5.1 INTRODUCTION

Lime is an essential ingredient of steel making industries [2]. Lime is very hygroscopic; therefore, it cannot be stored in the open atmosphere for a long period. [10,22]. Lime forms its hydroxide during storage in a humid environment (Rainy season) which may be caused for an accident during use in steelmaking practice, henceforth needs of fresh lime requirement increases due to use in each practice [7]. Integrated steel plants have their lime kiln and produce fresh lime according to their requirements, but small industries depend on others for their lime requirement. During transportation and storage, this fresh lime becomes hydrated by reacting in the humid environment. Similar nature is with DRI (sponge iron) which could be stored in closed boxes having inert atmosphere during the shipment/transport because of its highly reactive nature due to presence of higher porosity. Therefore, it is a very challenging task to provide safe and fresh lime to small industries for their steelmaking practices. Most of the small industries are used either induction melting furnace or electric arc furnace [59]. DRI (i.e. Directly Reduced Iron) can be used in both types of the furnace without any problem, but its storage is also a problem similar to storage of fresh lime. A high amount of ore fines (i.e. iron ore fines 67% and limestone fine fines50%) [4] are produced during mining and beneficiation process of iron ore and limestone in India, opens a new path to make highly fluxed DRI as pellets form. Highly fluxed DRI made in such a way that it contains the maximum amount of lime along with good strength which could be charged safely during steelmaking. Thus, by charging highly fluxed DRI external charging of lime can be avoided. Highly fluxed DRI will work as synthetic slag during melting because of calcium ferrites phase formation happened during their hardening process [92]. In the present work weathering behaviour of highly fluxed DRI was studied to examine the feasibility of their use in the steelmaking process. The present work aims to prepare highly fluxed DRI which may contain maximum amount of lime and can be stored for extended period of time without failure (cracks) and moisture gain.

5.2 EXPERIMENTAL

5.2.1 MATERIALS AND METHODS

In the present study, the highly fluxed DRI of different reduction level were selected for the study of their weathering behavior. From 68-98% reduced fluxed pellets of different basicity (i.e. 4, 6 and 8) were taken up for studying their weathering behavior. The hardening and reduction behavior of highly fluxed DRI are explained in detail in the previous chapter-3 and chapter-4 respectively.

5.2.2 EXPERIMENTAL PROCEDURE

Before starting the experiments following materials were procured: i) A hygrometer (for the measurement of humidity, temperature and time); ii) Electronic digital Balance (for the measurement of weight gain/ loss in the samples); iii) Slide Caliper (for the measurement of dimension of the samples); iv) Watch glasses/ Glass dishes(for keeping samples); v) Marker pen (Marking on the glass dishes for distinguishing samples); vi) Hollow cartoon cover (to avoid pick up of dust by samples from laboratory environment);

Initially, weight and diameter of each pellet were measured with the help of weighing on electronic digital balance and slide caliper respectively. After measuring weight and diameter, pellets of different level of reduction and basicity were kept separately on glass dishes respectively which were already marked with number. Glass dishes with samples were kept on a table in arrange way for the exposure in laboratory open atmosphere. The glass dishes with samples were covered by hollow packing carton as shown in **Figure-5.1** to protect weight gain by dust pick up from surrounding. Similar procedure was followed for hardened flux pellets as well.

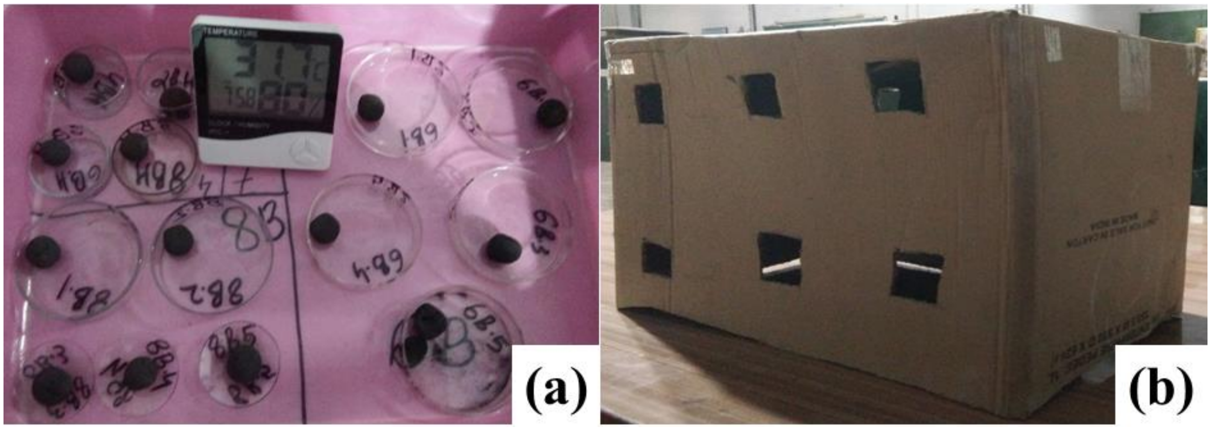


Figure-5.1 Arrangement of samples during weathering test; a) DRI on glass dishes with number; b) Hollow packing carton as cover

