aspect of this research is to estimate the total iron content of DRI. In exploitation of any mineral, it becomes mandatory to understand the main inherent properties and composition which determines its behavior during processing. Moreover, the characteristics of minerals also determine the economical aspect of commercial exploitation of deposits.

Storage of DRI – MIDREX Module

Scrap was considered as the main raw material for EAFs for a long time, but the importance of Sponge Iron (SPI) as a partial substitute for scrap has been increased day by day. Sponge Iron has its advantages and disadvantages compared with scrap.

The storage of sponge iron for long periods of time is affecting its metallization partially due to surface de-oxidation [33]. [33] The sponge iron will lose about 1 percent from its metallization after six months of storage in the open yard [34]. [34] This problem will not occur in the case of HBI storage where its re-oxidation rate is very slow due to less porosity.

Handling of SPI/HBI inside the plant is easy where a magnet or shovel loader can handle it, and be stacked, reclaimed and transferred by using belt conveyors. During handling, some dust will be created causing minor pollution. In case of HBI, a small percentage will be chipped off or broken but without affecting its performance [35]. [35]

Metallization of DRI is affected due to long storage periods in Storage yards. It's left uncovered in open atmosphere and obviously the atmosphere will have all sorts of negative effects on it until it's further processed. The following relationship is one the main reasons why DRI storage options for large DRI manufacturing plant must be evaluated for an efficient long-term storage, because if metallization is reduced then it would lead to financial loss in terms of low quality product or rejected raw material. Table 17 Relation between Time and

Metallization of DRI before and after storage**.** shows the relation between time and metallization [36]. [36]

Table 17 Relation between Time and Metallization of DRI before and after storage. [33]

Storage conditions	Months	DRI metallization before storage	DRI metallization after storage	Sampling Area
Not Exposed to rain	3	94.36%	94.35%	From 10 to 20cms depth
Exposed to rain	6	93.97%	91.76%	
	9	93.60%	87.00%	
	12	94.33%	83.70%	

Chemical and Sieve Analysis

The Abraham and his coworkers, (2012) investigating the chemical composition and microstructure of raw iron ore from the deposits in Muko area (south-western Uganda) by using X-ray diffraction and scanning electron microscopy. The samples were randomly collected from each six hills within a radius of about 10 meters. A sample of each hill was crushed and sieve analysis was performed. The necessary amount of sieve passage below 100μm was used for mineralogical and chemical analysis. The FeO and the total Fe contents were determined titrimetrically. Thereafter, the Fe_2O_3 content was calculated from those results. The contents of C and S in iron ore samples were determined using combustion and IR absorption. The Si and Al contents were determined using XRF after fusion in $Na_2B_4O_7$ [37]. [37]

Seyed Kazem Tahiri (1982) analyzed the sponge iron for the determination of total iron, metallic iron, carbon, and sulphur and phosphorus content using standard method of chemical PROCEDURE DR-4, DR-5, Midrex Corporation, U. S. A. [38].[38]

Ivana Angelini et. al (2004) collected glass samples and then chemically analyzed the glass samples of Bronze Age glasses. In their report they focused on the identifying the chemical composition of the glass [39]. [39]

A. D. Westland et. al (1958) conducted research on platinum-metal minerals by performing chemical analysis. The collected the iridosmine samples and they oxidized the micro-samples of iridosmine [40]. [40] Jenkins and his coworkers, (2005) described various techniques (Table 7) used for chemical and sieve analysis for mild steel. He emphasized that in a process of selecting any technique for chemical analysis, consideration of the particle size is the most important, as all techniques are perfect for a specific range of sieve size. He reported that previous studies of chemical analysis didn’t take into account the particle size, thus the results of those studies are not reliable. Therefore, he recommended to consider sieve analysis as a significant factor when investigating metal for chemical composition

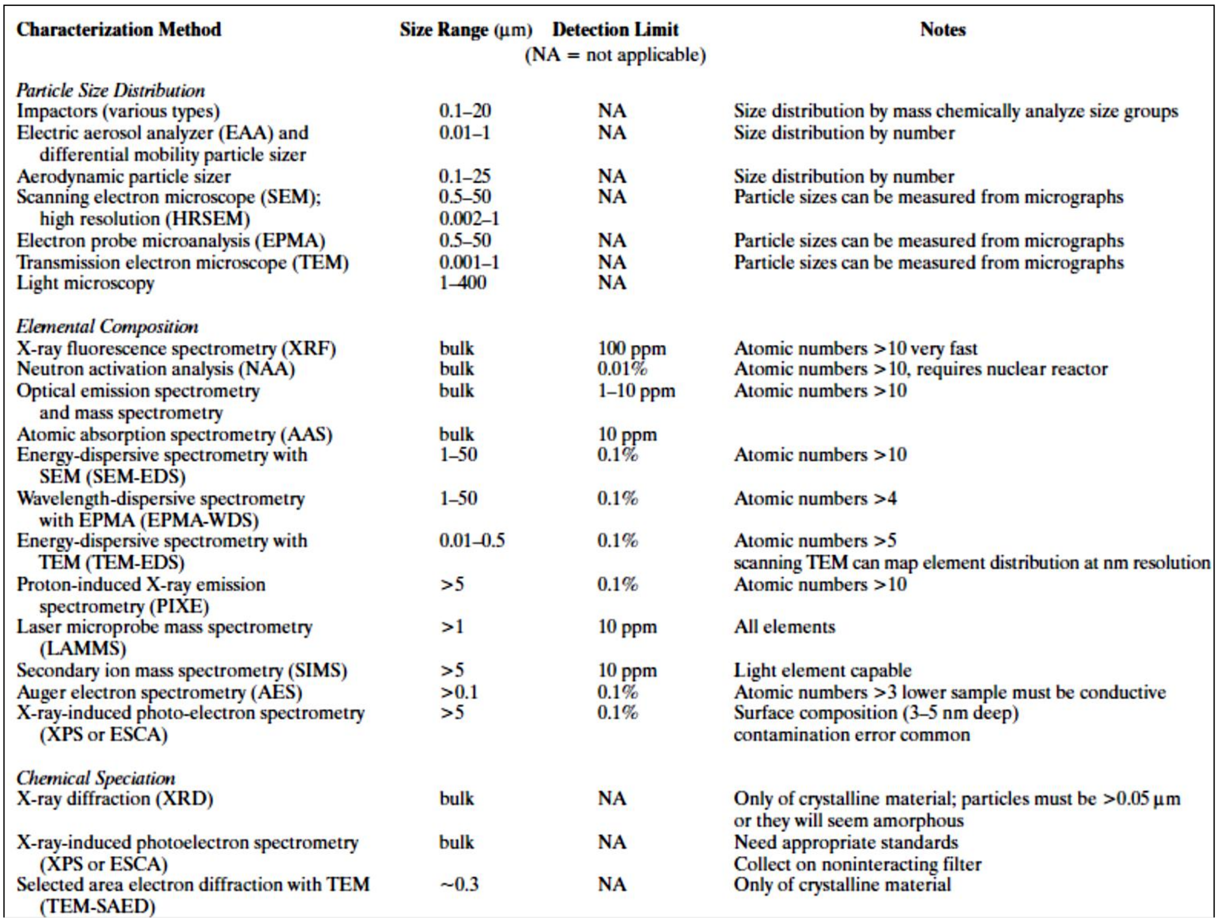
Elemental characterization techniques fall in two categories:

- one which measure proportional to the atomic number in which the data is represented in molar/atomic fractions
- one which measure proportional to the atomic mass in which the data is reported as weight percentage

The research focuses on sampling and separating the metal in small and large groups for testing purpose. Characterization is dependent on size and by bulk which is the mass-weighted average of the chemistry of the groups (large or small) in wt. % [41].[41]

Bernhardt (1994) explained that particle size carries the quantitative information regarding the size to size distribution of particles in the material. It is also a key factor in determining the optimum feed size for processing it at maximum efficiency. It is also crucial in determining the size which deteriorates the production quality [42].[42]

Table 18 Chemical composition and size characterization techniques for particles (Jenkins et al., 2005). [41]



Characterization Method	Size Range (μm)	Detection Limit (NA = not applicable)	Notes
Particle Size Distribution			
Impactors (various types)	0.1–20	NA	Size distribution by mass chemically analyze size groups
Electric aerosol analyzer (EAA) and differential mobility particle sizer	0.01–1	NA	Size distribution by number
Aerodynamic particle sizer	0.1–25	NA	Size distribution by number
Scanning electron microscope (SEM); high resolution (HRSEM)	0.5–50 0.002–1	NA	Particle sizes can be measured from micrographs
Electron probe microanalysis (EPMA)	0.5–50	NA	Particle sizes can be measured from micrographs
Transmission electron microscope (TEM)	0.001–1	NA	Particle sizes can be measured from micrographs
Light microscopy	1–400	NA	
Elemental Composition			
X-ray fluorescence spectrometry (XRF)	bulk	100 ppm	Atomic numbers >10 very fast
Neutron activation analysis (NAA)	bulk	0.01%	Atomic numbers >10, requires nuclear reactor
Optical emission spectrometry and mass spectrometry	bulk	1–10 ppm	Atomic numbers >10
Atomic absorption spectrometry (AAS)	bulk	10 ppm	
Energy-dispersive spectrometry with SEM (SEM-EDS)	1–50	0.1%	Atomic numbers >10
Wavelength-dispersive spectrometry with EPMA (EPMA-WDS)	1–50	0.1%	Atomic numbers >4
Energy-dispersive spectrometry with TEM (TEM-EDS)	0.01–0.5	0.1%	Atomic numbers >5 scanning TEM can map element distribution at nm resolution
Proton-induced X-ray emission spectrometry (PIXE)	>5	0.1%	Atomic numbers >10
Laser microprobe mass spectrometry (LAMMS)	>1	10 ppm	All elements
Secondary ion mass spectrometry (SIMS)	>5	10 ppm	Light element capable
Auger electron spectrometry (AES)	>0.1	0.1%	Atomic numbers >3 lower sample must be conductive
X-ray-induced photo-electron spectrometry (XPS or ESCA)	>5	0.1%	Surface composition (3–5 nm deep) contamination error common
Chemical Speciation			
X-ray diffraction (XRD)	bulk	NA	Only of crystalline material; particles must be >0.05 μm or they will seem amorphous
X-ray-induced photoelectron spectrometry (XPS or ESCA)	bulk	NA	Need appropriate standards Collect on noninteracting filter
Selected area electron diffraction with TEM (TEM-SAED)	~0.3	NA	Only of crystalline material

S. Akande et. al (2013) collected representative samples of iron-ore. Size preparation was followed by crushing, grinding and screening. It emphasizes that sieve analysis is a key to determining the quality of material [43].[43] Similarly the main purpose of this study is to study the chemical and physical properties of DRI to analyze the impact of environmental conditions over its properties during storage. Furthermore, it is also compared with market standards in order to assess its quality and determine the viability for further processing in EAF even after long storage intervals [31].

Chapter 3. Methodology

Methodology

It involves the progress and justification of this study. It gives us a broad view of how the work is conducted as well as why and in what way a specific method is chosen to achieve the aim. It is very important to get a persuasive research result, therefore the choosing of one or several suitable methods can be the vital part of the research work.

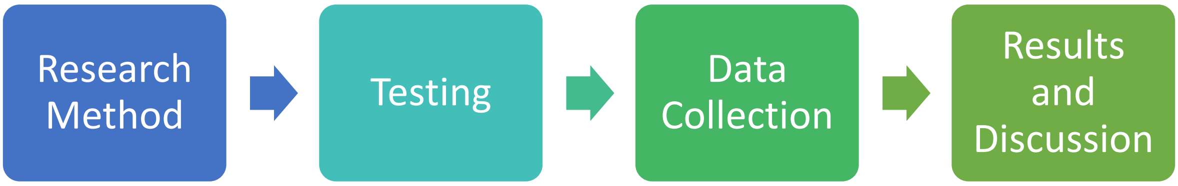


Figure 5. Steps involved in research methodology.

Type of Research

Applied Quantitative Research aims at evaluating the capability of various storage conditions for sustainable storage of DRI (Aliaga and Gunderson, 2002). Quantitative research is ‘Explaining phenomena by collecting numerical data that are analyzed using mathematically based methods (in particular statistics) [44]. [44]

Type of investigation

Sampling and Experimentation.

Consideration for Sampling and Sample preparation

For both sampling and sample preparation, three things are to be kept in mind: basic requirements for sampling and sample preparation, establishing a sampling scheme and system verification which is done according to international standards [45].[45]

Basic requirements

Correct sampling scheme requires DRI to be selected in the lot for analysis. Any deviation from this basic requirement can result in an unacceptable loss of accuracy and precision. An incorrect sampling scheme cannot be relied on to provide representative samples. The best sampling location is at a transfer point between conveyor belts and representative samples can be obtained by intercepting full cross-section of the DRI or HBI stream at regular intervals.

In situ sampling of ships, stockpiles, wagons, containers and bunkers is not permitted, because there is no sampling device that can be driven down to the bottom and then extract the full column. So, the whole lot do not have an equal opportunity to get sampled. The only effective procedure is sampling from a conveyor belt when the DRI or HBI is being conveyed to or from the ship, stockpile, container or bunker.

The methods used for sampling and sample preparation depend on the final choice of the sampling scheme, and on the steps necessary to minimize possible biases and obtain acceptable overall precision.

Sampling Scheme

The basis for sampling scheme is adopted from ISO 10835: 2007 which is as followed:

The lot was sampled from the existing moving stream of DRI plant at Karachi, owning to the fact that at the time of sampling plant was in operation and hence sampling from moving streams was a possibility. It was made sure that while collecting samples, the samples were of near-to- same size/mass. The vertical length of stream was reached by the shovels used to give all parts of the moving stream to be mixed and picked from during the sampling to minimize the biasness in sampling. Samples should be as dry as possible before crushing.

System Verification

Before conducting any bias tests, sampling and sample-preparation systems shall be first inspected to confirm that they conform to the correct design principles specified in the International Standard. Inspections shall also include an examination of whether any loading, unloading or reclaiming procedures could produce periodic variations in quality, in phase with the taking of increments, e.g. size distribution. When such cyclic variations occur, the source of the variations shall be investigated to determine the practicability of eliminating the variations. If not possible, stratified random sampling shall be carried out. [45]

Minimization of particle-size degradation

In order to avoid any particle size degradation, it is important to prevent/reduce free-fall drops. Minimization of particle-size degradation of samples used for determination of size distribution is vital to reduce bias in the measured size distribution. To prevent particle-size degradation, it is essential to keep free-fall drops to a minimum.

Extraction of increments

The increments of DRI were extracted in such a manner from the moving stream that it was made sure that all parts of the DRI conveyor were accessed and equally explored for samples, with key focus on mass, density, size of individual particles. If this step is not followed, then the sample cannot be considered to be representative sample and hence the analysis is not reliable.

Number of increments (cuts):

The number of increments for division using factional shoveling should have minimum of 20 increments. The increments is divided into partial samples and kept aside. The process is repeated various times and after over 100 partial samples are collected weighing 200gm each, then the activity of making gross sample is completed by repeating the same operations on the all partial samples collectively. When the gross sample is prepared, at that point base test is conducted to determine the current state physical and chemical characteristics of the gross sample. After the base testing, gross sample is then divided in 50 partial samples for testing.

