

4.1 INTRODUCTION

Reduction is the process which comprises a half reaction in which a chemical species loses its oxidation number, usually by gaining electrons. During the reduction of iron ore in which hematite (Fe_2O_3) converts into magnetite (Fe_3O_4) followed by conversion of wustite (FeO) and finally converts into iron. In general, a metal oxide (MO) when reacts with reductant (gas/Solid based) under suitable reaction condition may yield metal (M) and reductant Oxide (RO) as: $\text{MO} + \text{R} = \text{M} + \text{RO}$. This reaction would be feasible provided reductant (R) has more affinity for oxygen than metal (M) and its oxide (RO) is relatively more firm oxide than (MO). For reducing oxides of iron ($\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$) occurring in nature as mineral (hematite/magnetite), various reducing agents, like C, Si, Al, Mg, CO, H_2 etc. could be used as Evident by Ellingham Diagram which gives standard free energy (ΔG°) formation of oxides. Negative sign ($-\Delta G^\circ$) indicates the reaction proceed in forward direction. The reduction of iron oxide (Fe_2O_3) by CO or H_2 gas occurs in three stages as given below:

Fe_2O_3 (Hematite) (stage-I) \rightarrow Fe_3O_4 (Magnetite) (stage-II) \rightarrow FeO (Wustite) (Stage-III) \rightarrow Fe. Boudouard Reaction and carbon Deposition Reaction: $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$; the forward, highly endothermic reaction is known as Boudouard reaction and the reverse, highly exothermic, is termed as Carbon deposition reaction [88].

There are so many factors which influences the process of reduction of iron ore. Reduction influenced by the type of raw material (composition of iron ore and reductant), temperature of the reduction operation, holding time period, types of reductant (solid/gas), size of raw materials (iron ore and reductant) and type of process.

Energy is a very essential parameter for any type of process. Energy directly affects the cost of the process. Activation energy is the minimum amount of energy delivered to a chemical

system with potential reactants to result in a chemical reaction. If a reaction has low activation energy it means that it will start at earlier compared to the higher activation energy system. Therefore, study of the activation energy involved during reduction process is necessary. In this chapter, the reduction behavior of hardened flux iron ore pellets of different basicity from 2 to 8 at different temperature and reduction time interval have been studied. The values of activation energy for the reduction of different basicity iron ore pellets, using different models, are calculated in the present work.

4.2 EXPERIMENTAL

4.2.1 MATERIALS AND METHODS

In the present study, the highly fluxed iron ore pellets hardened at 1180°C temperature were selected for the study of their reduction behaviour. These highly fluxed iron ore pellets were made by using iron ore and lime fines with basicity 2, 4, 6 and 8. In the present study the coal was used as a reductant. Physical and chemical properties of hardened iron ore pellets and their raw materials had studied in chapter-3 and chapter-2 respectively. **Table-4.1** shows the chemical composition of fluxed iron ore pellets used for the reduction behaviour study.

Table-4.1 Chemical composition of fluxed iron ore pellets

Chemical composition of flux pellets (wt. %)						
Basicity (CaO/SiO ₂)	Fe ₂ O ₃	Al ₂ O ₃	MnO	SiO ₂	CaO	Rest
~2	86.95	3.48	0.09	2.76	5.70	1.02
~4	82.33	3.30	0.08	2.61	10.45	1.23
~6	78.63	3.15	0.08	2.50	14.25	1.39
~8	74.00	2.96	0.07	2.35	19.00	1.62

4.2.2 EXPERIMENTAL PROCEDURE

In this section all experiment which were conducted to optimize the reduction parameters of hardened flux iron ore pellets are explained in detail.

Figure-4.1 shows the process flow chart for reduction and characterization of hardened flux iron ore Pellets. The whole experiment was carried out at four different reduction temperature (900, 950, 1000 and 1050°C) and reduction time for 30, 45, 60, 90 and 120 minutes respectively. Each experiment was performed for a single pellet under isothermal condition.