Duration of the experiment was 1 July to 31 August (total of 60 days), these are peak days for humidity level of air in India. Weight and diameter of each exposed hardened/DRI pellets were measured at a regular interval of time (weight-1,5,10,15,20,25,30,60 days and diameter-1,10,20,30,60 days respectively). The physical appearance during test period was recorded by taking pellet photograph. Some selected pellets were tested for phase change by XRD and morphological changes by SEM/EDS. Fourier Transform Infrared Spectroscopy (FTIR) was used to know the presence of hydroxide and carbonate group in the pellets which may form during weathering in the form of calcium hydroxide and calcium carbonate.

5.3 RESULTS AND DISCUSSION

Weight gain in each pellet is calculated by using weight change in the hardened/DRI pellets (initial & final weight) and similarly, change in the diameter was used to calculate the volume change of the sample for fixed interval of exposure time. Weight and changes in weight of each flux hardened/reduced pellets days wise are given in the **Table-5.1** and their percentage weight gain are given in the **Table-5.2**. The diameters and their respective calculated volume are given in the **Table-5.3**. The percentage change in volume is calculated and given in the **Table-5.4**. Formula used to calculate the percentage weight gain and percentage volume change in the hardened/DRI pellets are given below:

%Weight Gain= (Weight change/Original weight of day first) x100;

%Volume Change= (Volume change/Original volume of day first) x100;

Table-5.1 Weight of flux hardened/reduced pellets and their respective changes in weight days wise

B	% R	Weight of the pellets with respect to days (gm.)								Change in weight with respect to days (gm.)						
		0	**5**	**10**	**15**	**20**	**25**	**30**	**60**	**5**	**10**	**15**	**20**	**25**	**30**	**60**
4	**UR**	11.73	11.73	11.73	11.73	11.73	11.73	11.73	11.73	0	0	0	0	0	0	0
	68.61	8.49	8.53	8.57	8.6	8.62	8.64	8.66	8.72	0.04	0.08	0.11	0.13	0.15	0.17	0.23
	72.42	7.89	7.93	7.98	8.01	8.03	8.05	8.07	8.14	0.04	0.09	0.12	0.14	0.16	0.18	0.25
	79.31	7.55	7.6	7.64	7.67	7.7	7.72	7.73	7.81	0.05	0.09	0.12	0.15	0.17	0.18	0.26
	96.43	8.66	8.75	8.81	8.86	8.89	8.92	8.94	9.04	0.09	0.15	0.20	0.23	0.26	0.28	0.38
	97.84	9.45	9.54	9.58	9.61	9.63	9.65	9.67	9.73	0.09	0.13	0.16	0.18	0.20	0.22	0.28
6	**UR**	10.19	10.19	10.19	10.19	10.19	10.19	10.19	10.19	0	0	0	0	0	0	0
	69.95	8.05	8.07	8.09	8.11	8.13	8.15	8.16	8.22	0.02	0.04	0.06	0.08	0.1	0.11	0.17
	80.34	7.98	8.03	8.09	8.14	8.2	8.23	8.27	8.31	0.05	0.11	0.16	0.22	0.25	0.29	0.33
	81.16	8.6	8.64	8.69	8.73	8.78	8.82	8.85	8.93	0.04	0.09	0.13	0.18	0.22	0.25	0.33
	96.91	8.37	8.41	8.45	8.51	8.56	8.63	8.79	**Br**	0.04	0.08	0.14	0.19	0.26	0.42	**Br**
	97.60	9.49	9.57	9.66	9.73	9.79	9.85	9.98	**Br**	0.08	0.17	0.24	0.30	0.36	0.49	**Br**
8	**UR**	10.11	10.11	10.11	10.11	10.11	10.11	10.11	10.11	0	0	0	0	0	0	0
	70.13	8.84	8.86	8.88	8.90	8.93	8.94	8.96	9.03	0.02	0.04	0.06	0.09	0.10	0.12	0.19
	82.96	8.67	8.71	8.74	8.77	8.79	8.81	8.83	8.90	0.04	0.07	0.10	0.12	0.14	0.16	0.23
	85.84	8.38	8.44	8.49	8.53	8.56	8.61	8.64	8.71	0.06	0.11	0.15	0.18	0.23	0.26	0.33
	96.92	8.93	9.08	9.15	9.21	9.26	9.31	9.38	**Br**	0.15	0.22	0.28	0.33	0.38	0.45	**Br**
	97.72	7.79	7.87	7.92	7.98	8.06	8.11	8.22	**Br**	0.08	0.13	0.19	0.27	0.32	0.43	**Br**