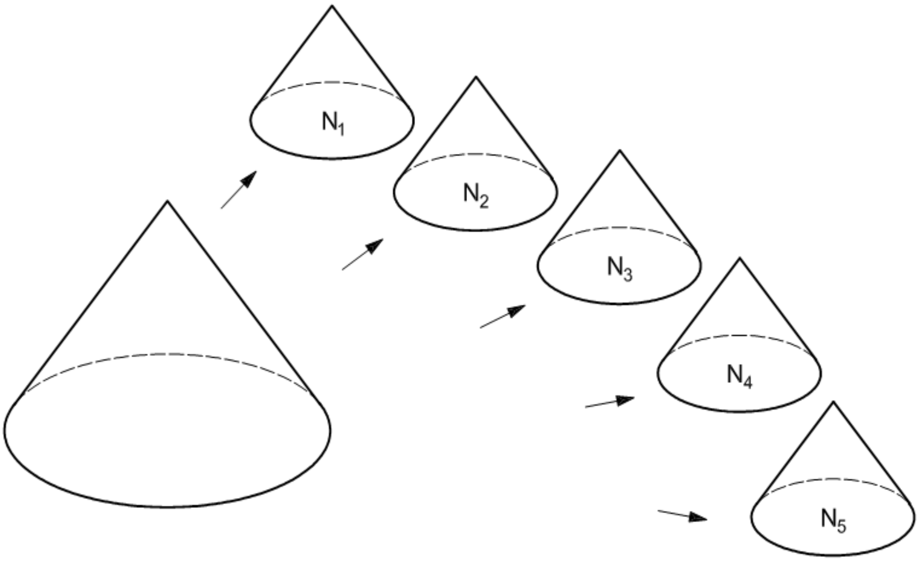


Figure 6. *Manual Sampling using Fractional Shoveling [45].*

Method of sampling: Mass-basis sampling

Increments were taken as if they are apparently uniform in mass. Size was another consideration. The particles were measured and weighed for uniformity and variation of increment masses was set less than 20% as per the ISO guidelines. Other remaining particles were not left out.

The coefficient of variation, CV, is defined as the ratio of standard deviation, σ_{mass}, to the mean value, $\underline{m}$, of the mass of the increments, expressed as a percentage as follows:

$$CV = \sigma_{mass}/\underline{m}$$

Example: If the average mass of DRI increment is to be 100 gm., then the increments should be collected in such a way that 95% of them may vary between 70 gm. to 130 gm., so that an average of 100 gm. is attained.

Sample preparation

During sample preparation of each partial sample, utmost care was taken in making sure no other material gets added in the sample and there's no effect on the quality of the material. A defined quantity of DRI or HBI collected as sample is passed through a series of operations, ranging from crushing, mixing and division in smaller partial samples.

Crushing and grinding

DRI is purged in the crusher and grinder equipment installed according to the size and hardness of the DRI taken from the increments. Utmost care should be taken not to get the DRI over grounded below a nominal top size of 160 µm, as this may lead to oxidation of the sample. The equipment was run in small intervals (i.e. 4-5 minutes cycle) as continuous run would have made the grinding equipment hot and this would have increased the temperature of DRI increments.

Mixing

Mixing the sample of DRI makes it more homogenous and it subsequently reduces the errors in sample division. Collection of samples from different piles of DRI makes mixing necessary. So, during sampling it is made sure that samples are taken in such a way that mixing is minimized.

Fractional shoveling

Division by fractional shovelling is applicable to DRI, HBI briquettes and crushed HBI. Its principle is based on the number of increments and the mass of divided sample. Division by fractional shoveling is applicable to DRI according to ISO 10835:2007 [45].

Mass of divided sample

When a gross sample is divided, the minimum mass of the divided sample shall be in accordance with Table 8. The gross sample shall not be divided further than the mass given in Table 4 for the nominal top size of the sample until it is crushed to a smaller particle size, subject to an absolute minimum of 500 g to satisfy the requirements for preparation of test samples for chemical analysis [45].

Table 19 Examples of minimum mass of divided gross sample for moisture determination and/or chemical analysis [45]

Size of DRI (mm)	Minimum mass of divided gross sample (kg)
100	1600
63.5	500
40	160
21.5	90
22.4	38
10	5
6.3	1.6
2.8	0.5
1.4	0.5
0.5	0.5
0.25	0.5

Note: The minimum masses are indicative and subject to confirmation through international tests

Chemical Analysis

DRI is used for the determination of total iron, metallic iron, ferrous iron, metallization and gangue.

Determination of Total Iron, Fe (T).

Total iron content was determined by Titrimetric method after tin (II) chloride reduction (ISO 2597-1: 2006) [46].[46] Figure 7 depicts the determination of total iron content as per the flow chart.

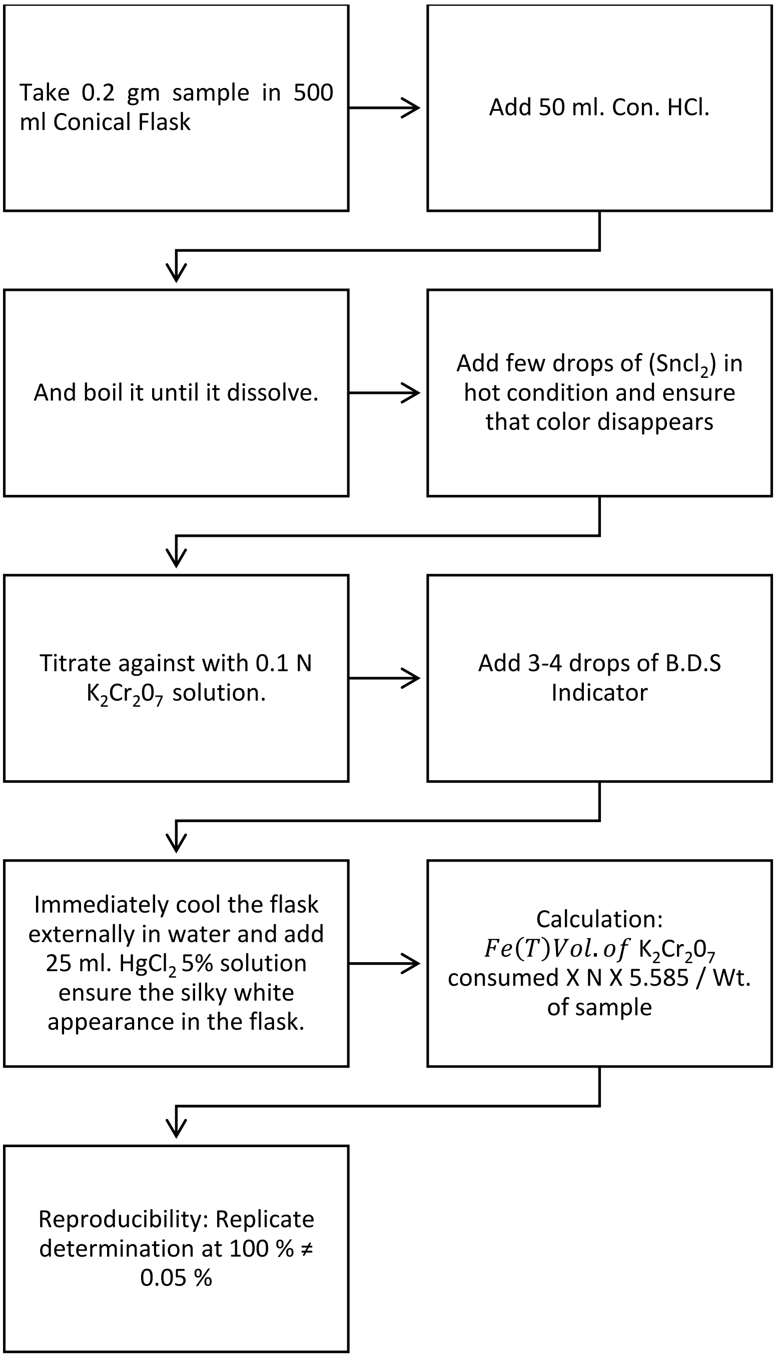


Figure 7 Flow chart depicting the procedure to determine the total iron Fe (T) in DRI sample. [47]

Metallic Iron, Fe (M)

Metallic iron content was determined by Bromine-Methanol Titrimetric Method (ISO 5416: 2006) [47]. [47] depicts the determination of metallic iron content as per the flow chart.

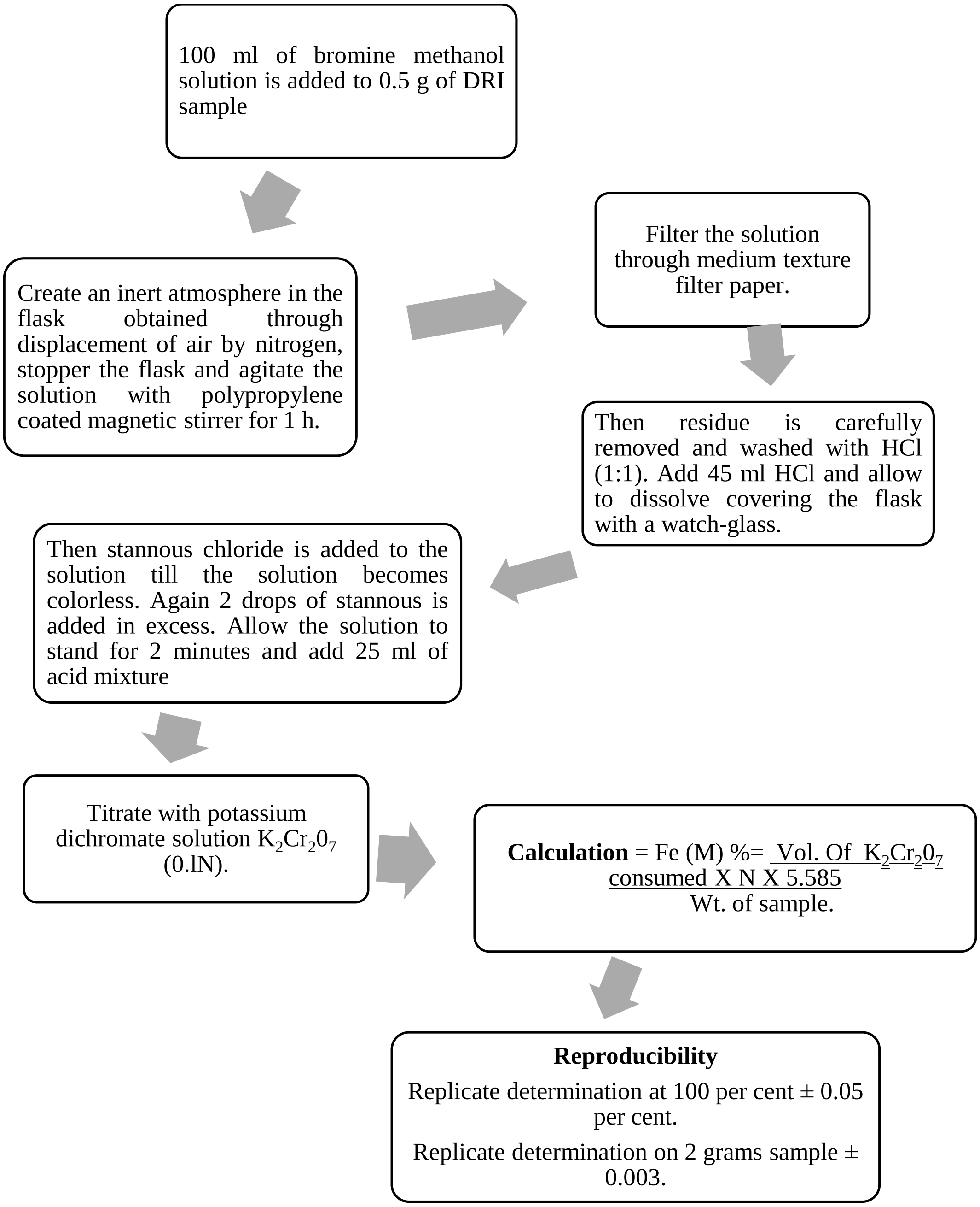
Principle of the Method:

It is based on the principle of dissolving metallic iron by treating it with bromine-methanol solution. The insoluble residue is separated by filtration. The iron in the filtrate is reduced to iron (II), which is titrated with potassium dichromate solution.

Reagents to be prepared [48]:[48]

For this analysis, reagents of analytical grade and water (according to grade 2 of ISO 3696) were used. Following reagents were prepared: HCl, ρ1, 16 g/ml to 1, 19 g/ml; H_2SO_4, ρ 1, 84 g/ml, diluted 1 + 1; CH_3OH, max. 0. 1 % H_2O; Bromine-methanol solution, 50 ml/l (5 ml of bromine in 95 ml of methanol which is used immediately after being prepared); H_2O_2 solution, 30 % (V/V): $SnCl_2$ (II) solution, 100 g/l which is prepared by dissolving 119 g of tin(II) chloride dihydrate ($SnC1_2$. $2H_2O$), in small amounts, with 200 ml of HCl by warming. This solution is cooled and diluted to 1 liter. $HgCl_2$ solution, 50 g/l; H_2SO_4;

Iron standard solution was prepared by dissolving 0. 800 g of high purity iron (III) oxide (Fe_2O_3! 99 %) in 40 ml of hydrochloric acid (4.1). Dilute to 1 000 ml and mix; Potassium dichromate ($K_2Cr_2O_7$) = 0,016 67 mol/l; Sodium diphenylamine sulfonate, 2 g/l solution was prepared by dissolving 0.2 g of sodium diphenylamine sulfonate ($C_6H_5NHC_6H_4SO_3Na$) in 100 ml of water. Store the solution in a brown glass bottle.



100 ml of bromine methanol solution is added to 0.5 g of DRI sample

Create an inert atmosphere in the flask obtained through displacement of air by nitrogen, stopper the flask and agitate the solution with polypropylene coated magnetic stirrer for 1 h.

Filter the solution through medium texture filter paper.

Then residue is carefully removed and washed with HCl (1:1). Add 45 ml HCl and allow to dissolve covering the flask with a watch-glass.

Then stannous chloride is added to the solution till the solution becomes colorless. Again 2 drops of stannous is added in excess. Allow the solution to stand for 2 minutes and add 25 ml of acid mixture

Titrate with potassium dichromate solution $K_2Cr_20_7$ (0.lN).

Calculation = Fe (M) %= $\frac{\text{Vol. Of } K_2Cr_20_7 \text{ consumed X N X 5.585}}{\text{Wt. of sample.}}$

Reproducibility

Replicate determination at 100 per cent ± 0.05 per cent.

Replicate determination on 2 grams sample ± 0.003.

Figure 8 Flow chart depicting the procedure to determine the metallic iron in DRI sample.

Apparatus required

Pipettes (one-mark), Volumetric flasks (one-mark), Burette, Conical flask without concave base, watch-glass if working outside a fume cupboard, Magnetic stirrer, magnetic stirring bar with PTFE coating, Filtering apparatus, with a pore size of > 1µm.

Outline of the Method

Bromine and methanol mixture is added to the DRI sample leading to the dissolution of the metallic iron. HCl is added to the filtered residue which contains oxides of Fe^{2+} and Fe^{3+}. This dissolves the FeO present. The addition of stannous chloride, reduces all the Fe^{2+} present in the residue Fe^{3+}, excess of which is eliminated by reaction with $HgCl_2$. The amount of combined iron is determined. The difference between total iron and the combined iron is equal to the amount of metallic iron.

- $2Fe + 3\,Br_2 \rightarrow 2\,Fe^{3+} + 6\,Br-$
- $Fe^{3+} + Sn^{2+} \rightarrow 2Fe^{2+} + Sn^{4+}$
- Sn^{2+} (excess) $+ 2\,Hg^{2+} \rightarrow Sn^{4+} + 2\,Hg^{+}$
- $6Fe^{2+} + Cr_2O_7^{-2} + 14\,H^{+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

Procedure

100 ml of bromine methanol solution is added to 0.5 g of DRI sample in ground glass joint flask. The flask is fixed to reflux condenser. The residue obtained is cooled, filtered and washed with distilled water, then with methanol and again with distilled water. Then residue is carefully removed and washed with HCl (1:1). Add 45 ml HCl and allow to dissolve covering the flask with a watch-glass. Then stannous chloride is added to the solution till the solution becomes colorless. Again 2 drops of stannous is added in excess. Allow the solution to stand for 2 minutes and add 25 ml of acid mixture. Add 3-4 drops of indicator and titrate with 0.1 N of $K_2Cr_2O_7$ solution. As a result the solution changes its color from colorless to yellow, green and end point is purple.