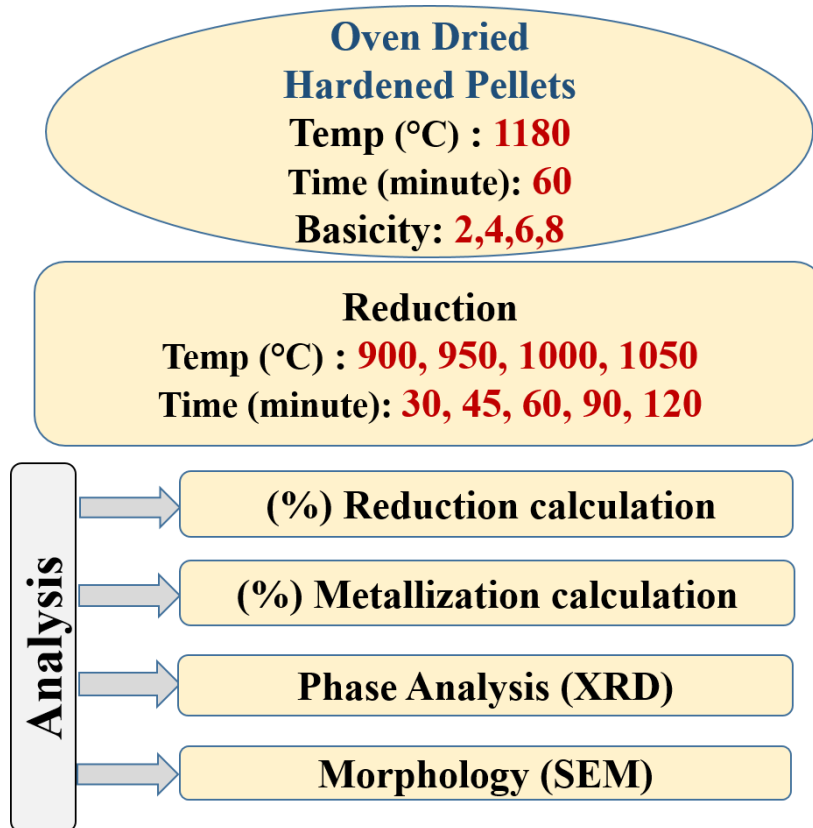


Figure 4.1 Flow chart for reduction and characterization Of hardened flux iron ore Pellets

Figure-4.2 shows the reduction cycle used in the current study. Each hardened flux iron ore pellets were weighed and placed separately inside the bed of coal in the steel crucible (60 mm height and 25mm inside diameter) which was covered using grog (crushed refractory powder).

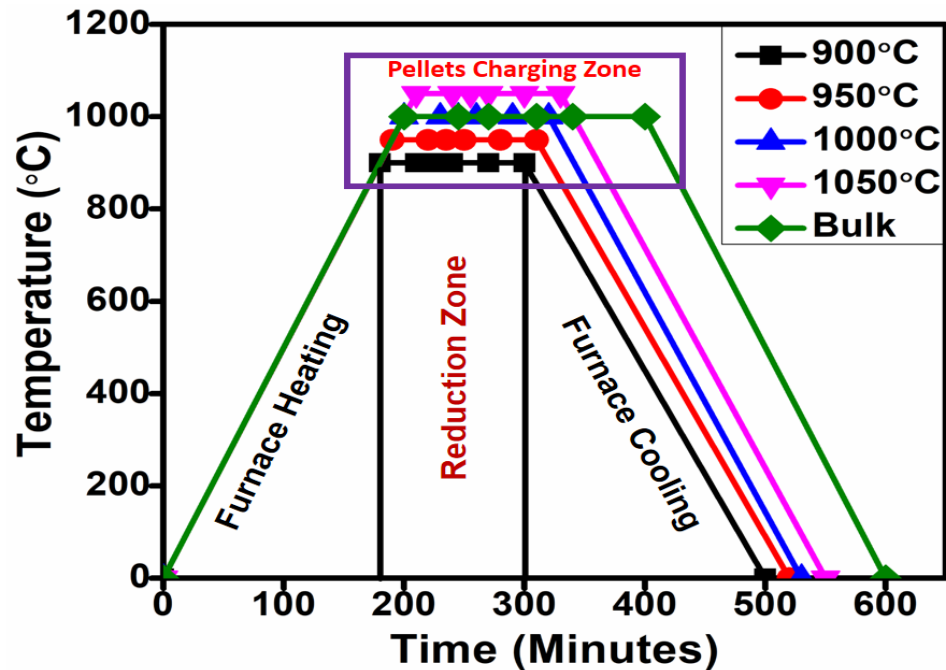


Figure-4.2 Reduction Cycle used for hardened flux iron ore pellets

Figure-4.3 shows the schematic diagram of the setup used in the experiment. Figure-4.3(a) shows the resistance heating furnace and Figure-4.3(b) shows crucible arrangement, in which position of pellet in the bed of coal with grog at the top of crucible is shown. The crucibles containing pellet were kept inside the resistance furnace at the scheduled reduction temperature. After reduction, the crucibles were taken out from the furnace one by one after a given interval of reduction time.

The degree of reduction (%R) was calculated using formula based on the weight loss obtained for the different set of experiments respectively. Bulk (1kg) tests were also performed to obtain reduced flux iron ore pellets of required percent reduction value which are applied in the study of steel making process.