Note:- B-Basicity, **R**-Reduction, **UR**-Unreduced, **Br**-Break

Table 5.2 Percent weight gain of flux hardened/reduced pellets during studying

Weight gain by reduced pellets during weathering test (%)							
Basicity	**Days**	**Weight gain during weathering test with respect to days (%)**					
		unreduced	68.61%R	72.42%R	79.31%R	96.43%R	97.84%R
4	0	0	0	0	0	0	0
	5	0	0.47	0.5	0.66	1.03	0.95
	10	0	0.94	1.14	1.19	1.73	1.37
	15	0	1.29	1.52	1.58	2.3	1.69
	20	0	1.53	1.77	1.98	2.65	1.9
	25	0	1.76	2.02	2.25	3	2.11
	30	0	2	2.28	2.38	3.23	2.32
	60	0	2.7	3.16	3.44	4.38	2.96
6							
		unreduced	69.95%R	80.34%R	81.16%R	96.91%R	97.6%R
	0	0	0	0	0	0	
	5	0	0.24	0.62	0.46	0.47	0.84
	10	0	0.49	1.37	1.04	0.95	1.79
	15	0	0.74	2	1.51	1.67	2.52
	20	0	0.99	2.75	2.09	2.27	3.16
	25	0	1.24	3.13	2.55	3.1	3.79
	30	0	1.36	3.63	2.9	5.02	5.16
	60	0	2.11	4.13	3.83	Break	Break
		unreduced	70.13%R	82.96%R	85.84%R	96.92%R	97.72%R
	0	0	0	0	0	0	0
	5	0	0.22	0.46	0.71	1.67	1.02
	10	0	0.45	0.8	1.31	2.46	1.67
8	15	0	0.67	1.15	1.78	3.13	2.43
	20	0	1.01	1.38	2.14	3.69	3.47
	25	0	1.13	1.61	2.74	4.25	4.11
	30	0	1.35	1.84	3.1	5.03	5.52
	60	0	2.14	2.65	3.93	Break	Break

Table 5.3 Diameter of reduced pellets and their respective volume

Basicity	Days	Diameter of reduced pellets(mm)				Volume of reduced pellets(mm^3)				
		68.61 %R	72.42 %R	79.31 %R	97.84 %R	Days	68.61 %R	72.42 %R	79.31 %R	97.84 %R
4	0	21.08	20.14	19.54	20.96	0	4906.65	4279.09	3907.93	4823.33
	10	21.17	20.27	19.68	21.09	10	4967.00	4365.10	3991.50	4912.56
	20	21.23	20.32	19.71	21.14	20	5011.16	4392.49	4010.65	4946.81
	30	21.24	20.34	19.72	21.14	30	5021.47	4406.18	4017.30	4952.11
	60	21.26	20.34	19.76	21.16	60	5036.68	4408.32	4041.14	4959.83
6		69.95 %R	80.34 %R	81.16 %R	97.60 %R		69.95 %R	80.34 %R	81.16 %R	97.60 %R
	0	20.2	19.73	20.13	20.93	0	4317.45	4023.04	4272.72	4802.65
	10	20.31	19.85	20.29	21.07	10	4388.69	4096.26	4376.55	4897.26
	20	20.33	19.88	20.30	21.15	20	4401.64	4117.18	4382.10	4955.85
	30	20.34	20.01	20.34	21.38	30	4407.25	4198.04	4409.02	5118.18
	60	20.44	20.04	20.40	**Break**	60	4472.01	4217.35	4445.77	**Break**
8		70.13 %R	82.96 %R	85.84 %R	97.72 %R		70.13 %R	82.96 %R	85.84 %R	97.72 %R
	0	20.13	19.91	20.55	20.56	0	4272.72	4134.16	4545.78	4549.10
	10	20.23	20.04	20.68	20.76	10	4333.82	4215.84	4633.97	4686.48
	20	20.30	20.11	20.75	20.81	20	4381.25	4261.69	4677.15	4723.79
	30	20.36	20.16	20.86	21.08	30	4421.41	4293.92	4751.70	4905.75
	60	20.39	20.20	20.88	**Break**	60	4442.77	4319.53	4771.71	**Break**