Blank test

Blank test was determined by using all reagents but adding 10 ml of standard iron solution in place of the test portion. Add 25 ml of HCl to the standard iron solution. Then Add some water, rinsing the walls of the beaker, and heat again until fuming takes place. Cool, carefully add about 140 ml of water and 25 ml of HCl and boil until all salts are re-dissolved. Then, tin (II) chloride solution is added to the boiling solution, drop by drop until the solution becomes colorless. The walls of the beaker are rinsed and cool quickly, then diluted with water to 300 ml. Then 15 ml of mercury (II) chloride solution is added. Wait for about 5 min until slight turbidity appears, add 25 ml of sulfuric acid/phosphoric acid mixture and 1,0 ml of sodium diphenylamine sulfonate solution and titrate with potassium dichromate solution until one drop produces a change in color from green to purple. Subtract 1,00 ml from the volume of potassium dichromate solution required for the titration of the blank test solution. The result is the blank test value to be subtracted from the titration value obtained for the test portion.

Summary

The samples of DRI are collected from respective storage yard. Initially properties (physical/chemical) are recorded by testing them at DRI of manufacturing plant as depicted in Figure 9 Flow of Sampling to Testing. Later on, samples of DRI are kept closed storage and open storage conditions (Open storage and closed storage) for 24 weeks and testing is carried out weekly to identify impact of storing them for such duration and variance analysis for choosing between options of storage for effective utilization of the products and for intermittent production [49].[49] Repeated testing gives the opportunity to visually inspect the material under those conditions.

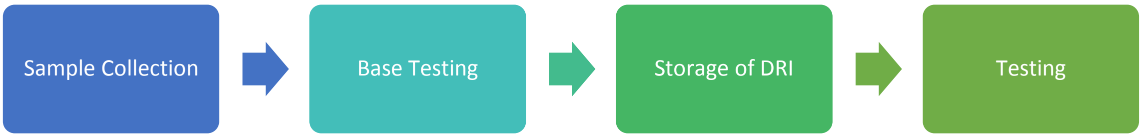


Figure 9 Flow of Sampling to Testing

Storage Types and Testing

After the initial sample collection, Base testing is done to make sure that the original properties of samples collected are recorded before keeping them in any storage for analysis. Then, gross samples are split to make partial samples and in this way two types of partial samples are kept under two modified storage conditions.

Disparate Storage

Existing Storage will also be monitored so that various relationships/comparisons may be used for analysis as depicted in

Figure 10 Flow chart depicting the two storage options used for the analysis of DRI..

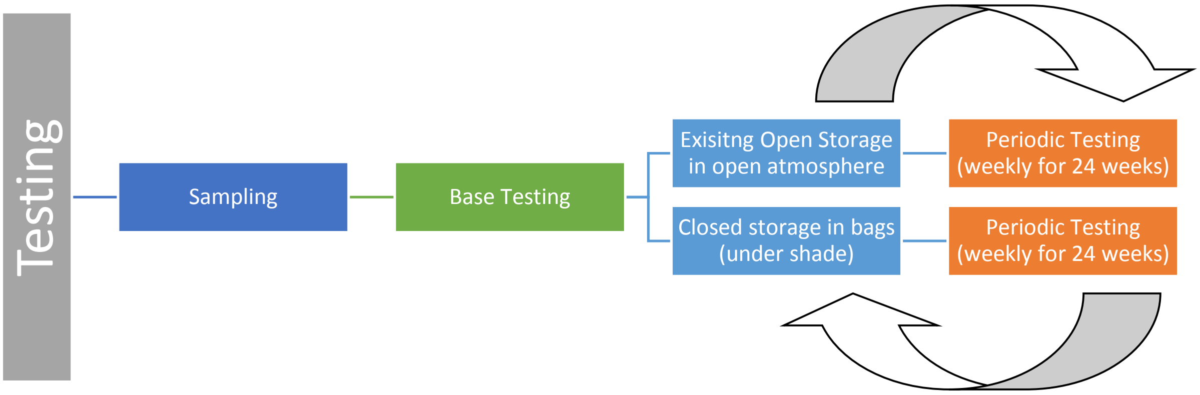


Figure 10 Flow chart depicting the two storage options used for the analysis of DRI.

Purpose of Selection of Storage Options

Two storage options are used for the analysis as depicted in the chart above. Originally, the storage of DRI is storage bags (without shadow) at DRI manufacturing plant. For this research setting, we have modified the storage options to evaluate the possible storage options.

1. **DRI (Inside New Storage Yard):** DRI manufacturing plant has constructed a new facility for storing DRI, a shed having temperature controlled situations for DRI. DRI are bagged inside these storage sheds and weekly tests are carried out from the samples kept for analysis purpose.
2. **DRI (Outside Storage):** Old storage area also analyzes comparison without any changes to study the impact of storage condition.

Figure 11 View of existing open storage yard of DRI

Figure 12 Bag containing DRI ready to shift in closed storage

Properties to be analyzed

The following tests analyze the key parameter of DRI, therefore they are sufficient for the analysis to determine the best storage options in given conditions.

Chemical Analysis (% w/w)

1. Metallic Iron (Fe)
2. Ferrous Oxide (FeO)
3. Total Iron (TFe)
4. Metallization
5. Gangue

Sieve Analysis (% w/w)

1. Size 9.5~19 MM
2. Size 5.0~9.5 MM
3. Size -5.0~5.0 MM

Laboratory Testing

Laboratory testing has been done at DRI Laboratory, DRI manufacturing plant, Bin Qasim, Karachi - Pakistan

Number of tests

- 1 Base Test
- 24 Tests of each sample: 24x2 = 48

Testing

To find out the impact of storage conditions, repeated tests are carried on periodical basis (weekly) for 24 weeks at DRI manufacturing plant laboratory. The aim of these experiments is to know the exact difference of degradation in properties of DRI by testing the samples from those storage. Artificial condition of shed for DRI is created along with the existing open storage yard. The observations from experiments/tests are noted and analysis is done on the basis of test results. Graphical representation of each week's tests are plotted for easy analysis of results.

- **Sampling**: Representative sample collection is done from whole DRI storage yard
- **Base Testing**: It is carried out to know the current status of Chemical Properties and sieve sizes.
- **Sample's Storage**: Samples are separated for two storages (existing which is outside shed and new which was artificially prepared).
- **Testing**: Testing was carried on weekly basis at the DRI manufacturing plant Laboratory and results were recorded.
- **Discussion**: Discussion on the results is undertaken

Chapter 4. Results

Test Graphs

As per the aim, the study of “Comparative analysis of ageing effect on DRI under closed and open storage conditions at DRI manufacturing plant” was carried out with the use of 2 DRI similar samples. Each DRI sample placed under two different storage conditions were analyzed for continuous 24 weeks with the gap of 7 days. They were being analyzed every Monday of the week. This analysis was based on two techniques: chemical analysis and Sieve analysis. The result were electronically documented every week by the testing procedure of ISO 2597-1 (2006), ISO 5416:2006.

Chemical Analysis

During this analysis, the total iron content, metallic iron content, ferrous oxide content, extent of metallization and gangue impurity were determined in percentage. The total iron content was assessed by trimetric method after tin (II) chloride reduction (ISO 2597-1: 2006). Metallic iron content was determined by Bromine-Methanol Titrimetric Method (ISO 5416: 2006). To show the chemical analysis of a DRI sample of every weeks till 24rth week is difficult to show, so the electronic document of chemical analysis 1st and 24rth week are outlined as sample in Annexure I (A-B). Annexure II gives the summary of test results (% w/w) whereas Annexure III summarizes the percentage deviation obtained from test results.

Total Iron

Figure 13 depicts the total iron w/w percentage (in Y- axis) has decreased over the length of 24 weeks (X- axis) in both storage conditions. The simple black curve shows the decrease in total iron content in closed storage whereas distorted black line shows the reduction in open storage condition. With the production of 93.78% of total iron content in DRI sample, the blank sample showed similar total iron content of 93.62% in both open and closed storage with only 0.16% loss within 4 days which confirms its fast reduction in the air. So, total iron content in blank test sample was taken as control to compare further reduction in content in either of the storage conditions with the passage of time. During the first week of analysis, the total iron content was found to be 93.49% and 92.72% as compared to control which corresponds to 0.13% and 0.90% decrease. With the passage of time, the reduction in total iron content decreased by 1.37% and 5.20% during the 11th week of analysis under closed and open storage conditions. This reduction further increased to 1.73% and 6.04% during 24th week of analysis under closed and open storage conditions. The reduction in total iron content in open storage was 3.49 folds the reduction in closed storage condition.

So, a clear difference can be observed in the existing storage as compared to new storage system. The material outside the shed has deteriorated considerably and hence for a period of 20-30 weeks, the inside storage apparently is the best choice in given conditions.

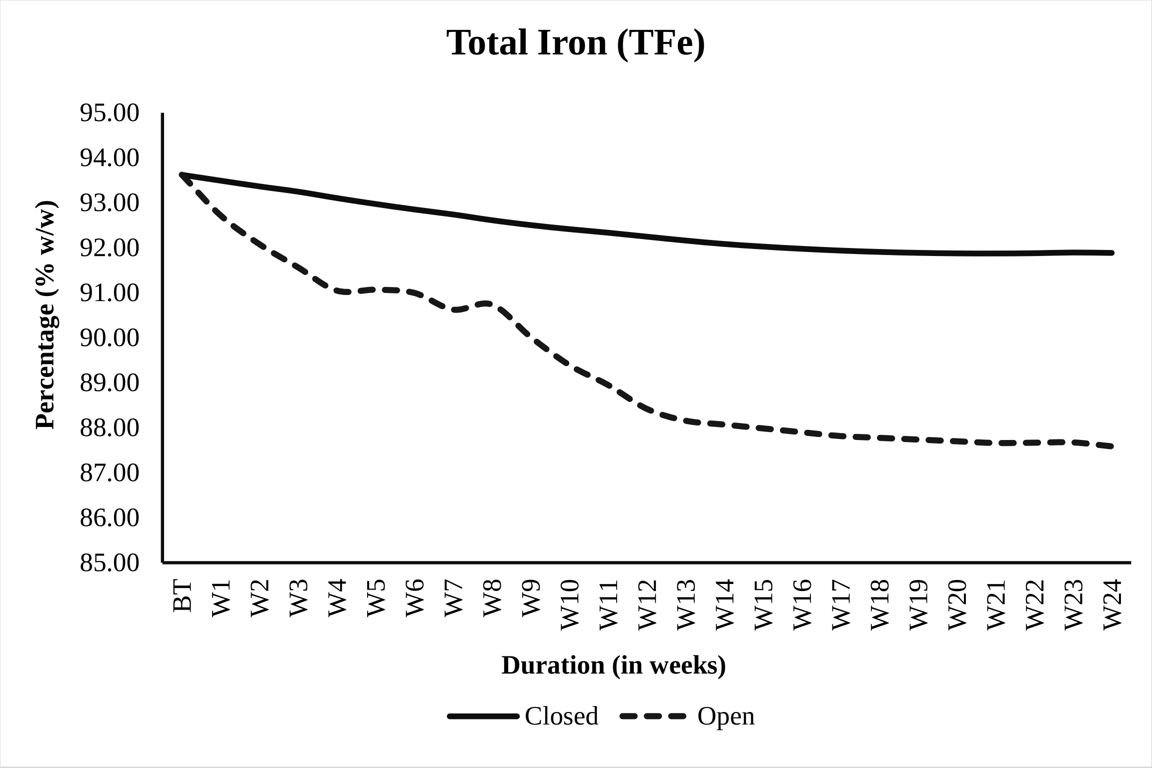


Figure 13 Effect of Storage on Total Iron (w/w %)

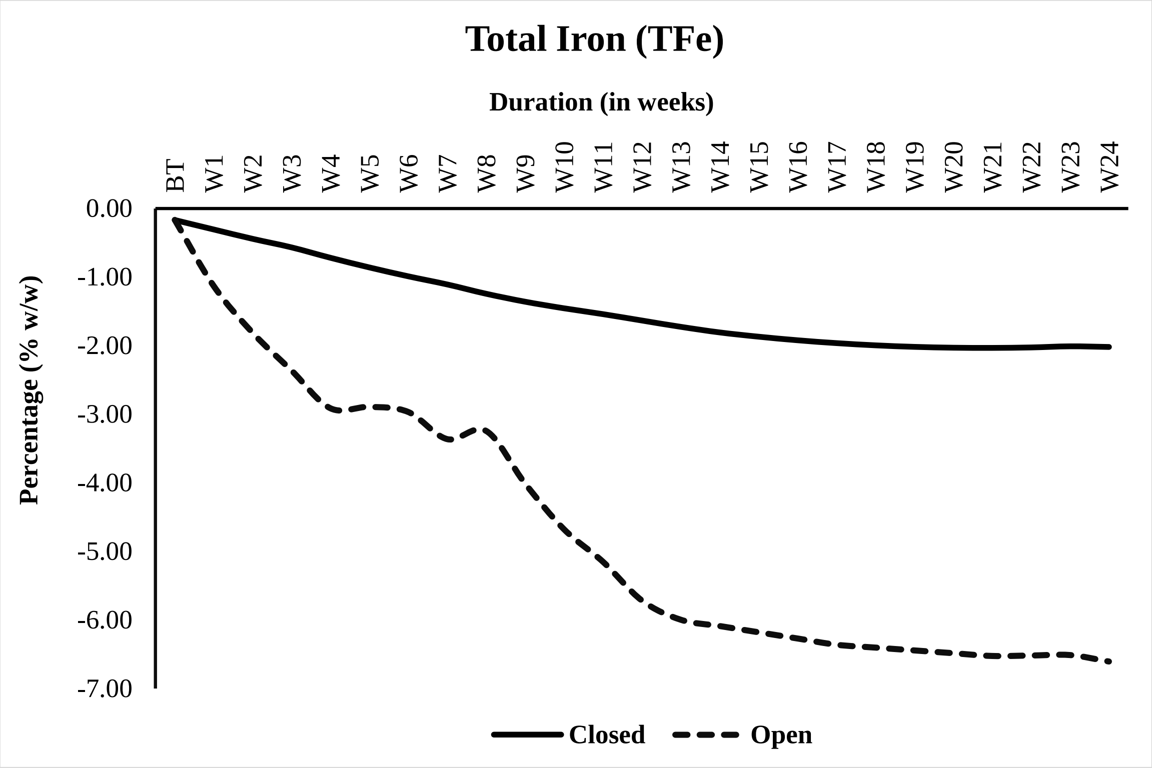


Figure 14 Overall percentage variation in Total Iron

Further Figure 14 shows the rate of percentage degradation from the actual base test percentage of the total iron. The S-curves may look similar, but in actual it’s the representation of the amount of percentage it reduced over the length of 24 weeks. Both samples have degraded at a certain rate, but there’s a big difference between the degradation of inside (almost -2 %) and outside (-6.5+ %).

Metallic Iron

Figure 15 depicts the metallic iron w/w percentage (in Y- axis) has decreased over the length of 24 weeks (X- axis) in both storage conditions. The simple black curve shows the decrease in metallic iron in closed storage whereas distorted black line shows the reduction in open storage condition. With the production of 88.28% of metallic iron in DRI sample, the blank sample showed similar total iron content of 88.12% in both open and closed storage with only 0.16% loss within 4 days which confirms its fast reduction in the air. So, metallic iron in blank test sample was taken as control to compare further reduction in content in either of the storage conditions with the passage of time. During the first week of analysis, the metallic iron was found to be 87.99% and 87.19% as compared to control which corresponds to 0.13% and 0.93% decrease. With the passage of time, the reduction in metallic iron increased by 1.51% and 5.87% during the 11th week of analysis under closed and open storage conditions.

This reduction further increased to 2.11% and 7.81% during 24th week of analysis under closed and open storage conditions. The reduction in metallic iron in open storage was 3.70 folds the reduction in closed storage condition. So, closed storage condition is preferential for the outcome to the steel maker. These results supports more the exposure of DRI to oxygen present in air, more is its reduction so lesser the content of metallic iron content in DRI. This decrease can leads to the severe loss to the steel maker.