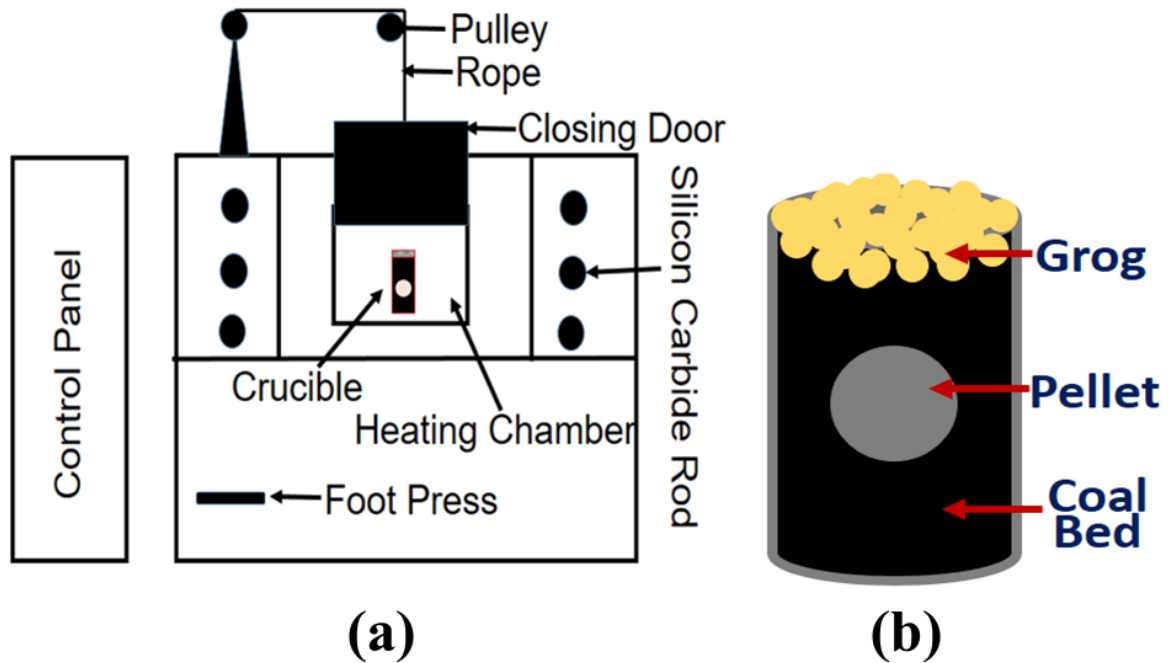


Figure-4.3 Schematic diagram of the crucible and resistance heating furnace used in the experimental study: a) Resistance heating furnace; b) Crucible arrangement.

Figure-4.4 shows the condition of crucible before and after reduction. **Figure-4.4(a)** shows the prepared crucible filled with sample, **Figure-4.4(b)** shows the running condition of the reduction process and **Figure 4.4(c)** shows the condition of the crucible with sample after reduction. The same procedure was followed for all basicity (2, 4, 6 and 8) pellets at temperature (900, 950, 1000, and 1050°C) respectively for different reduction time interval (30, 45, 60, 90 and 120 minutes)

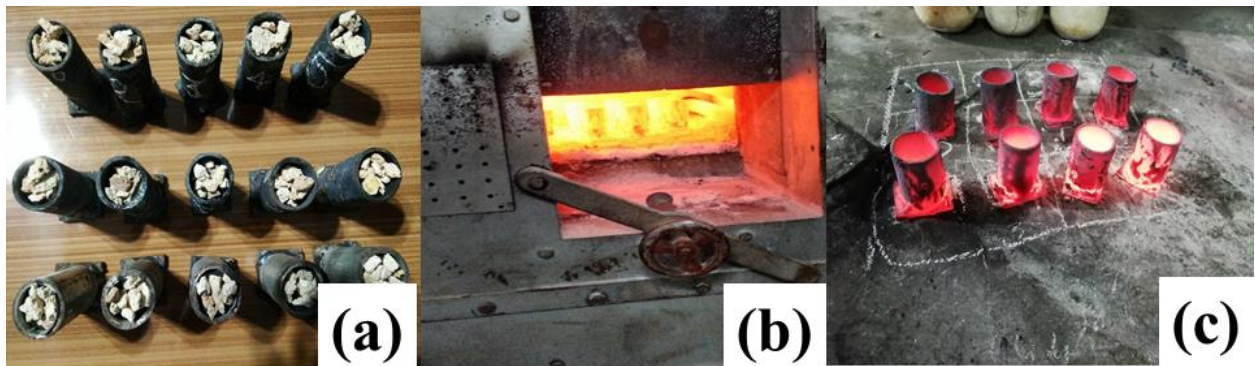


Figure-4.4 condition of crucibles: a) before reduction; b) during reduction; c) after reduction

Scanning Electron Microscope (SEM) and EDS (Model ZEISS EVO-18, OXFORD instrument with software INCA ENERGY 300, acceleration voltage=20 kV, beam current~5nA) used to identify the microstructure and chemical composition of the samples. X-Ray Diffraction (XRD) (Model Rikagu Miniflex-600 model with Dtex ultra detector and Co-K α radiation $\lambda=0.179\text{nm}$, acceleration voltage=40 kV, current=15mA) was used to determine the phases present in the reduced pellets. Samples were scanned at the rate of 2°/ minute from 20° to 110°. *Expert High Score* and *PCPDF* Software used to determine the phases of the material.