Table.5.4 Change in volume of reduced pellets due to weathering effect

Basicity	Days	Volume changed of reduced pellets (%)			
4		**68.61%R**	**72.42%R**	**79.31%R**	**97.84%R**
	0	0	0	0	0
	10	1.23	2.01	2.16	1.85
	20	2.13	2.65	2.65	2.56
	30	2.34	2.97	2.82	2.67
	60	2.65	3.02	3.43	2.83
6		**69.95%R**	**80.34%R**	**81.16%R**	**97.60%R**
	0	0	0	0	0
	10	1.65	1.82	2.43	1.97
	20	1.95	2.34	2.56	3.19
	30	2.08	4.35	3.19	**6.57**
	60	3.58	4.83	4.05	Break
8		**70.13%R**	**82.96%R**	**85.84%R**	**97.72%R**
	0	0	0	0	0
	10	1.43	2.05	1.94	3.02
	20	2.54	3.16	2.89	3.84
	30	3.48	3.94	4.53	**7.84**
	60	3.98	4.56	4.97	Break

The effect of basicity and % reduction of fluxed DRI on the weathering behavior are discussed in following sub-sections:

5.3.1 EFFECT OF BASICITY ON THE WEATHER RESISTANCE

Figure 5.2 shows the effect of weathering days (exposure time) under humidity 81±5% on weight gain by fluxed DRI having different basicity (i.e. 4, 6, 8) and % reduction (68-98%) and similarly, **Figure 5.3** shows the effect of weathering days under same humidity limit on volume change in same fluxed DRI. From the **Figures 5.3 & 5.4**, it is depicted that there is no change observed in the weight gain and volume change for the unreduced samples (i.e. hardened condition fluxed pellets of basicity-4, 6, 8). It means that basicity does not play a major role in weight gain and volume change for the hardened pellets up to 60 days exposure time. For the reduced pellets of different % level, weight gain and volume change are observed significantly with respect to increasing basicity. Weight gain and volume change of fluxed DRI pellets increase with increasing basicity. The maximum weight gained and volume changed in 8-basicity DRI pellets are obtained below 6 wt. % and ~8% respectively in 30 days of exposure time on humidity 81±5% level.

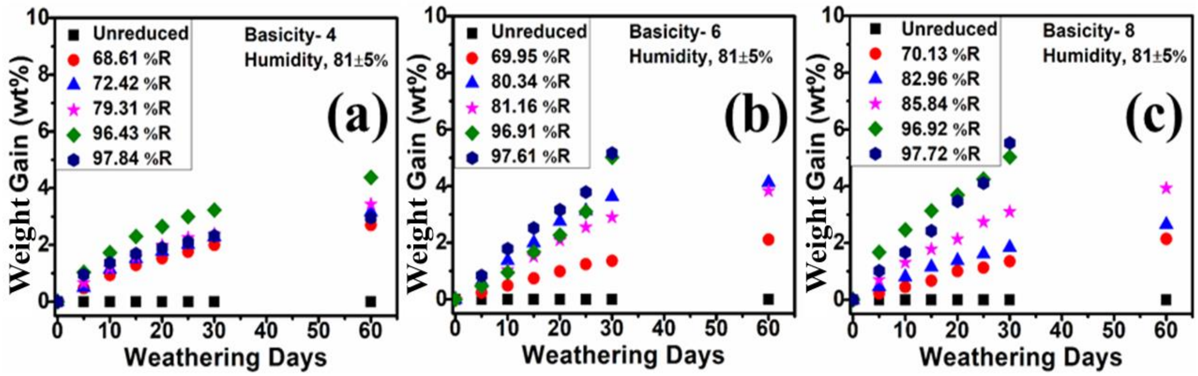


Figure-5.2 Weight gain of hardened/DRI pellets with respect to weathering time; a) 4 basicity DRI, b) 6 basicity DRI, c) 8 basicity DRI

5.3.2 EFFECT OF PERCENT REDUCTION LEVEL ON WEATHER RESISTANCE

The fluxed DRI when exposed to air ((humidity 81±5%) showed increase in its weight and volume as shown in **Figure-5.2&5.3** respectively. It is interesting to note that the highly humid air (~85% humidity) exposure for 30 days did not cause weight gain beyond 6 wt%. The oxygen (O_2), carbon dioxide (CO_2) and moisture (H_2O) molecules surrounding the fluxed DRI tries to react with iron and lime present in it. The porous morphology of DRI allows diffusion of oxygen (O_2) and moisture (H_2O) molecules to the interior surfaces to react with iron and lime. Theoretically oxygen and moisture can oxidize reduced iron and moisture can hydrate CaO at room temperature which are present in the DRI. Presence of carbon dioxide (CO_2) in the atmosphere may react with free lime to form calcium carbonate. The oxidation of iron and hydration & calcination of lime would cause increase in DRI weight. The oxidation behavior of freshly reduced iron has been studied by many workers and reported by Singh & Gupta [2]. It is reported [2] that the rate of iron oxidation without flowing air at room temperature is extremely slow and no weight gain is expected in 30 days exposure time. In view of this the DRI weight gain can be attributed only due to moisture adsorption.