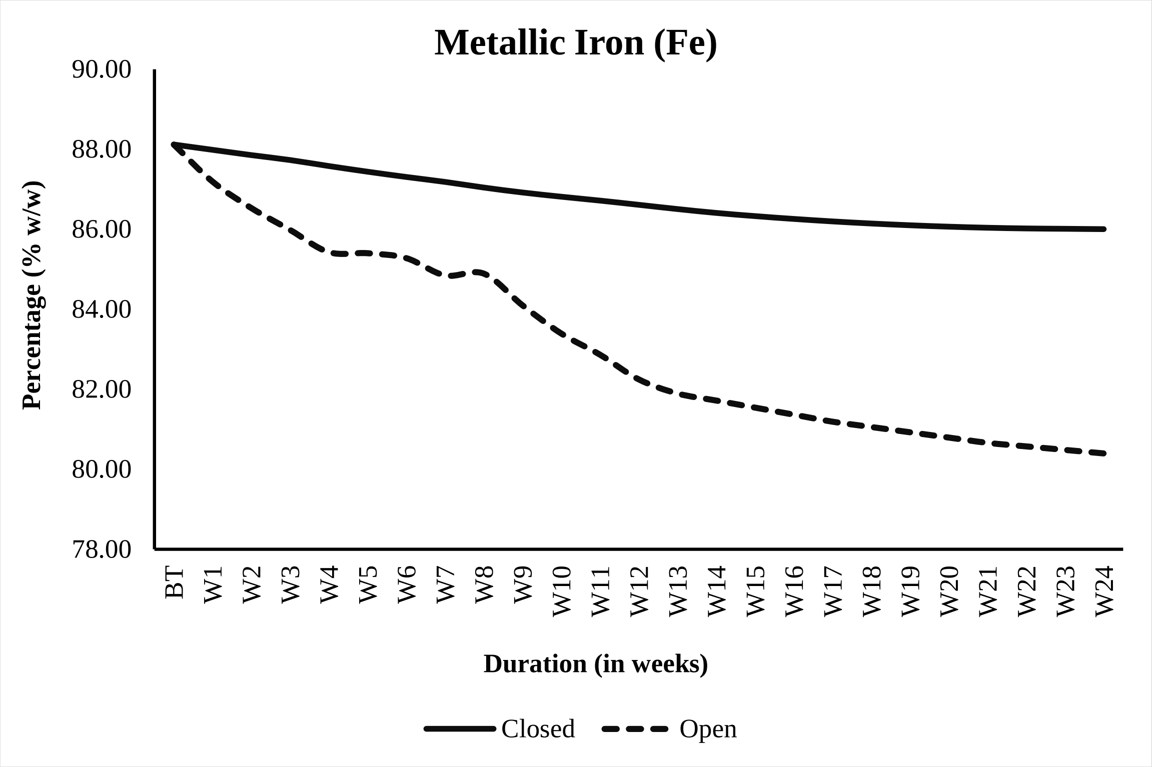


Figure 15 Effect of Storage on Metallic Iron (w/w %)

Further Figure 16 shows the rate of percentage degradation from the actual base test percentage of the metallic iron. Metallization is a key in further processing of the DRI. The EAF route is specifically chosen to reduce the energy and cost related issues, and ultimately get the maximum value for the money invested. But, as the trend shows the metallization has reduced almost 9 percentage in the outside atmosphere compared to 2+ percentage of inside, it’s pretty much clear that outside conditions massively impact the metallization of the material. Further, these results are only of 24 weeks, but considering the utilization of the material at remote, the material usually has to wait for another 15-20 weeks further to get into further processing unit. In such situation, the material will not produce the results required as desired from the DRI which could have been used as a continuous manufacturing process at the source of production.

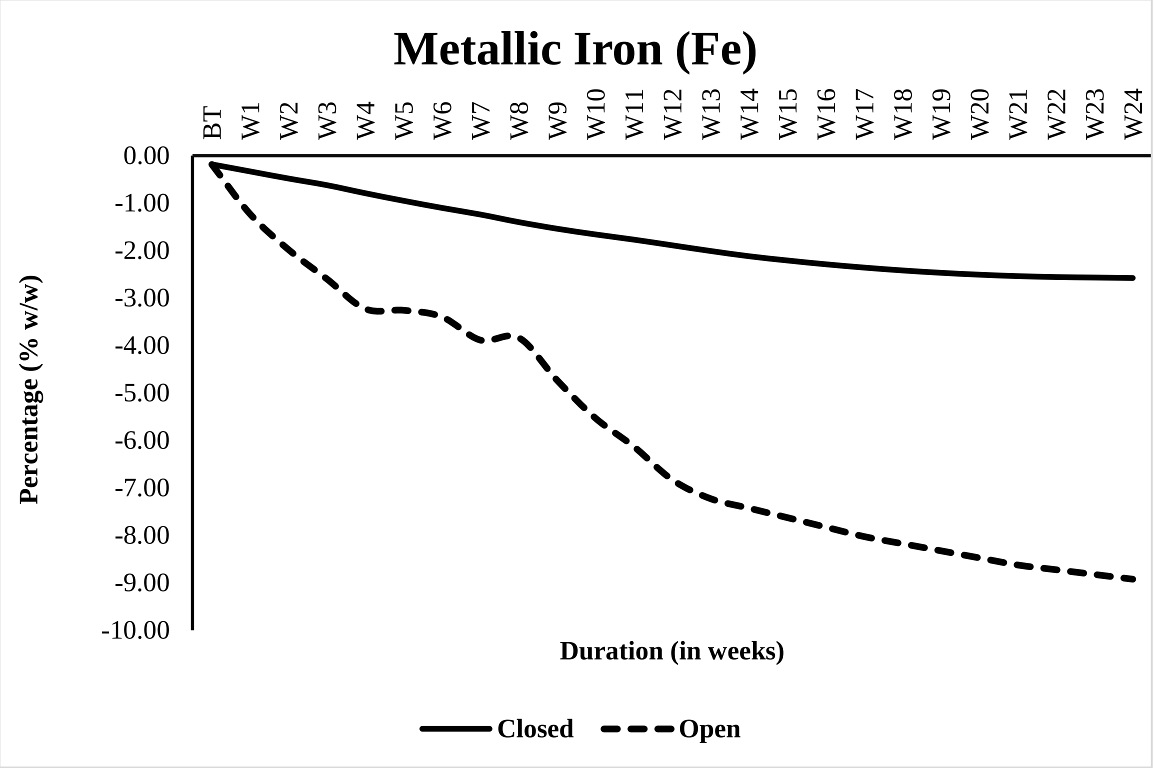


Figure 16 Overall percentage variation in Metallic Iron (Fe)

Ferrous Oxide

As Figure 17 depicts the percentage increase in ferrous oxide. As 100% reaction is not achieved during iron ore reduction, therefore even after production of DRI, still some FeO remain in the product which is found to be 5.50% in blank test sample. It was observed that during the storage of DRI, there is still some chances for DRI to get oxidized. In results, the open storage has increased the percentage of ferrous oxide in the DRI sample. The content of ferrous oxide increased from 0.02% in 1st week of analysis to 1.68% in 24th week.

Whereas, the content of ferrous oxide was found to be low ranging from 0.00% in 1st week to 0.38% in 24th week. So the average content of ferrous oxide in open storage is found to be 6.23% and 5.43% in closed storage. So, in the existing system, there’s more deviation over time than the new storage system and the FeO content has increased which is reverse of the passivation process/reduction process.

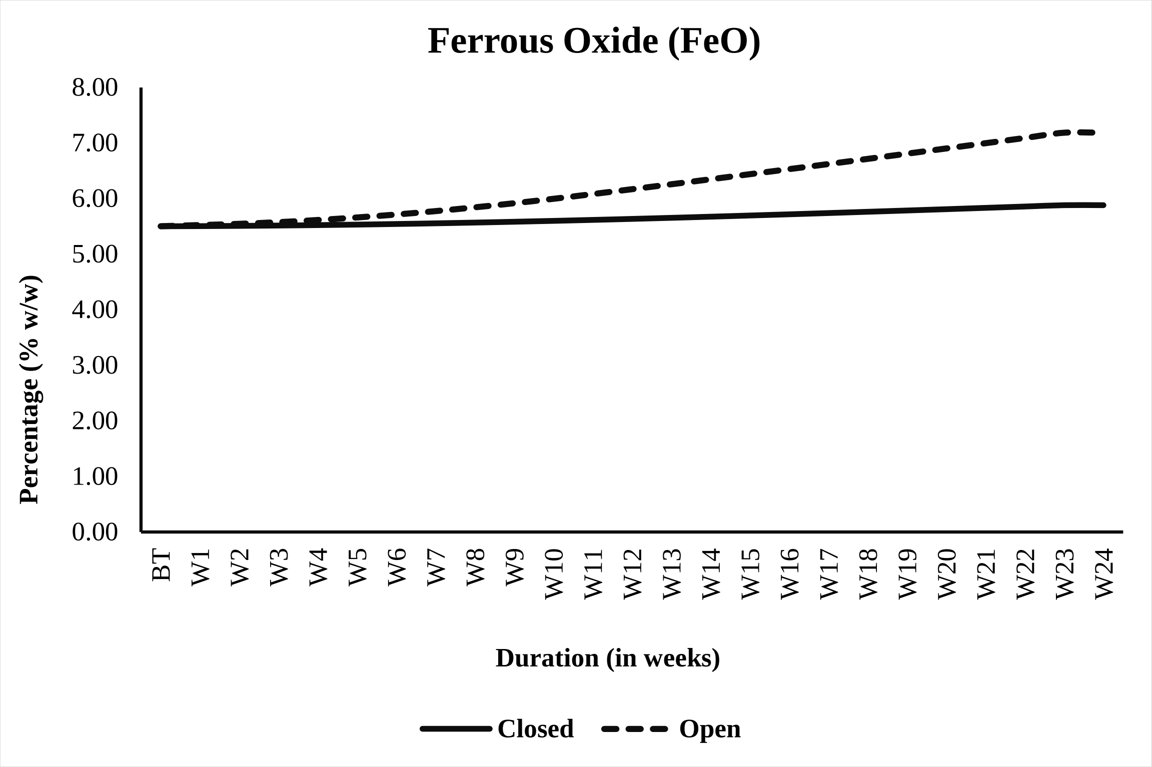


Figure 17 Effect of Storage on Ferrous Oxide (FeO) (w/w %)

Further Figure 18Figure 17 shows that the rate of percentage increase from the actual base test percentage of the ferrous oxide. This is due to the fact the DRI (reduction process) has reversed during the storage period, and hence the porous area of DRI pellets has been filled-in by oxygen to form FeO, ultimately increasing its overall percentage. This is negative impact on the material, as the material’s non-metallic content has increased. The DRI in open conditions has dramatically increased with FeO percentage over 30% compared to 7 % of the closed conditions.

Encouraging the use of closed conditions for period of 20-30 weeks in given conditions is the best options. Results may vary depending upon the time elapsed in months and for years even. Therefore, such results must be revisited for a detailed analysis for any given durations in particular.

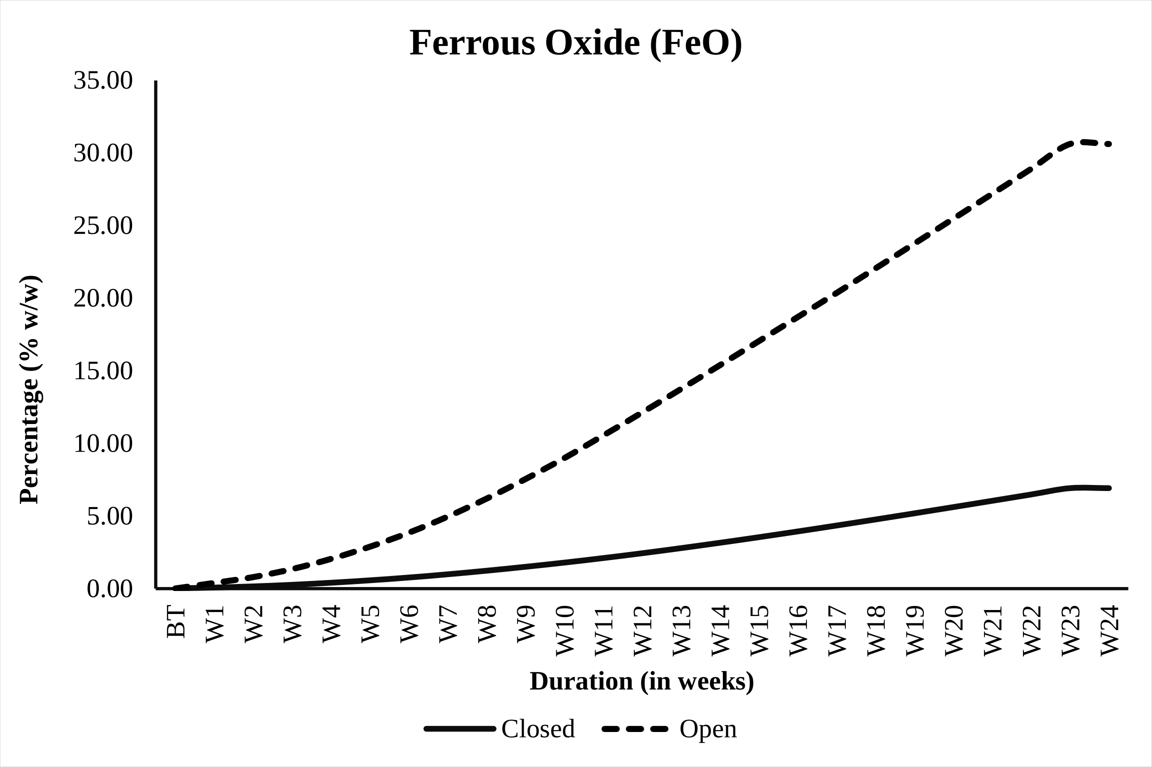


Figure 18 Overall percentage variation in Ferrous Oxide (FeO)

Metallization

Figure 19 shows the extent of metallization (in w/w percentage) of DRI sample under analysis. The result shows that the metallization has reduced as the process of passivation has reversed in this case and oxygen has again found places in the porous area of DRI, ultimately reducing the overall Iron, Metallic Iron and Metallization percentage. As the metallization has reduced, this will make the DRI with low percentage will be more difficult to melt as well as it will require more energy for melting. In blank test sample, the extent of metallization was 94.12% in both closed and open storage condition.

Whereas, the extent of metallization decreased by 0.01% and 0.08% during 1st week of analysis in closed and open storage conditions. This reduction in metallization further reached to 0.52% and 2.32% in closed and open environment. It gives us clear-cut idea that closed storage condition may prevent DRI sample towards metallization.