4.3 RESULTS AND DISCUSSION

In this section observation of the above mentioned experiment shown in the form of result and discussed in detail. Effect of basicity, temperature and time on the reduction of flux iron ore are discussed here. Calculation of activation energy based on the percentage reduction values are explained using different type of kinetic models.

4.3.1 CALCULATION OF DEGREE OF REDUCTION FOR FLUXED IRON ORE PELLETS

Percentage reduction is calculated with the help of weight loss method. Results obtained from calculation are given in the **Table-4.2**. Formula used to calculate percentage of reduction as given below:

$$\text{Degree of Reduction (\%R)} = (\text{weight of } O_2 \text{ removed during process} / \text{weight of removable } O_2 \text{ in Initial fluxed iron ore pellet}) * 100 \dots\dots\dots 4.1$$

Where,

$$(W_3) = (W_1) - (W_2)$$

$$(W_5) = (W_1) * (W_7)$$

$$(W_6) = (W_5) * 0.925$$

$$(W_4) = (W_6) \cdot (W_8)$$

Theoretical O₂ content in Fe₂O₃ (W₈) = $(16 \times 3) / [(56 \times 2) + (16 \times 3)] = 48/160 = 0.3$;

W₁- Initial weight of flux iron ore pellets

W₂- Final weight of flux iron ore pellets

W₃- Weight loss or weight of O₂ removed

W₄- Weight of removable O₂ in initial flux iron ore pellets

W₅- Weight of iron ore in the initial flux iron ore pellets

W₆- Weight of Fe₂O₃ in the initial flux iron ore pellets

W₇- Percentage weight of Iron ore in the initial flux iron ore pellets

Example of %R calculation for 2 basicity reduced iron ore pellets:-

1. Initial weight of flux iron ore pellet (W₁) = 9.431 g ; (From Table 4.2)
2. Final weight of flux iron ore pellet (W₂) = 8.713 g
3. 2 Basicity pellet means mixture of (lime 6% + iron ore 94%)
4. Weight of iron ore in initial pellet (W₅)= $(9.431 \times 94) / 100 = 8.8657$ g;
5. Weight of Fe₂O₃ in iron ore (W₆) = $(8.8657 \times 92.5 / 100) = 8.200$ g;
6. Weight of O₂ in initial flux iron ore pellet (W₄) = $8.200 \times 0.3 = 2.46$ g;
7. Weight loss in pellet during reduction (W₃) = $(W_1 - W_2) = 0.718$ g;
8. %R = $(\text{wt. loss in pellet} / \text{wt. O}_2 \text{ in initial flux iron ore pellet}) \times 100 = (0.718 / 2.46) \times 100 = 29.18\%$
- 9.

When reduction exceeds 30%, then metallic iron begins to form and its presence increases with degree of reduction. Extent of metallic iron formation is expressed as [3]:

$$\% \text{ Fe}_{\text{Met.}} = 1.4294 \times \%R - 42.3.$$

%Metallization (%Fe_{Met.}) = (Weight of metallic iron / Total iron weight in sample) X 100.

Table 4.2 shows the calculation for % Reduction & % Metallization for the reduced flux iron-ore pellets of basicity from 2 to 8 at different temperature and time.