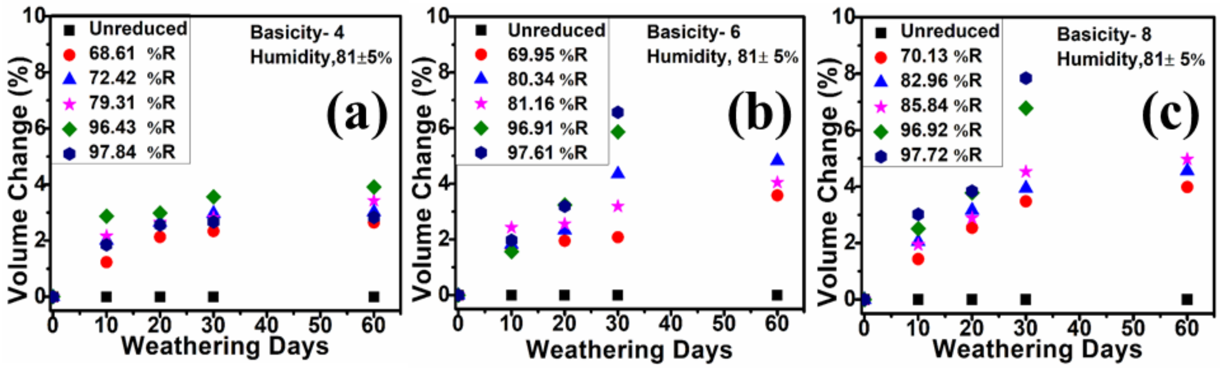


Figure-5.3 Volume change of Hardened/DRI pellets with respect to weathering time; a) 4 basicity DRI, b) 6 basicity DRI, c) 8 basicity DRI

Fluxed DRI, which was used to explain the weathering behaviour for their physical and chemical happening during exposure in humid environment, contains highest basicity (8 out of 4, 6, 8) and percentage reduction (98% out of 68-98%) because it was cracked at first. If highly fluxed and reduced pellets can controlled under weather condition than lower basicity and less reduced pellets will be controlled easily. The changes in the physical appearance of 8 basicity and ~98%R reduced fluxed DRI with respect to weathering exposure time (days) are shown in **Figure-5.4**. From the figure, it was observed that highly fluxed and highly reduced DRI is initiated cracking after 30 days exposure time in highly humid (81±5%) conditions. It means that these DRI (~98%R) could be stored up to 30 days safely during rainy season's condition. The cracked DRI was tested and analyzed for further investigation to know the reason of failure.

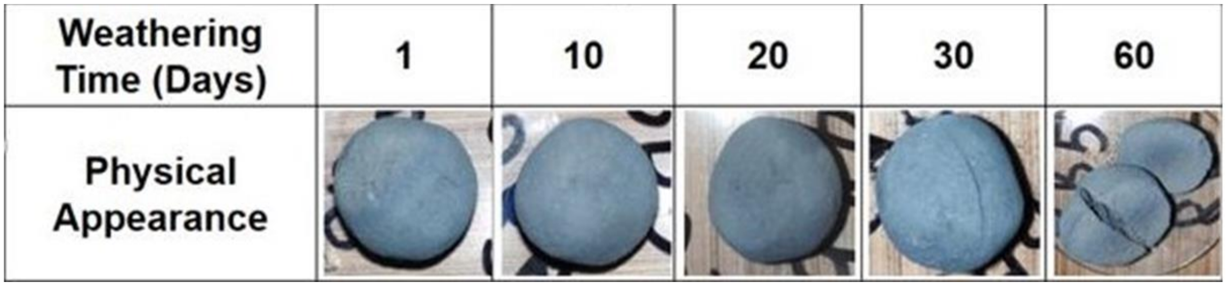


Figure-5.4 Physical appearance of DRI with respect to weathering time

The adsorbence of lime hydration by air moisture is further confirmed by XRD analysis as no lime hydroxide phase was noted **(Figure 5.5 a)** in DRI having high lime content (basicity 6 & 8). It may be due to the limitations of XRD techniques which cannot detect the phases which are less than 5% (wt/volume) in the sample.