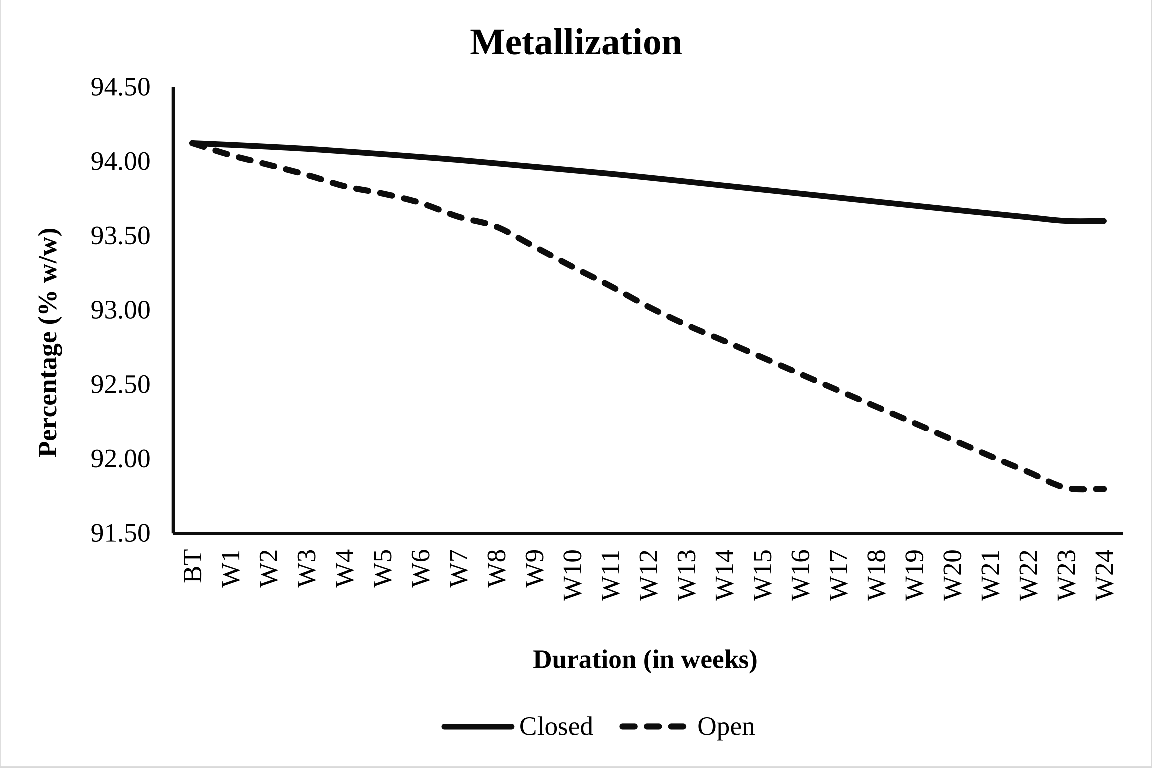


Figure 19 Effect of Storage on Metallization (w/w %)

Figure 1 reflects again the similar trend where the rate of percentage metallization has decreased to a negative range. Considering both conditions, as show in Figure 20 the percentage metallization degradation in closed condition is near to minimum, and overall in open conditions is also -2.5% which is concerning, as the metallization and Metallic Iron percentages are not only reason for buying the DRI is its Iron percentages nearing 100%, even 95+% at times in total iron but if even that is going to reduce, then the buyers will not be interested.

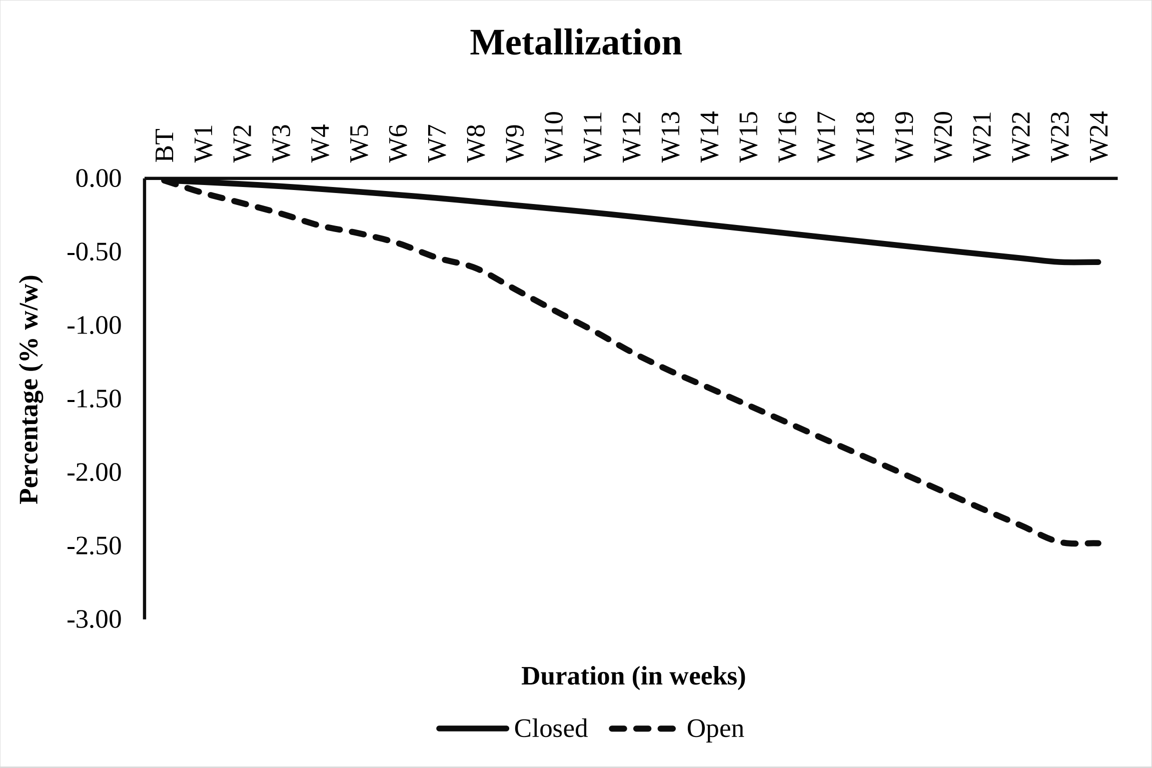


Figure 20 Overall percentage variation in Metallization

Gangue

Figure 21 shows the percentage of gangue (including all other elements in the composition of DRI which are very less in percentage and importance) w/w % has increased in both closed and open storage conditions. In blank test sample, it was found to be 6.38% in both conditions of storage but increased to 8.11% and 12.42% in respective closed and open conditions. The increase in percentage of gangue is 2 times and 1.27 times more in case of closed and open storage conditions as compared to blank test sample. This refers to the major shift in open environment as the metallic iron percentage has reduced due to the reaction of oxygen with DRI. The oxygen reacts and forms MgO, CaO, and SiO etc. Figure 22 reflects a huge variance in percentage increase of gangue, which is almost 30% for DRI in closed conditions compared to the 100% increase (double of the actual w/w %). This is very clear from all the graphs in general and this one in particular that closed conditions are the best and has the least impact at least for a duration time of 20-30 weeks.

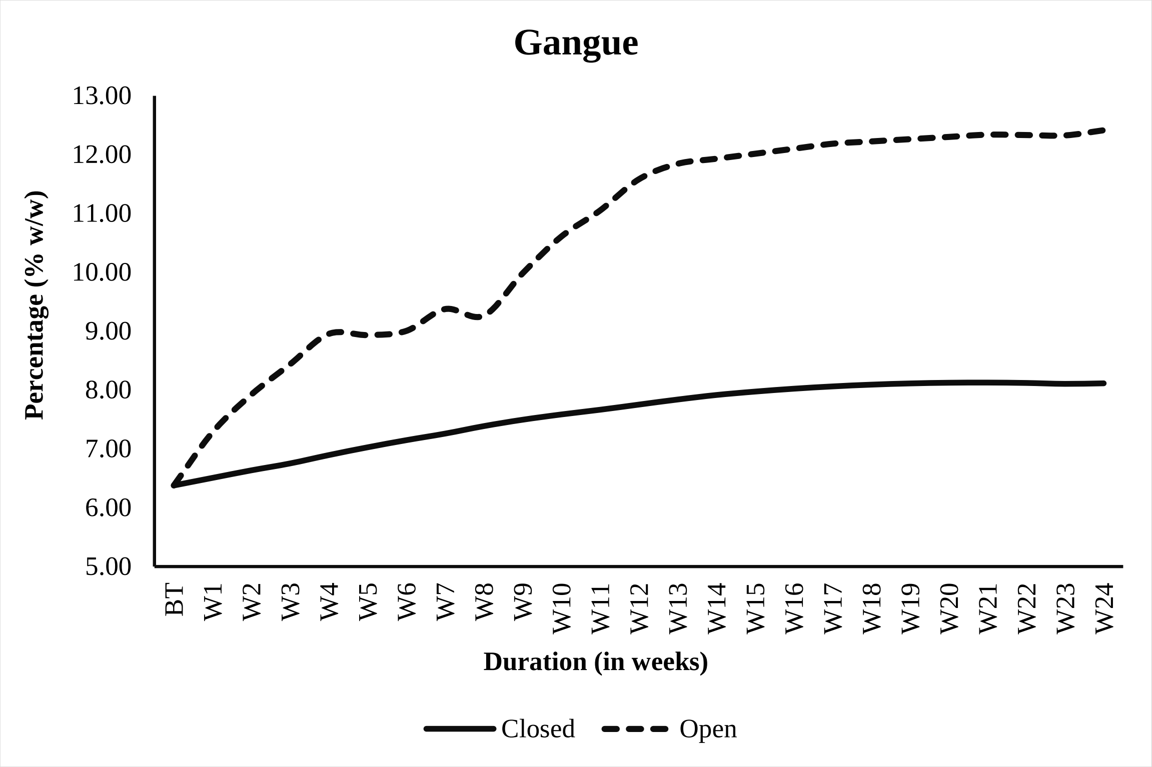


Figure 21 Effect of Storage on Gangue (w/w %)

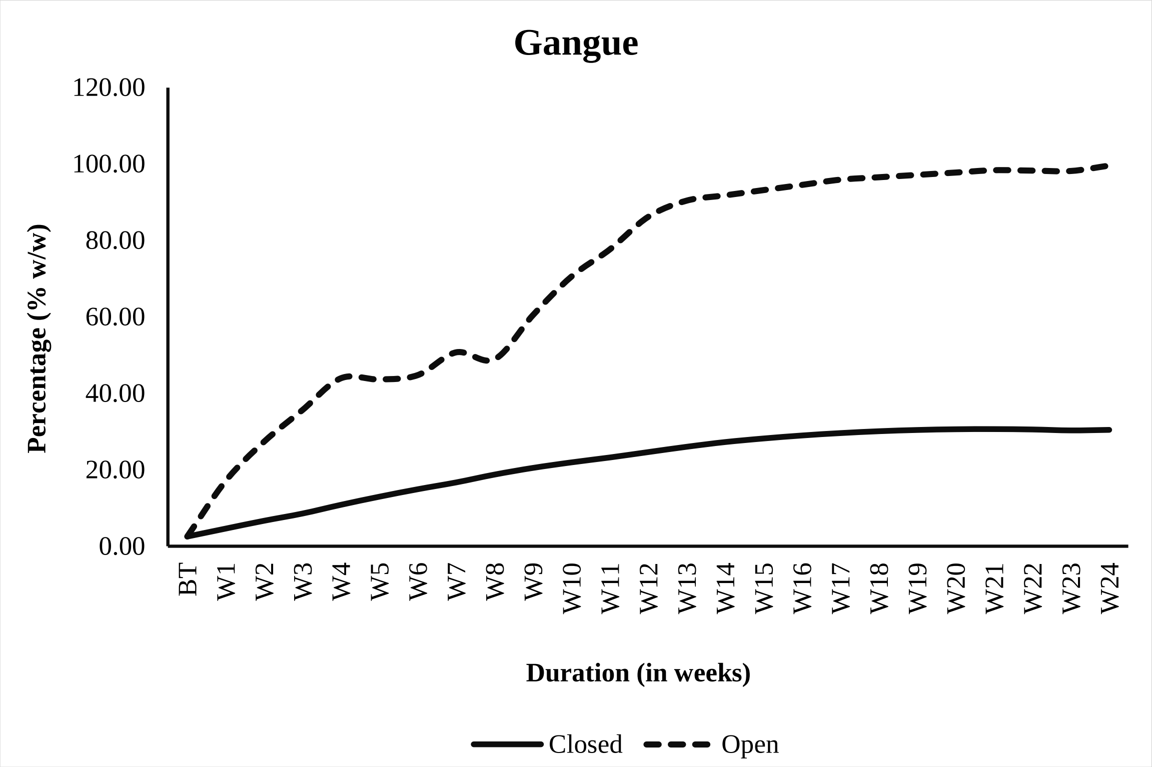


Figure 22 Overall percentage variation in Gangue

Sieve Analysis

Sieve Analysis Size A (Large) Size 9.5~19 MM

Figure 23 shows that during sieve analysis the size of DRI pellets has reduced over the period of 24 weeks in both storages. During 1st week of analysis, 95.31% and 95.16% of DRI pellets showed the reduction in their size as compared to 95.45% during blank test sieve analysis in closed and open storage conditions. This percentage of DRI pellets further reduced to 93.16% and 91.63% during the 24th week of sieve analysis in closed and open storage conditions. The fine generation have resulted due to initial and intermediate handling of the DRI pellets as well as due to the crack formation subject to the storage conditions the DRI is storage in. The difference between the both storage conditions is not significant, but it is very important to point that the curve is continuously on the decline in abrupt manner in open and closed storage conditions.

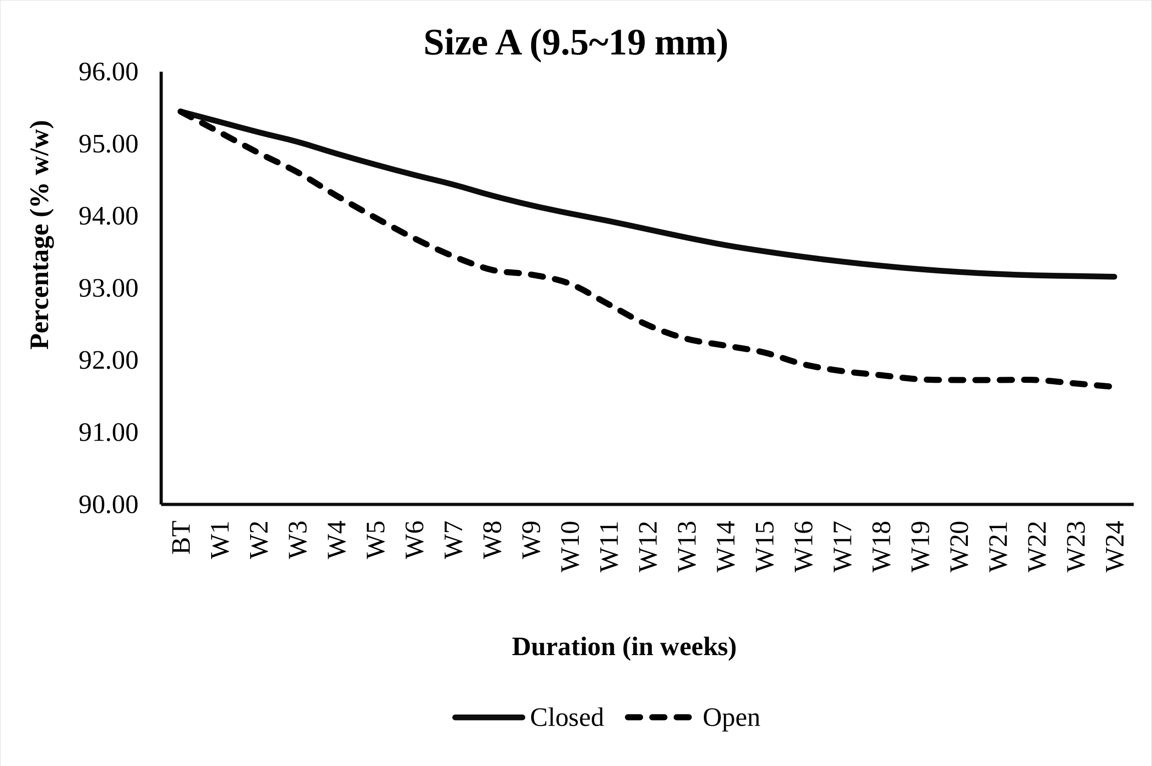


Figure 23 Effect of Storage on Sieve Size A

This reduction might be due to the reduction of DRI pellets in both the storage conditions. It can be assumed that the fine generation is possible further at same rate for more duration. Figure 24 depicts the percentage degradation has double difference almost and again there's evident better situation is the closed storage conditions.