Basicity	Temp. (°C)	Time (min)	Initial Weight of Pellet (gm.) (W ₁)	Final Weight of Pellet (gm.) (W ₂)	Weight loss (gm.) (W ₃)	Initial Weight of oxygen in Pellet (gm.) (W ₄)	Degree of Reduction R (%)	Metallization (%)	Rate (dR/dt)
2	900	30	9.431	8.713	0.718	2.461	29.185	-0.583	0.973
		45	9.717	8.692	1.025	2.535	40.412	15.465	0.898
		60	8.798	7.546	1.252	2.295	54.565	35.695	0.909
		90	10.023	8.397	1.626	2.615	62.205	46.615	0.691
		120	9.865	8.061	1.804	2.573	70.098	57.898	0.584
	950	30	10.736	9.790	0.946	2.800	33.778	5.982	1.126
		45	9.936	8.609	1.327	2.591	51.223	30.918	1.138
		60	12.026	10.147	1.879	3.136	59.919	43.348	0.999
		90	12.162	10.056	2.106	3.172	66.401	52.613	0.738
		120	11.137	8.990	2.147	2.905	73.931	63.376	0.616
	1000	30	11.301	9.384	1.917	2.947	65.051	50.683	2.168
		45	10.508	8.697	1.811	2.741	66.084	52.161	1.469
		60	10.585	8.584	2.001	2.761	72.497	61.327	1.208
		90	9.125	6.838	2.288	2.380	96.165	95.158	1.068
		120	10.841	8.093	2.748	2.827	97.146	96.561	0.809
	1050	30	9.583	7.788	1.795	2.499	71.808	60.342	2.394
		45	10.744	8.299	2.445	2.802	87.235	82.393	1.939
		60	10.069	7.557	2.512	2.626	95.656	94.431	1.594
		90	9.949	7.433	2.516	2.595	96.955	96.287	1.077
		120	10.423	7.781	2.642	2.718	97.187	96.619	0.809
4	900	30	8.057	7.369	0.688	1.989	34.601	07.158	1.153
		45	8.327	7.439	0.888	2.056	43.221	19.481	0.961
		60	8.951	7.642	1.309	2.210	59.231	42.364	0.987
		90	8.724	7.272	1.452	2.154	67.394	54.032	0.749
		120	9.005	7.368	1.637	2.224	73.621	62.934	0.614
	950	30	8.777	7.837	0.940	2.167	43.392	19.725	1.446
		45	10.667	9.253	1.414	2.634	53.683	34.434	1.193
		60	10.591	8.983	1.608	2.615	61.494	45.599	1.025
		90	9.931	8.167	1.764	2.452	71.948	60.542	0.799
		120	12.584	10.203	2.381	3.107	76.623	67.224	0.639
	1000	30	8.081	6.711	1.370	1.995	68.613	55.775	2.287
		45	9.379	7.702	1.677	2.316	72.421	61.218	1.609
		60	9.633	7.747	1.886	2.379	79.311	71.067	1.322
		90	9.911	7.546	2.365	2.447	96.643	95.842	1.074
		120	11.192	8.488	2.704	2.764	97.846	97.561	0.816
	1050	30	9.593	7.871	1.722	2.369	72.691	61.604	2.423
		45	10.731	8.415	2.316	2.651	87.371	82.588	1.942
		60	11.256	8.601	2.655	2.779	95.512	94.224	1.592
		90	11.485	8.749	2.736	2.836	96.462	95.582	1.072
		120	10.327	7.838	2.489	2.551	97.607	97.219	0.813

Ba sici ty	Temp. (°C)	Time (min)	Initial Weight of Pellet (gm.) (W ₁)	Final Weight of Pellet (gm.) (W ₂)	Weight loss (gm.) (W ₃)	Initial Weight of oxygen in Pellet (gm.) (W ₄)	Degree of Reduction R (%)	Metalliz ation (%)	Rate (dR/dt)
6	900	30	8.523	7.725	0.798	2.011	39.718	14.472	1.324
		45	8.058	7.129	0.929	1.901	48.928	27.637	1.087
		60	8.281	7.023	1.258	1.953	64.414	49.773	1.074
		90	8.083	6.642	1.441	1.906	75.555	65.698	0.839
		120	8.384	6.849	1.535	1.977	77.667	68.717	0.647
	950	30	9.108	8.127	0.981	2.148	45.682	22.997	1.523
		45	9.494	8.165	1.329	2.239	59.389	42.591	1.320
		60	9.721	8.177	1.544	2.292	67.387	54.022	1.123
		90	7.754	6.313	1.441	1.828	78.817	70.361	0.876
		120	8.992	7.201	1.791	2.121	84.412	78.358	0.703
	1000	30	8.823	7.368	1.455	2.081	69.953	57.691	2.332
		45	8.986	7.283	1.703	2.119	80.347	72.548	1.785
		60	7.256	5.867	1.389	1.711	81.161	73.711	1.353
		90	8.339	6.433	1.906	1.966	96.901	96.211	1.077
		120	8.602	6.621	2.081	2.028	97.607	97.219	0.813
	1050	30	8.181	6.763	1.418	1.929	73.509	62.773	2.451
		45	8.875	6.996	1.879	2.093	89.783	86.035	1.995
		60	9.654	7.471	2.183	2.277	95.896	94.773	1.598
		90	8.672	6.697	1.975	2.045	96.588	95.762	1.073
		120	10.3	7.929	2.371	2.429	97.625	97.245	0.814
8	900	30	8.276	7.459	0.817	1.861	43.972	20.553	1.466
		45	8.491	7.438	1.053	1.908	55.202	36.605	1.227
		60	8.892	7.438	1.454	1.998	72.778	61.728	1.213
		90	7.615	6.267	1.348	1.711	78.778	70.305	0.876
		120	7.939	6.478	1.461	1.784	81.915	74.789	0.683
	950	30	10.964	9.707	1.257	2.464	51.011	30.615	1.701
		45	10.251	8.764	1.487	2.304	64.544	49.959	1.434
		60	11.118	9.312	1.806	2.499	72.305	61.052	1.205
		90	11.626	9.392	2.234	2.613	85.512	79.931	0.951
		120	11.384	9.119	2.265	2.558	88.518	84.227	0.738
	1000	30	8.284	6.979	1.305	1.862	70.132	57.946	2.337
		45	8.421	6.851	1.571	1.892	82.955	76.275	1.843
		60	8.301	6.690	1.611	1.865	85.841	80.401	1.431
		90	9.502	7.431	2.071	2.135	96.921	96.238	1.077
		120	9.337	7.286	2.051	2.098	97.728	97.392	0.814
	1050	30	8.561	7.129	1.432	1.924	74.457	64.128	2.482
		45	10.673	8.457	2.216	2.399	92.371	89.735	2.053
		60	9.464	7.428	2.036	2.127	95.739	94.549	1.596
		90	9.619	7.527	2.092	2.162	96.769	96.021	1.075
		120	8.041	6.286	1.755	1.807	97.032	96.397	0.809