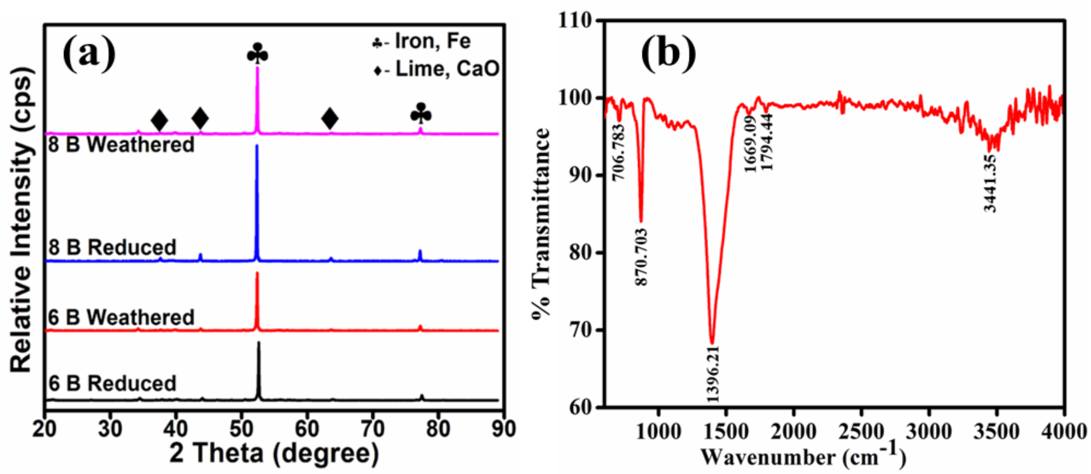
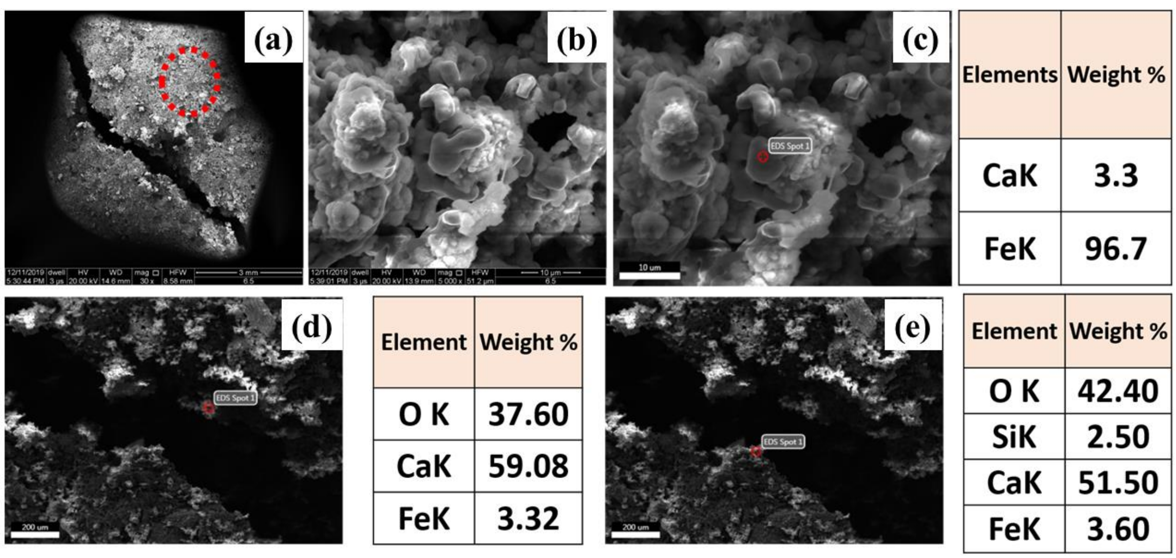


Figure-5.5 a) X-Ray Diffraction pattern of 6 & 8 basicity DRI pellets (~98%R) before and after weather test, b) FTIR spectrum of 8basicity ~98%R weathered DRI (pellet)

FTIR technique was used to confirm the presence of hydroxide and carbonate phases in the sample. **Figure-5.5(b)** shows the FTIR analysis of the sample. From the figure it can be observed that the presence of hydroxide phase can be confirmed by the peak at 3441.35 cm^{-1} due to O-H stretching. Hydroxide phase wavenumber may vary from 3300 to 3500 cm^{-1} due to presence of other elements in the sample. Calcite phase is confirmed by characteristic peak at 706.783, 1794.44 and 1396.21 cm^{-1} due to out of plane and bending vibration and splitting in plane vibration respectively. H-O-H group is confirmed by the presence of peak at 1669.09 cm^{-1}. Mayenite phase [$Ca_{12}Al_{14}O_{32}(OH)_2$] is confirmed by the presence of peak at 870.703 cm^{-1}. FTIR analysis confirm the presence of hydroxide phase with moisture and carbonates in the sample. The presence of moisture content up-to 7- 8% has been reported by Ahmad [93] as common and reportedly acceptable for use by steel makers. In-view of this the 6 wt% of adsorbed moisture in fluxed DRI may be acceptable for use in steel making.