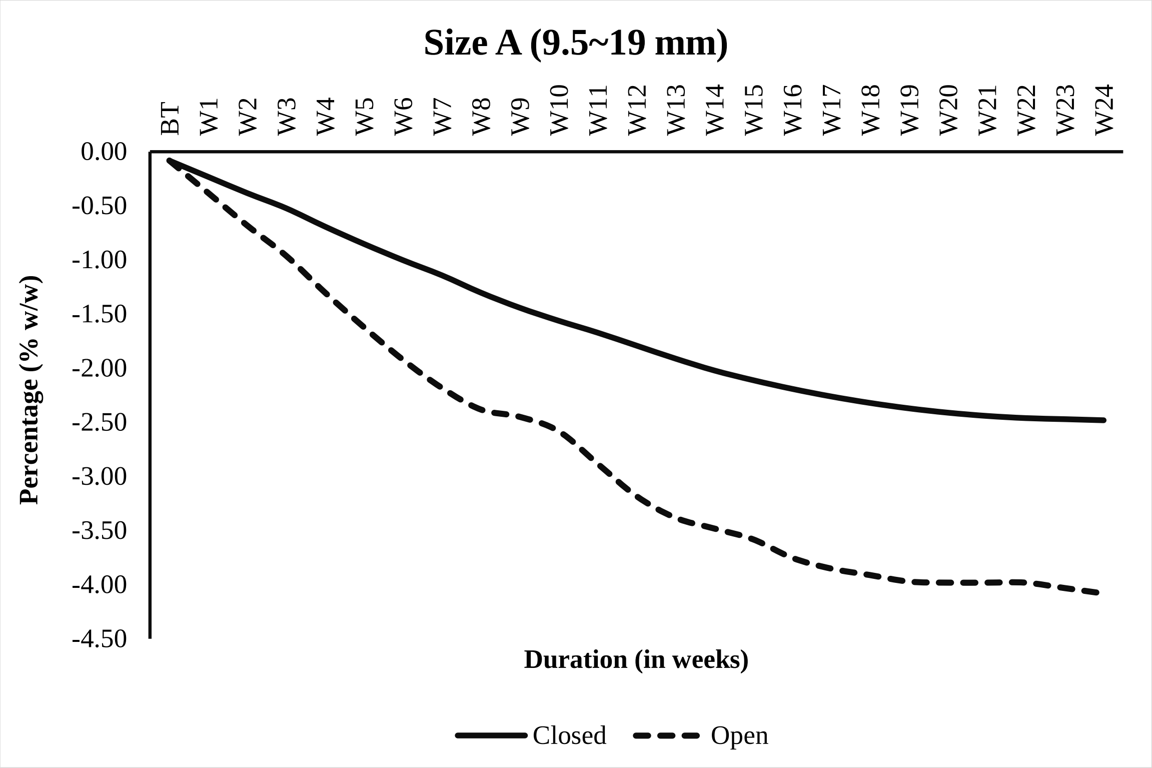


Figure 24 Overall percentage variation in Sieve Size A

Sieve Analysis (Medium) Size B 5.0~9.5 MM

Figure 25 shows the fine generation has taken place in both cases. It has been observed that DRI in closed storage and open storage conditions has smoothened curve at the end of 24 weeks, which reflects the possibility of storage of further fine generation over the length of period. During 1st week of analysis, 4.09% and 4.07% of DRI pellets showed the reduction in their size as compared to 4.10% during blank test sieve analysis in closed and open storage conditions. This percentage of DRI pellets further reduced to 4.00% and 3.71% during the

24th week of sieve analysis in closed and open storage conditions. But for actual results, same may be evaluated in greater detail using the same procedure.

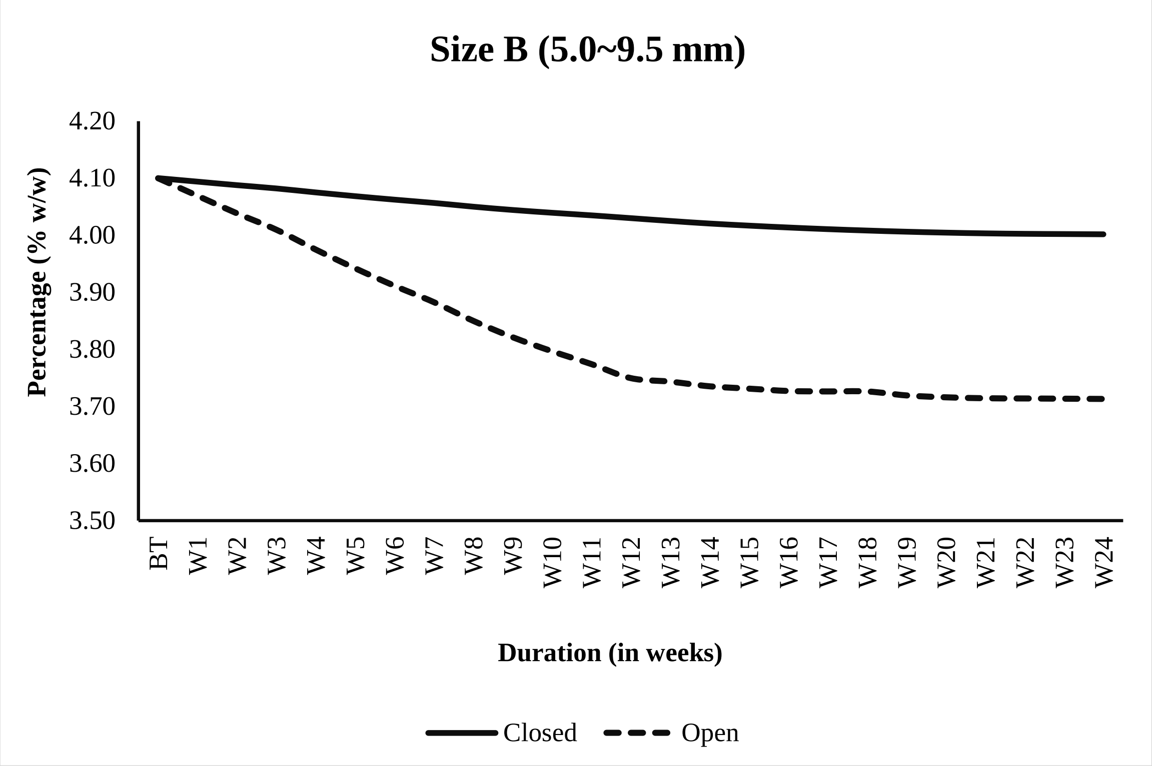


Figure 25 Effect of Storage on Sieve Size B

Figure 26 shows that there’s a percentage difference of almost -8% and again like most of the previous results, the open storage has been effected most by the conditions.

Sieve Analysis (Medium) C Size -5 MM

Figure 27 shows a different result from most of the DRI graphs above. There’s only a 0.01 difference from the base test to the final 24th week result in the closed conditions, which perhaps may be considered as the precision error. Though the open storage has degradation, but as the scale is less than 1, hence it is not of major importance for the overall result analysis.

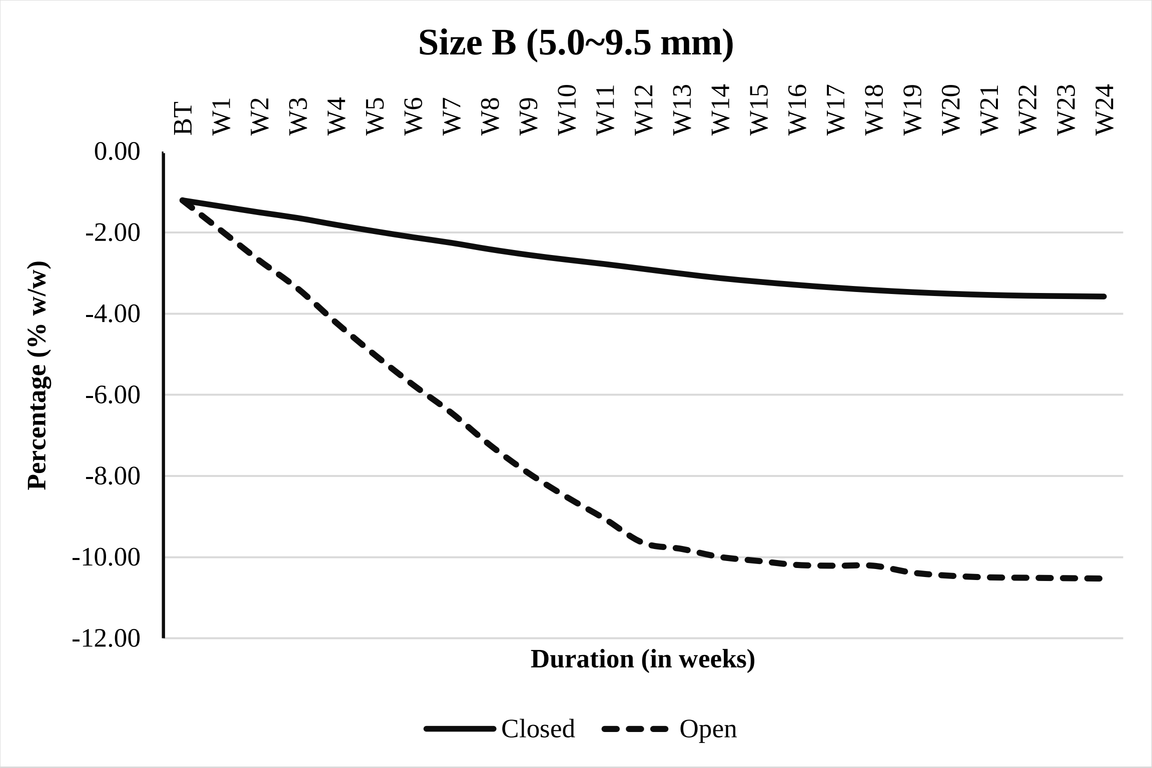


Figure 26 Overall percentage variation in Sieve Size B

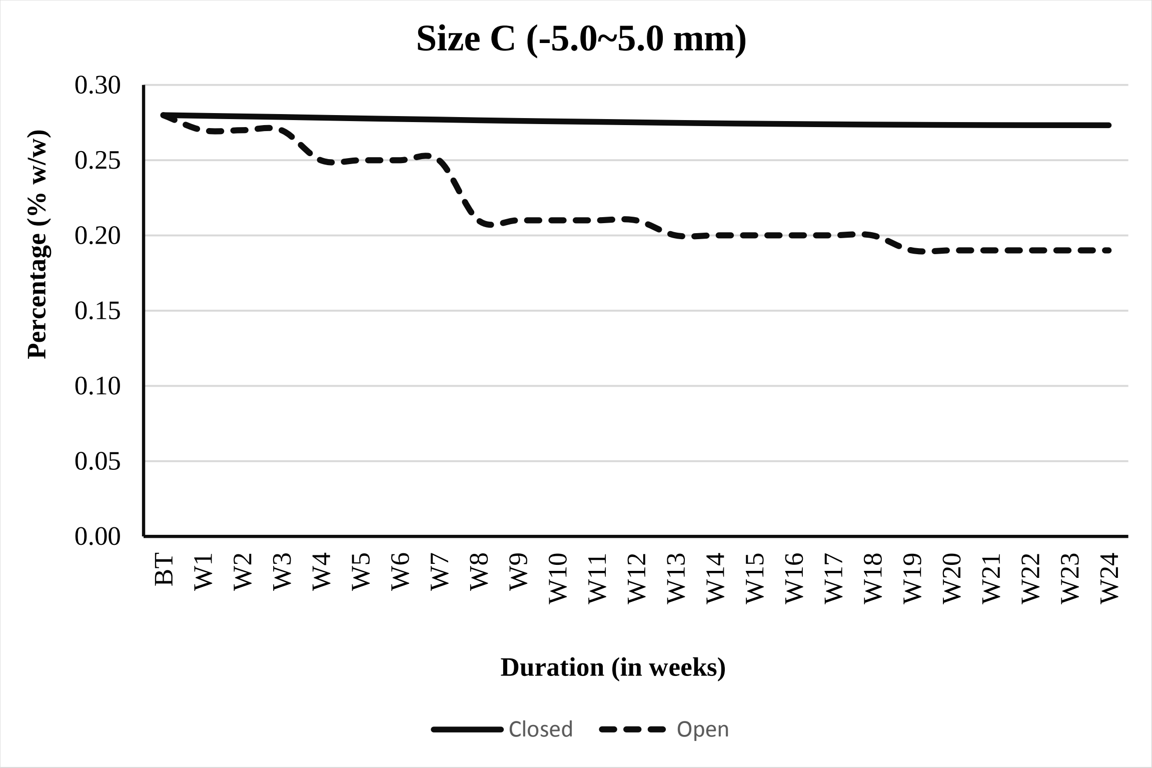


Figure 27 Effect of Storage on Sieve Size C

Figure 28 shows almost 0% deviation in closed conditions, but there's a deviation of -40% from the base test results in open conditions. Though, the percentage is huge, but as the importance and quantity of this Size C (Small) category is very small, hence it is of least importance in the overall analysis of the storage impact on DRI in open and closed conditions.

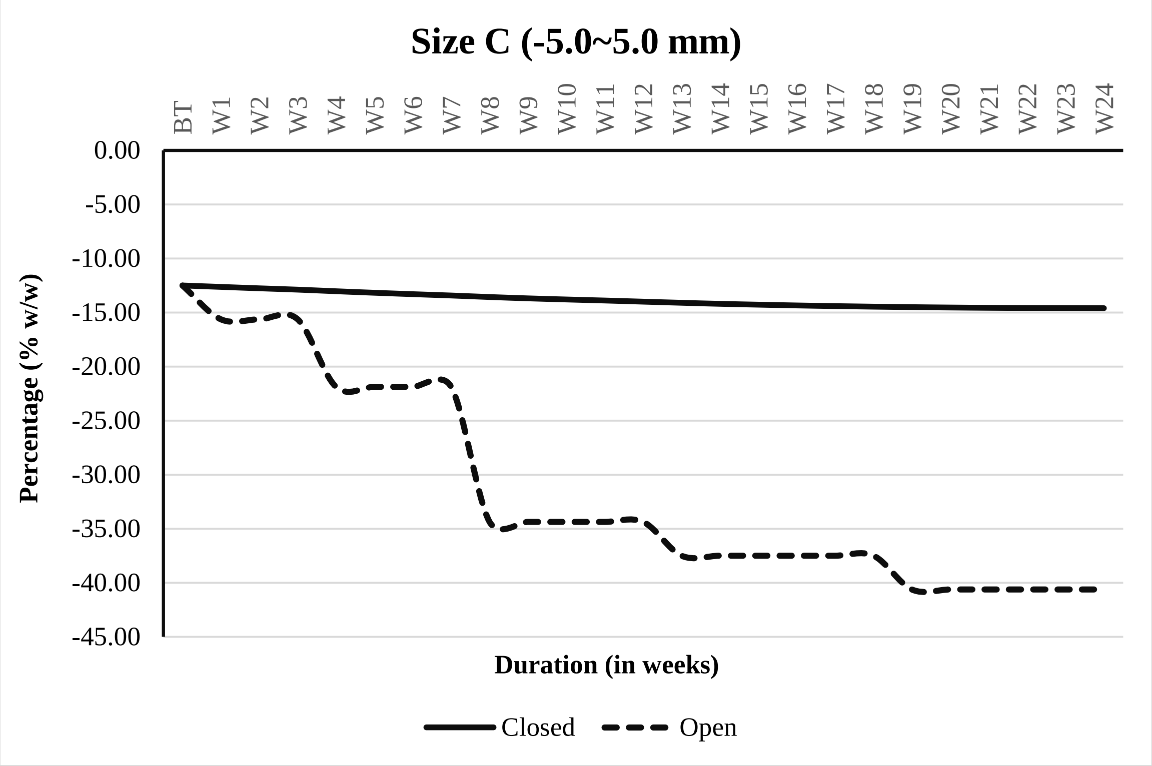


Figure 28 Overall percentage variation in Sieve Size C

Chapter 5. Discussion

Effect of storage options used, on composition on DRI

Our first objective was to examine the effect of storage. Testing results depict that almost all properties of DRI are impacted in both the storage conditions, so it generally satisfy the time and metallization loss as literature supports in Table 17 Relation between Time and Metallization of DRI before and after storage. [33].

Total Iron

The total iron degrades by 1.89 w/w% in the closed storage. Whereas in open storage the DRI degrades by 6.2 w/w %. Therefore it is clear that closed storage has more impact on that of total iron during this storage.