4.3.2 EFFECT OF TEMPERATURE ON THE DEGREE OF REDUCTION

Calculation and values of percentage reduction are given in the **Table-4.2**. With the use of calculated values of percent reduction with respect to reduction time in minutes **Figure 4.5** is drawn in which effect of temperature on the reduction behavior of hardened iron ore pellets of basicity 2, 4, 6 and 8 are shown respectively.

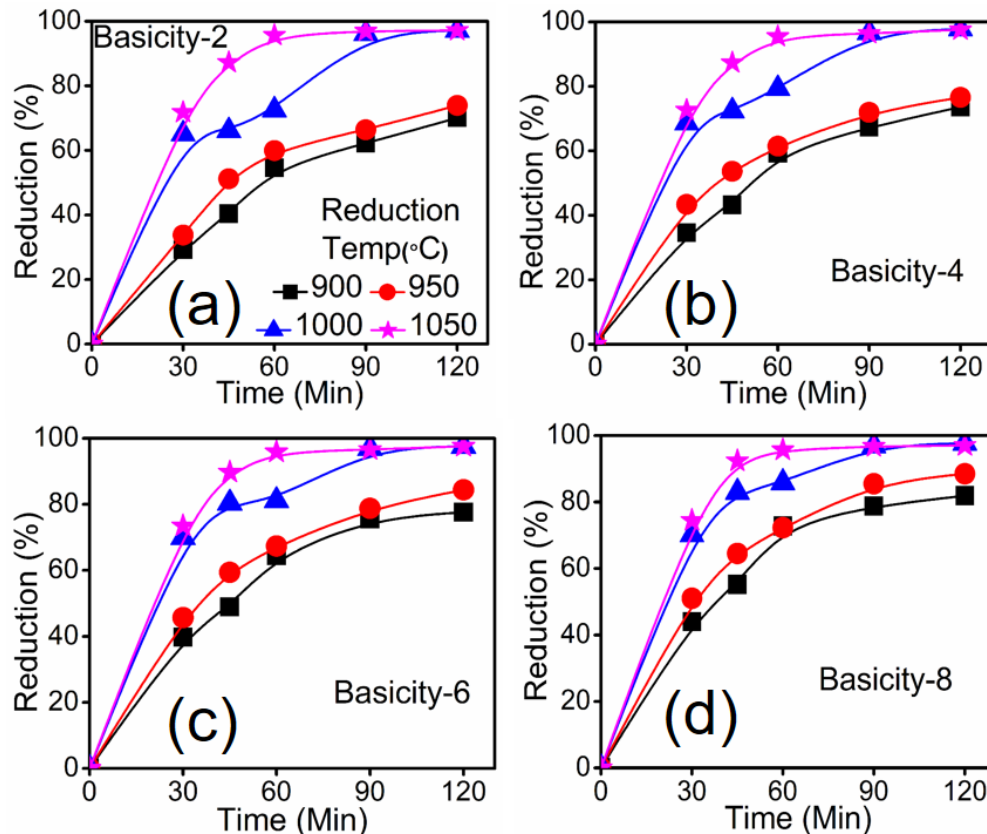


Figure- 4.5 Effect of temperature on the reduction behavior of iron ore pellets for: a) 2 basicity; b) 4 basicity; c) 6 basicity; d) 8 basicity

It is evident from the **Figure-4.5** that the percent reduction of fluxed iron ore pellets increases with increasing reduction temperature for a fixed composition of lime (basicity) [40,50].