5.3.3 SCANNING ELECTRON MICROSCOPY ANALYSIS OF FLUXED DRI

On the behalf of above results, 8-basicity, 98% reduced pellets (DRI) was selected for the failure examination. **Figure-5.6** shows the SEM/EDS analysis of cracked DRI.



Elements	Weight %
CaK	3.3
FeK	96.7

Element	Weight %
O K	37.60
CaK	59.08
FeK	3.32

Element	Weight %
O K	42.40
SiK	2.50
CaK	51.50
FeK	3.60

Figure-5.6 SEM/EDS analysis of; a) Cracked DRI, b) Morphology of spotted area, c) EDS of spots away from the crack, d) EDS on one side of the crack, e) EDS on another side of the crack

There are two distinct areas selected for the failure analysis. One area is selected away from the crack and another area selected near the crack marked by small & big red line dotted circles. The area which is away from the crack shows iron-rich region while the area near crack on both sides is calcium-rich. Chemical analysis of the cracked DRI at different points shows that crack is propagated in the calcium-rich region. It may be due to high volume expansion (drastic) by the formation of calcium hydroxide phases.

5.3.4 TENTATIVE MECHANISM OF CRACK FORMATION

Figure-5.7 shows the sequence of crack formation on the pellet and its propagation along with reasons for physical changes.

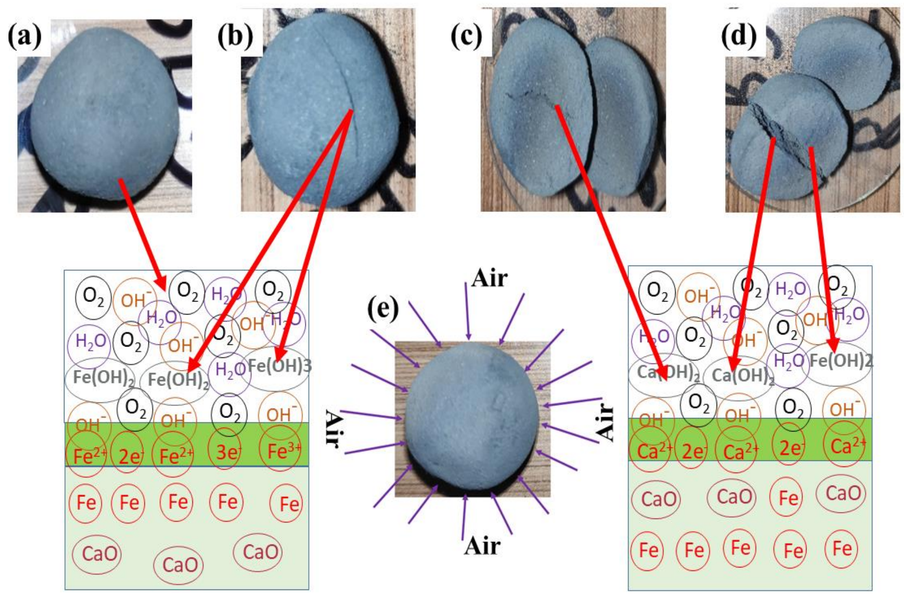


Figure-5.7 Tentative mechanism of crack formation; a) Fresh DRI, b) DRI after 30 days (External crack), c) DRI after 60days (Internal crack), d) DRI after 60 days (internal crack propagation) e) Schematic presentation of the sample.