Metallic Iron

The metallic iron degraded by 2.27 w/w% in the closed storage, whereas the degradation in open storage was 7.88 w/w % after 24 weeks. Again there’s apparently big difference between the two and this shows that closed storage has least effect on the DRI properties.

Ferrous Oxide

The ferrous oxide increased by 0.38 w/w% in the closed storage. Though, it was ensured that the porous part of DRI is not filled-in by oxygen by letting the passivation take place after the manufacturing of DRI, but due to storage impacts, still there’s evident increase in the FeO and the same has contributed to degrade the other variables. Whereas, the open storage was also having passivized DRI, but as it was in open air, it was very much expected that oxygen will form bonding with the iron and therefore the results show an increase of 1.68 w/w%. This FeO increase has reversed the reduction process and therefore the total quality of the material has been disturbed. The closed storage though has least impact of the two, and as the open storage has more degradation, the closed storage is better than the open.

Metallization

The metallization according to the literature review Table 17 Relation between Time and Metallization of DRI before and after storage. [33] is lost during storage of DRI. And it degrades more in rain/water/open conditions. This literature result was proved true during our tests as well, when the metallization of closed storage degraded by a percentage of 0.54 w/w% and comparatively the open storage DRI was affected more due to the humid and moisture conditions at the sea coast here in Karachi (the sea in hardly 500 meters away from the storage/ DRI manufacturing plant) and degradation of metallization was about 2.34 w/w% in a duration of 6 months. Therefore, it depicts that the storage is not feasible in open storage for such long durations, as more the time will pass, the degradation will be more and therefore the usability of the DRI will be same is the raw material (iron oxide) itself. That is why the steel melting plants are in continuous operation along with a DRI plant so that the DRI is not stored for long durations to ensure it is processed when it’s at best composition.

Gangue

The gangue (including all other elements in the composition of DRI which are very less in percentage and importance) w/w% in closed was increased by 1.89 due to the reaction of oxygen with other elements and the composition changed and the gangue increase in the open storage was about 6.2 w/w%, which again shows the fact that closed storage is the best available option, if we are really going to store DRI.

As all the compositions are interrelated and the change in one will impact the change in others, therefore when all the results are showing the close storage having least impact of the two storage conditions monitored, then it is fair enough to say that close storage is the best possible alternate.

Effect of storage on sieve size of DRI

Sieve Analysis Size A (Large) Size 9.5~19 MM

The sieve of large size A (9.5~19 mm) was reduced by 2.37 w/w% in closed storage and by 3.90 w/w% in the open storage conditions. Close storage has again the least impact on the storage and the fine generation during storage and handling of the samples was least in closed storage compared to that of the open storage. One point worth noting is that there’s no significant difference in the results, and as over 90% of the DRI pellets are of that size, then this deviation is acceptable for the sieve only.

But if we consider the total composition degradation, then naturally the impact is big, so when there’s case of the DRI being sold on the basis of size, then we can keep in for 4-6 months in open storage and deal with the minor degradation. But, when the quality of DRI is critical to the melter, then even that small difference will be big to the manufacturer and hence it is encourage that closed storage to be used.

Sieve Analysis (Medium) Size 5.0~9.5 MM

The sieve of medium Size B (5.0~9.5 mm) was degraded by 0.15 w/w% and in open the damage was about 0.44 w/w% and therefore the difference in the low overall percentage possessing size is negligible based on the results of the sieve as discussed above. Generally speaking, the closed storage advantage remains true for the sieve analysis results as well and hence with the least degradation in the sieve.

Sieve Analysis (Small) Size 5.0~-5.0 MM

The sieve of small size has degraded about 0.05 and 0.13 w/w% in closed and open storage respectively and as the case remains same for all the sieve results that the variation in the results is not significant, therefore such a minor difference may be considered negligible or ignorable as this will technically not make much difference due to its overall low weightage in percentage of the quantity of DRI.

Close storage is best option for storing DRI

According to all the results and discussion, the close option is by far the best option available for DRI manufacturing plant in discussion. Though, there are still losses in closed storage, but are much lesser than that of the open storage which is existing at the plant.

Condition which has least effect on its characteristics/properties.

As the storage impact results are discussed, the closed storage is by-far the better option of the two. But, other small changes may be made to make the closed option a much better place for the DRI to live long without becoming the iron dust and the possible changes are discussed in future works (chapter 6).

Critical properties which degrade more during the storage phase.

The properties which have degraded more in the storage are of the open storage chemical properties, all of them. Though the same storage has made the sieve size reduce, but the difference is not significant compared to that of the closed storage. The close storage has been better in keeping the degradation to the lowest possible.

Chapter 6. Conclusion

Conclusion

Considering the detailed regular/weekly analysis results, it’s very clearly evident that the open storage conditions negatively impacted seriously the DRI chemical and physical characteristics. Overall, in most results, the **close storage** had a very little and even almost **negligible impact** of the degradation and the percentage degradation of the DRI characteristics (both chemical and physical).

Considering the trends of all chemical and physical (sieve) tests for the given conditions, close storage option has the least impact than open storage of DRI pellets in testing site of DRI manufacturing plant with a given duration of 24 weeks (say 20-30 weeks). The DRI samples in open conditions had deteriorated significantly and it is advisable to use the closed conditions for this given period of storage, provided the DRI pellet is used after 20 weeks or so, but if the storage and handling is increased even after the period of 24 weeks, then it might be feasible and a detailed analysis of other storage condition may be carried out, which should be designed for any period of time.

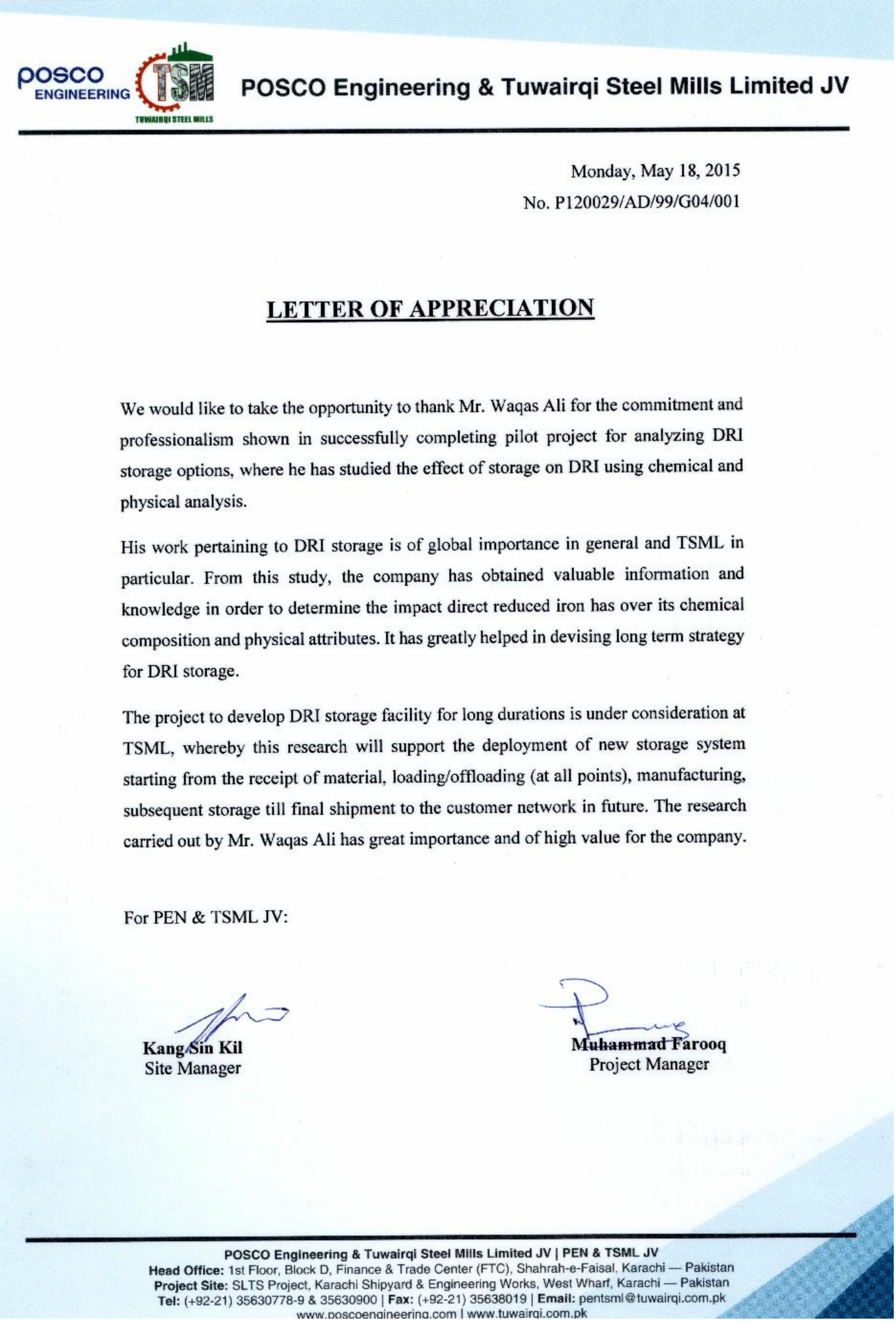
The sieve analysis results has the least variation, as the major size A which comprises of the 90+ of the total volume has deformed 2-3 percent which is usual and acceptable in most cases. The most important thing in case of Sieve Size A is that the line was still declining, so it possible that the results may show further negative effect after a period of extending 24 weeks, as the curve was having sharp decline.

Future Work

The future recommendations are as follows:

1. The analysis may be repeated at a different plant site in any other part of the world which have different conditions from those of Karachi, Pakistan.
2. The analysis duration may be increased from 24 weeks to 50 or even 100 weeks
3. Other possible storage options may be designed and evaluated in similar manner.
    a. Like closed conditions of a masonry room (unlike the shaded space used in our case).
    b. Close conditions in masonry room but DRI may not be packed in any bag and piled like similar heap/pile as in our case was used for open storage conditions
4. Various other condition changes may be evaluated as following:
    a. One sample may be kept dry and while other sub-merged in water
    b. One sample may be kept dry, second one sub-merged in water and third one with any combination of dry and wet like:
        i. 1 week dry and 1 week wet
        ii. 1 day dry and 1 day wet
    c. One sample may be kept at clean space and other in ship for detailed analysis with respect to sea handling conditions
    d. One sample may be kept dry and other one in raining conditions
    e. One sample may be kept in dry, second in rainy and third in acid rain

Annexure – I | Letter of Appreciation



POSCO ENGINEERING TSM TUWAIRQI STEEL MILLS
POSCO Engineering & Tuwairqi Steel Mills Limited JV

Monday, May 18, 2015
No. P120029/AD/99/G04/001

LETTER OF APPRECIATION

We would like to take the opportunity to thank Mr. Waqas Ali for the commitment and professionalism shown in successfully completing pilot project for analyzing DRI storage options, where he has studied the effect of storage on DRI using chemical and physical analysis.

His work pertaining to DRI storage is of global importance in general and TSML in particular. From this study, the company has obtained valuable information and knowledge in order to determine the impact direct reduced iron has over its chemical composition and physical attributes. It has greatly helped in devising long term strategy for DRI storage.

The project to develop DRI storage facility for long durations is under consideration at TSML, whereby this research will support the deployment of new storage system starting from the receipt of material, loading/offloading (at all points), manufacturing, subsequent storage till final shipment to the customer network in future. The research carried out by Mr. Waqas Ali has great importance and of high value for the company.

For PEN & TSML JV:

Kang Sin Kil
Site Manager

Muhammad Farooq
Project Manager

POSCO Engineering & Tuwairqi Steel Mills Limited JV | PEN & TSML JV
Head Office: 1st Floor, Block D, Finance & Trade Center (FTC), Shahrah-e-Faisal, Karachi — Pakistan
Project Site: SLTS Project, Karachi Shipyard & Engineering Works, West Wharf, Karachi — Pakistan
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Annexure – II | Award

POSCO ENGINEERING

TUWAIRQI STEEL MILLS

Employee Recognition Award

This award is being presented to

Mr. Waqas Ali

(Deputy Manager – Project Management) (P-0942)

in recognition of the overall exceptional performance during 2014.

Kang Sin Kil
Site Manager

Muhammad Farooq
Project Manager

Dated: June 6, 2015

POSCO Engineering & Tuwairqi Steel Mills Limited Joint Venture | PEN & TSML JV | www.posco.com | www.tuwairqi.com.pk

Annexure – III | Summary of Test Results

Summary of Test Results

ANALYSIS OF DIRECT REDUCED IRON

POSCO & TUWAIRQI STEEL MILLS LIMITED JV

Test results of ageing effect on DRI under closed & open storage conditions at TSML | Tests (production, base sample test & weekly storage from Week 1 to Week 24)

CHEMICAL ANALYSIS

Parameter	Detail	UOM	Production	Storage	Testing Results																								
					BT	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24
Total Iron (TFe)	A	% w/w	93.78	Closed	93.62	93.49	93.36	93.25	93.11	92.97	92.85	92.74	92.61	92.50	92.41	92.33	92.25	92.16	92.08	92.03	91.98	91.94	91.91	91.89	91.88	91.87	91.88	91.89	91.89
				Open	93.62	92.72	92.08	91.56	91.05	91.07	91.00	90.62	90.74	90.02	89.39	88.95	88.42	88.16	88.07	87.98	87.90	87.81	87.77	87.74	87.70	87.66	87.67	87.67	87.58
Metallic Iron (Fe)	B	% w/w	88.28	Closed	88.12	87.99	87.86	87.73	87.58	87.44	87.31	87.19	87.04	86.92	86.82	86.72	86.61	86.51	86.41	86.33	86.26	86.20	86.15	86.10	86.07	86.04	86.02	86.01	86.01
				Open	88.12	87.19	86.53	85.99	85.43	85.41	85.28	84.85	84.89	84.10	83.40	82.87	82.25	81.90	81.72	81.55	81.37	81.19	81.06	80.93	80.80	80.67	80.58	80.49	80.40
Ferrous Oxide (FeO)	C=A-B	% w/w	5.50	Closed	5.50	5.50	5.51	5.52	5.52	5.53	5.54	5.55	5.57	5.58	5.60	5.62	5.63	5.65	5.67	5.70	5.72	5.74	5.76	5.79	5.81	5.83	5.86	5.88	5.88
				Open	5.50	5.52	5.54	5.58	5.61	5.66	5.71	5.77	5.84	5.92	6.00	6.08	6.17	6.26	6.35	6.44	6.53	6.62	6.71	6.81	6.90	6.99	7.09	7.18	7.18
Metallization	D=B/A*100	% w/w	94.14	Closed	94.12	94.11	94.10	94.09	94.07	94.05	94.03	94.01	93.99	93.96	93.94	93.92	93.89	93.87	93.84	93.81	93.78	93.76	93.73	93.70	93.68	93.65	93.63	93.60	93.60
				Open	94.12	94.04	93.98	93.91	93.83	93.79	93.72	93.63	93.56	93.43	93.29	93.16	93.02	92.90	92.79	92.68	92.57	92.46	92.35	92.24	92.13	92.02	91.91	91.81	91.80
Gangue	E=100-A	% w/w	6.22	Closed	6.38	6.51	6.64	6.75	6.89	7.03	7.15	7.26	7.39	7.50	7.59	7.67	7.75	7.84	7.92	7.97	8.02	8.06	8.09	8.11	8.12	8.13	8.12	8.11	8.11
				Open	6.38	7.28	7.92	8.44	8.95	8.93	9.00	9.38	9.26	9.98	10.61	11.05	11.58	11.84	11.93	12.02	12.10	12.19	12.23	12.26	12.30	12.34	12.33	12.33	12.42

SIEVE ANALYSIS

Parameter	Detail	UOM	Production	Storage	Testing Results																								
					BT	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24
Size A	9.5~19 MM	% w/w	95.53	Closed	95.45	95.31	95.16	95.03	94.87	94.72	94.57	94.44	94.29	94.15	94.04	93.93	93.82	93.70	93.60	93.51	93.44	93.37	93.31	93.26	93.23	93.20	93.18	93.17	93.16
				Open	95.45	95.16	94.88	94.61	94.29	93.98	93.69	93.45	93.25	93.19	93.06	92.78	92.49	92.30	92.20	92.11	91.95	91.85	91.79	91.74	91.73	91.73	91.73	91.68	91.63
Size B	5.0~9.5 MM	% w/w	4.15	Closed	4.10	4.09	4.09	4.08	4.07	4.07	4.06	4.06	4.05	4.04	4.04	4.03	4.03	4.02	4.02	4.02	4.01	4.01	4.01	4.01	4.00	4.00	4.00	4.00	4.00
				Open	4.10	4.07	4.04	4.01	3.97	3.94	3.91	3.88	3.85	3.82	3.80	3.77	3.75	3.74	3.74	3.73	3.73	3.73	3.73	3.72	3.72	3.71	3.71	3.71	3.71
Size C	-5.0~5.0 MM	% w/w	0.32	Closed	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27	0.27
				Open	0.28	0.27	0.27	0.27	0.25	0.25	0.25	0.25	0.21	0.21	0.21	0.21	0.21	0.20	0.20	0.20	0.20	0.20	0.20	0.19	0.19	0.19	0.19	0.19	0.19

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This report is prepared by Mr. Waqas Ali Tunio for his MS dissertation at NUST, Pakistan under the guidance and supervision of Indigenous Mineral Utilization Cell (IMUC), POSCO & TSML JV.