In the case of lower temperature (900 & 950°C) and all basicity, the percentage of reduction increases up to maximum level (~80%) for 120 minutes while for the higher temperature (1000 & 1050°C) and all basicity, the reduction increases up to maximum level (~95%) for 90

minutes afterwards it becomes constant. It may be due to increasing coal reaction (carbon gasification) with an increasing temperature and holding time which enhanced the degree of reduction [89]. The result of this experiment agrees with the result of Kumar et al who achieved more than 90 percent reduction in 2 hours at 900°C [64] and Nargin et al who achieved more than 90 percent metallization in 90 minutes at 1000°C [70].

4.3.3 EFFECT OF BASICITY ON THE DEGREE OF REDUCTION

Figure-4.6 shows the reduction of flux iron ore pellets increases with increasing amount of lime (basicity) at a constant temperature.

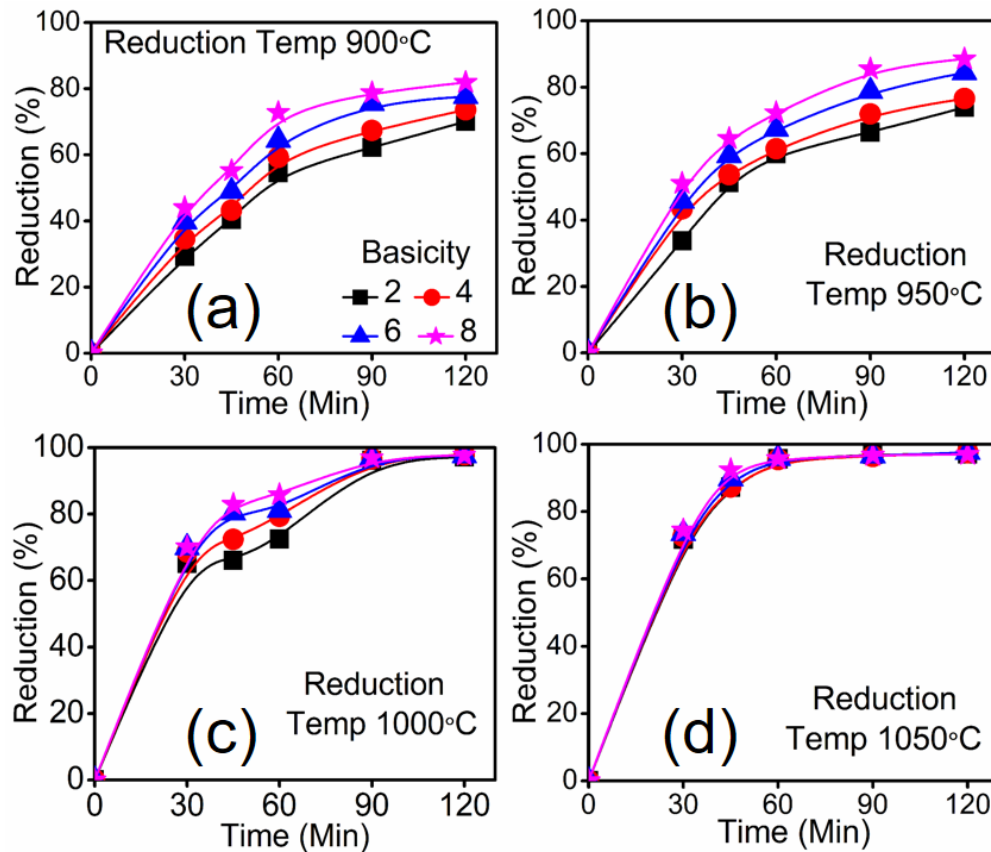


Figure-4.6 Effect of basicity on the reduction behavior of iron ore pellets at temperature: a) 900°C; b) 950°C; c) 1000°C; d) 1050°C

As the percentage of lime increases the creation of calcium ferrite phases in the pellets increases which may be responsible for the higher reduction degree with increasing amount of lime or flux [3,31,41,46,65]. At the lower temperature (900 & 950°C) reduction of pellets increases with basicity for each interval of time from 30 to 120 minutes. At temperature 1000°C reduction increases up to 90 minutes while for 1050°C temperature it increases up to 60 minutes only afterwards it become constant. At lower temperature lime have an important effect on the behavior of reduction but at higher temperature, it does not play a significant role. It may be either due to slow diffusion rate of reducing gases at lower temperature compare to higher temperature or lower gasification rate of carbon at lower temperature compare to higher temperature.