Figure-5.7(a) shows the image of first-day exposure and **Figure-5.7(b)** shows the image of physical appearance after 30 days of weathering exposure of fluxed DRI respectively. From these diagrams, it is evident that a minor crack on the surface (external crack) was observed on the sample of 30 days exposure time. **Figure-5.7(c)** shows the physical appearance of fluxed DRI after 60 days weathering exposure time. Here DRI was not separated in two pieces till 30 days, but in the case of 60 days exposure time sample, an internal crack was shown very clearly and DRI breaks into two pieces as shown in **Figure 5.7(d).** In this figure, the internal crack propagation was shown and still exposed in the open atmosphere which is surrounded by air and humidity. Air contains oxygen and humidity contains oxygen and hydrogen along with moisture. Highly reduced DRI contains a high amount of iron with lime on the surface. This free iron available on the surface may react with the oxygen available in the surrounding to form their oxides. The volume of DRI expanded due to oxides formation. This expanded volume may be responsible for the crack formation on the surface. As the crack formed on the surface, free lime and lime-rich phases available in the DRI come into the contact with oxygen and hydrogen ions of moisture available in the environment. Hydrogen available in the surrounding will react with lime and formed calcium hydroxide phases. Possible reactions may occurred during the process is shown in **Table 5.5**.

Table-5.5 List of possible reactions occurred during weathering process [94]

Possible Reactions	
Iron Hydroxide formation	**Calcium Hydroxide formation**
$Fe \longrightarrow Fe^{2+} + 2e^-$	$Ca \longrightarrow Ca^{2+} + 2e^-$
$Fe \longrightarrow Fe^{3+} + 3e^-$	$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$
$O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$	$4Ca^{2+} + 4OH^- \longrightarrow Ca(OH)_2 + 2H^+$
$4Fe^{2+} + 4OH^- \longrightarrow Fe(OH)_2 + 2H^+$	$CaO + CO_2 \longrightarrow CaCO_3$
$4Fe^{3+} + 4OH^- \longrightarrow Fe(OH)_3 + 2H^+$	

Formation of calcium hydroxide phases increases the volume abruptly, which may be responsible for the crack propagation and failure of DRI into several pieces. For explanation of reactions happened in between, an imaginary interface **(Figure-5.8)** is asumed in between surface of solid mass (fluxed DRI) and surronded Gaseous Environment (moist air). Reactants of soild phase present towards interface are reduced iron of DRI and calcium of lime. Similarly reactants of gaseous phase present towards interface are as clustures of oxygen, hydrogen, moisture in the form of ions, atoms & molecules.

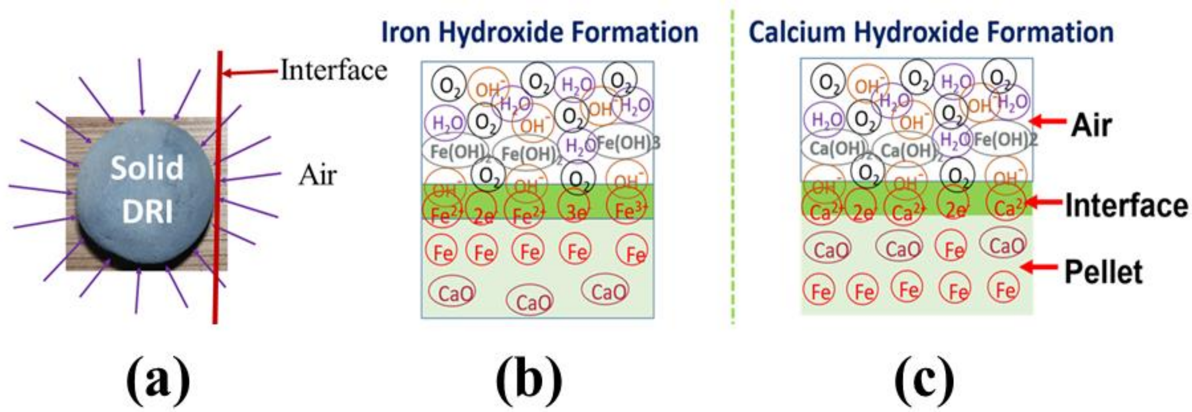


Figure-5.8 Possible reactions of iron and calcium with oxygen and hydrogen

Thermodynamically these species are reacting and to form stable products in the form of oxides/hydroxides.There are mainly two types of reactions happen during weathering. Formation of oxides and hydroxides with iron is one type while the formation of hydroxide with calcium is another type. Formation of hydroxide may be responsible for the failure of highly fluxed DRI.

5.4 FINDINGS

The study resulted in the following conclusions:

- Highly fluxed reduced pellets (DRI) having 4, 6 and 8 basicity and 65-98 % R when exposed to humid atmosphere (81±5% humidity at 30±5°C temperature) for 30 days did not show any visible physical change.
- The gain in weight by such fluxed DRI in 30 days exposure time was less than 6 wt% which could be due moisture adsorption on available surfaces or formation of few hydroxide and carbonate phases of lime.
- The present study gives indication that the high fluxed DRI (up-to basicity 8) could be safely stored in static humid (~ 85%) air at ~30°C.