Summary of Percentage Deviation from Production Results

ANALYSIS OF DIRECT REDUCED IRON

POSCO & TUWAIRQI STEEL MILLS LIMITED JV

Test results of ageing effect on DRI under closed & open storage conditions at TSML | Tests (production, base sample test & weekly storage from Week 1 to Week 24)

CHEMICAL ANALYSIS

Parameter	Detail	UOM	Production	Storage	Testing Results																								
					BT	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24
Total Iron (TFe)	A	% w/w	93.78	Closed	-0.17	-0.31	-0.44	-0.57	-0.72	-0.86	-0.99	-1.11	-1.24	-1.36	-1.46	-1.54	-1.63	-1.73	-1.81	-1.87	-1.92	-1.96	-2.00	-2.02	-2.03	-2.03	-2.03	-2.01	-2.02
				Open	-0.17	-1.13	-1.81	-2.36	-2.92	-2.89	-2.97	-3.37	-3.25	-4.01	-4.68	-5.15	-5.72	-6.00	-6.09	-6.18	-6.27	-6.36	-6.40	-6.44	-6.49	-6.53	-6.52	-6.51	-6.61
Metallic Iron (Fe)	B	% w/w	88.28	Closed	-0.18	-0.33	-0.48	-0.62	-0.79	-0.95	-1.10	-1.24	-1.40	-1.54	-1.66	-1.77	-1.89	-2.01	-2.12	-2.21	-2.29	-2.36	-2.42	-2.47	-2.51	-2.54	-2.56	-2.57	-2.58
				Open	-0.18	-1.23	-1.98	-2.60	-3.23	-3.26	-3.40	-3.88	-3.83	-4.73	-5.53	-6.13	-6.83	-7.23	-7.43	-7.63	-7.83	-8.03	-8.18	-8.33	-8.48	-8.63	-8.73	-8.83	-8.93
Ferrous Oxide (FeO)	C=A-B	% w/w	5.50	Closed	0.03	0.08	0.16	0.27	0.41	0.58	0.77	0.99	1.24	1.51	1.80	2.11	2.44	2.80	3.17	3.55	3.95	4.35	4.77	5.19	5.62	6.05	6.49	6.93	6.93
				Open	0.03	0.41	0.81	1.36	2.06	2.90	3.86	4.97	6.21	7.55	9.00	10.55	12.14	13.75	15.39	17.05	18.70	20.36	22.05	23.75	25.47	27.18	28.89	30.61	30.61
Metallization	D=B/A*100	% w/w	94.14	Closed	-0.01	-0.02	-0.04	-0.05	-0.07	-0.09	-0.11	-0.13	-0.16	-0.18	-0.21	-0.23	-0.26	-0.29	-0.32	-0.34	-0.37	-0.40	-0.43	-0.46	-0.49	-0.51	-0.54	-0.57	-0.57
				Open	-0.01	-0.10	-0.17	-0.24	-0.32	-0.37	-0.44	-0.54	-0.61	-0.75	-0.89	-1.03	-1.18	-1.31	-1.43	-1.54	-1.66	-1.78	-1.89	-2.01	-2.13	-2.25	-2.36	-2.47	-2.48
Gangue	E=100-A	% w/w	6.22	Closed	2.55	4.63	6.68	8.56	10.85	12.97	14.92	16.71	18.76	20.50	21.95	23.23	24.64	26.03	27.26	28.19	28.98	29.61	30.09	30.42	30.61	30.65	30.55	30.31	30.45
				Open	2.55	17.09	27.36	35.65	43.96	43.64	44.77	50.74	48.93	60.49	70.55	77.68	86.19	90.43	91.82	93.19	94.55	95.92	96.55	97.17	97.78	98.39	98.30	98.19	99.61

SIEVE ANALYSIS

Parameter	Detail	UOM	Production	Storage	Testing Results																								
					BT	W1	W2	W3	W4	W5	W6	W7	W8	W9	W10	W11	W12	W13	W14	W15	W16	W17	W18	W19	W20	W21	W22	W23	W24
Size A	9.5~19 MM	% w/w	95.53	Closed	-0.08	-0.23	-0.38	-0.52	-0.69	-0.85	-1.00	-1.14	-1.30	-1.44	-1.56	-1.67	-1.79	-1.91	-2.02	-2.11	-2.19	-2.26	-2.32	-2.37	-2.41	-2.44	-2.46	-2.47	-2.48
				Open	-0.08	-0.38	-0.68	-0.96	-1.30	-1.62	-1.92	-2.18	-2.38	-2.45	-2.58	-2.88	-3.18	-3.38	-3.48	-3.58	-3.75	-3.85	-3.91	-3.97	-3.98	-3.98	-3.98	-4.03	-4.08
Size B	5.0~9.5 MM	% w/w	4.15	Closed	-1.20	-1.35	-1.50	-1.64	-1.81	-1.97	-2.11	-2.25	-2.41	-2.55	-2.67	-2.78	-2.89	-3.01	-3.12	-3.21	-3.29	-3.36	-3.42	-3.47	-3.51	-3.54	-3.56	-3.57	-3.58
				Open	-1.20	-1.95	-2.69	-3.38	-4.22	-5.01	-5.75	-6.44	-7.23	-7.92	-8.52	-9.06	-9.65	-9.80	-10.00	-10.10	-10.20	-10.21	-10.21	-10.38	-10.46	-10.50	-10.51	-10.52	-10.53
Size C	-5.0~5.0 MM	% w/w	0.32	Closed	-12.50	-12.63	-12.76	-12.89	-13.03	-13.17	-13.31	-13.43	-13.57	-13.69	-13.80	-13.89	-14.00	-14.10	-14.20	-14.28	-14.35	-14.41	-14.46	-14.50	-14.54	-14.57	-14.58	-14.59	-14.60
				Open	-12.50	-15.63	-15.63	-15.63	-21.88	-21.88	-21.88	-21.88	-34.38	-34.38	-34.38	-34.38	-34.38	-37.50	-37.50	-37.50	-37.50	-37.50	-37.50	-40.63	-40.63	-40.63	-40.63	-40.63	-40.63

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References

---

[1] [1] ISO 11323

[2] [2] A. Ajbar et. al, Model-Based Energy Analysis of an Integrated MIDREX-Based Iron/Steel Plant, Chemical Engineering Communications, Volume: 201 Issue: 12 Pages: 1686-1704, Published: 2014 (page 1)

[3] [3] The MIDREX® Process – The world's most reliable and productive Direct Reduced Technology, retrieved from http://www.midrex.com/assets/user/media/MIDREX_Process-Brochure.pdf on January 15, 2015 (page#6)

[4] [4] Direct from MIDREX (2nd Quarter 2013) pg. 17-18, (Retrieved on November 30, 2014 from http://www.midrex.com/uploads/documents/MDX_2013_DFM2ndQTR7.31.pdf)

[5] [5] The MIDREX Processes, MIDREX Plants (Page No.23) (Retrieved on November 30, 2014 from http://www.midrex.com/pdfs/MIDREX_Process-Brochure.pdf)

[6] [6]MIDREX Plant Reference List, retrieved from http://www.midrex.com/assets/user/media/MIDREX_Plant_Reference_List.pdf on January 15, 2015 (page#2)

[7] [7] Rehren T, et al, "5,000 years old Egyptian iron beads made from hammered meteoritic iron", Journal of Archaeological Science 2013

[8] [8] F. Grobler and R.C.A. Minnit, "The increasing role of direct reduced iron in global steel making", The Journal of The South African Institute of Mining and Metallurgy, March-April 1999

[9] [9] Midrex® Process & HOTLINK® Process, Kobe Steel Limited, retrieved from http://www.kobelco.co.jp/english/engineering/products/dri/dri04.html on January 14, 2014

[10] [10] MIDREX Technologies Inc., USA, "Technical Specification for a MIDREX MEGAMOD Plant" pg. 13-14, March 2006

---

[11] [11] The MIDREX® Process – The world's most reliable and productive Direct Reduced Technology, retrieved from http://www.midrex.com/assets/user/media/MIDREX_Process-Brochure.pdf on January 15, 2015 (page#6)

[12] [12] Indian Sponge Iron Industry in Global Perspective October (2001).

[13] [13] HOUSEMAN, D. H. Direct Ironmaking Processes, Steel Times, vol. 206(4), 1978. pp. 326–333.

[14] [13] BROWN, J. W. Alternative Routes to Steel, *Iron and Steel Engineer,* June 1976, pp. 37–38.

[15] [15] Scarnati, T.M. Use of DRI and HBI in electric furnace steelmaking: Quality and cost considerations, Iron and Steel Engineer, April 1995. pp. 86–89.

[16] [16] BONOMO, F. and FEDERICO, G. DRI: Production and Utilization, International Conference—Pre-Reduced Products and Europe, Milan, September 1996, 35 p.

[17] [17] Use of DRI in EAF's , Qualities and Storage of Direct Reduced Iron by Gregory L. Dressel

[18] [18] MTD 30 (5066), Indian Standard, Sponge Iron/Direct Reduced Iron (DRI), Hot Briqueted Iron(HBI)/Cold Briquetted Iron (CBI) for steel making in induction furnace, (page no.3)

[19] [19] Advanced Explorations Inc

[20] [20] "Typical Applications of Midrex Iron," Midrex Corporation USA, 1993.

[21] [21] R.D. Morales, et. al.,"The Slag Foaming Practice in EAF and Its Influence on the Steelmaking Shop Productivity," ISIJ International, Vol. 35 (1995) No. 9, pg. 1057.

[22] [22] ISO/DIS 11258 Iron ores for shaft direct-reduction feed stocks — Determination of the reducibility index, final degree of reduction and degree of metallization

---

[23] [23] ore. (2013). In *Encyclopedia Britannica*. Retrieved from http://www.britannica.com/EBchecked/topic/431610/ore (dated June 20, 2014)

[24] [24] IS 10852 (2012), MTD 30: Sponge Iron and Smelting Reduction, BIS 2012

[25] [25] IS 10852 (2012), MTD 30: Sponge Iron and Smelting Reduction, BIS 2012

[26] [26] Stevenson and Smailer, ed., Direct Reduced Iron, Iron and Steel Society, 1980, pg. 10

[27] [27] Use of DRI in EAF's. (Part I: Qualities and Storage of Direct Reduced Iron) Gregory L. Dressel Technologies, Pawley's Island, SC, USA

[28] [28] A.K.Biswas, Principles of Blast Furnace Iron Making, SBA Publications, Calcutta, India, 2005.

[29] [29] G. G. O. O. Uwadiale, “Upgrading Nigerian iron ores, “Minerals and Metallurgical Processing, vol. 6, no. 3, pp. 117–123, 1989.

[30] [30] B. D. Sparks and A. F. Sirianni, “Beneficiation of a phosphoriferous iron ore by agglomeration methods,” International Journal of Mineral Processing, vol. 1, no. 3, pp. 231–241, 1974.

[31] [31] C. Y. Cheng, V. N. Misra, J. Clough, and R. Mun, “Dephosphorization of Western Australian iron ore by hydrometallurgical process,”Minerals Engineering, vol. 12, no. 9, pp. 1083–1092, 1999.

[32] [32] Platts, “Methodology and Specification Guide: Iron Ore,” The McGraw Hill Companies, 2010, (http://www.platts.com/IM.Platts.Content/MethodologyReferences/MethodologySpecs/ironore.pdf.) retrieved on April 12, 2015

[33] [33] Direct From Midrex 2nd Quarter 1999, page no. 4. (retrieved from http://www.midrex.com/assets/user/media/DFM1999Q2.pdf) dated May 12, 2015

---

[34] [34] B V R Raja & N Pal, Indian Sponge Industry-Status, Potential & Prospects, Vol. No.9, No.2, April 2006, IIM Metal News (retrieved from http://ecacwb.org/editor_upload/files/7278460-Indian-Sponge-Iron-Status-Potential-Prospects-05rarajapal0406.pdf) dated May 12, 2015

[35] [35] Utilization of Sponge Iron in Electric Arc Furnaces by Nabil Daoud Takla, Qatar Steel Company Limited (QASCO). Paper was presented at AISU's 2nd Electric Furnace Symposium in Damascus, Syria, October 19-20, 1998.

[36] [35] Direct from MIDREX 2nd Quarter 1999, Utilization of DRI in EAF (retrieved from http://www.midrex.com/uploads/documents/Utilization%20of%20Sponge%20Iron%20in%20EAF1.pdf)

[37] [37] Characterization of Chemical Composition and Microstructure of Natural Iron Ore from Muko Deposits, Abraham et. al, Volume 2012, Article ID 174803,9 pages, (http://www.diva-portal.org/smash/get/diva2:624387/FULLTEXT01.pdf) (dated November 14, 2015)

[38] [38] Syed Kazem Tahiri, (1982), Direct Reduction of Iron Ore in Rotary Kiln, Brunel University, Great Britain

[39] [39] Ivana et. al, Chemical Analyses of Bronze Age glasses from Frattesina di Rovigo, Northern Italy, Journal of Archaeological Science 31 (2004) (page: 175-1184)

[40] [40] A. D. Westland and F. E. Beamish, (1958), The Chemical Analysis of Iridosmines and other platinum-metal minerals, The American Mineralogist, Vol. 43, May-June 1958 (page: 503-516)

[41] [41] N.T. Jenkins and T.W. Eager, Chemical Analysis of Welding Fume Particles, The Welding Journal, June 2005 (page: 87-93)

[42] [42] Bernhardt, C. (1994): Particle Size Analysis, Chapman & Hall London. Glasgow. U.K. Pp 198

---

[43] [43] S. Aknade, B. Adebayo, J. M. Akande, Comparative Analysis of Grindability of Iron-ore and Granite, Journal of Mining World Express Volume 2 Issue 3, July 2013 (page: 55-62)

[44] [44] Aliaga, M. and Gunderson, B. (2002) Interactive Statistics. [Thousand Oaks]: Sage.

[45] [45] ISO 10835:2007. Direct Reduced Iron and Hot Briquetted Iron — Sampling and Sample Preparation

[46] [46] ISO 2597-1: 2006

[47] [47] ISO 5416: 2006

[48] [48] ISO 3696

[49] [49] Waqas Ali Tunio, Analysis of Direct Reduced Iron, POSCO & Tuwairqi Steel Mills Limited (http://www.scribd.com/doc/255062812/Direct-Reduced-Iron-by-Waqas-Ali-Tunio) dated April 1, 2015.

[50] Waqas Ali Tunio, Tuwarqi Steel Mills Limited Internship, (http://www.scribd.com/doc/47377940/Tuwairqi-Steel-Mills-Limited-TSML-Internship-Report-by-Waqas-Ali-Tunio) dated April 1, 2015.