The percentage of free lime inside the iron ore pellets increases as the basicity increases from 6 to 8 (Evident from XRD **Figure-4.10b**) it may be due to the reduction of calcium ferrite phases which formed earlier during hardening process. An increasing amount of free lime creates more porosity in the iron ore pellets which may provide additional free sites/surfaces for the reaction.

4.3.4 EFFECT OF TEMPERATURE AND BASICITY ON RATE OF REDUCTION

The effect of basicity and temperature on the rate of reduction for flux iron ore pellets are shown in **Figure-4.7**. Temperature and basicity both were increasing the rate of reduction, and apparently as the time of reduction increases the rate of reduction decreases. Coal, which is used as reductant in the present study, contains 14.7% volatile matter. The rate of dissociation of hydrocarbons into the hydrogen and carbon increases with increasing temperature and time which may favor the high rate of reduction in the initial stage [63,73,76,78,80].

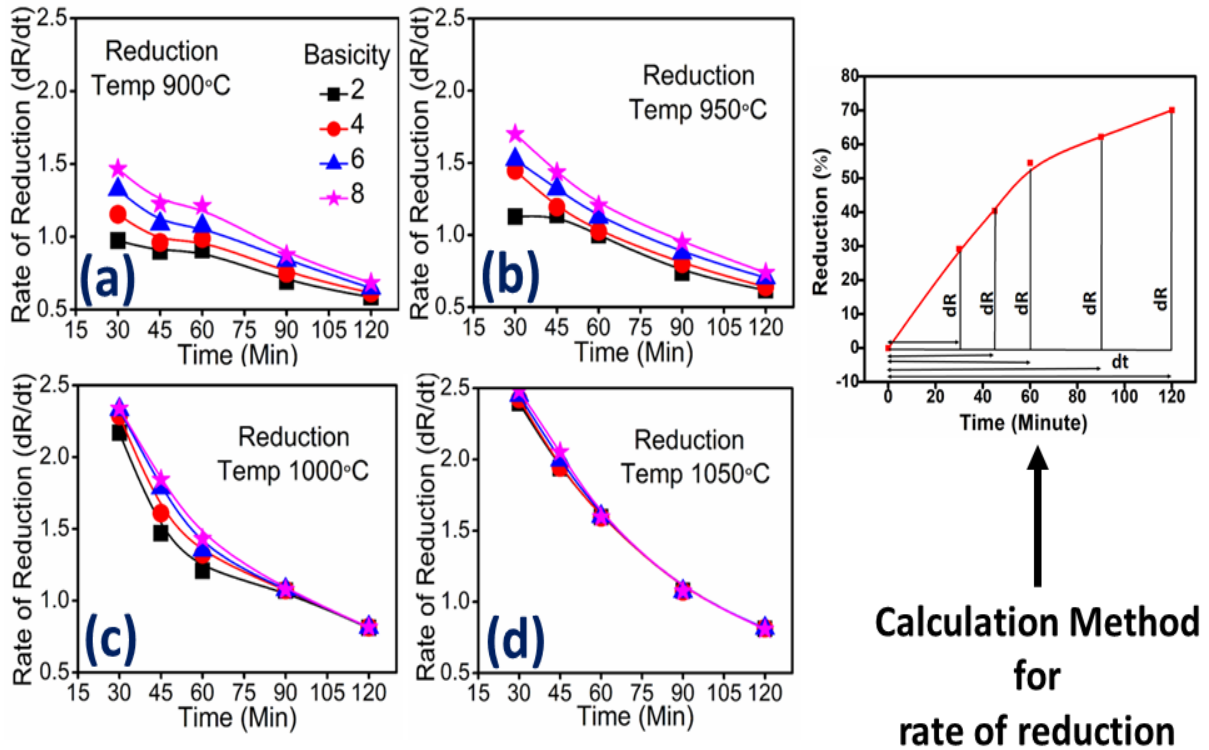


Figure -4.7 Effect of Basicity on the Rate of Reduction for fluxed iron ore pellets at temperature: a) 900°C; b) 950°C; c) 1000°C; d) 1050°C

Figure-4.8 shows the topographical representation of reduction behavior of iron ore pellet which is marked by interface of Fe-CO layer, concentric layers of iron (Fe) followed by wustite (FeO), magnetite (Fe₃O₄) and hematite (Fe₂O₃). The metallized iron layer on the top and hematite in the core are clearly marked. In initial stage, the amount of unreduced iron ore (Fe₂O₃) is high, as the time of reduction increases the thickness of metallic layer (Fe) also increases which may offer resistance to the diffusion of reducing gases (CO) for further reduction, which may reduce the rate of reduction with increase in time.

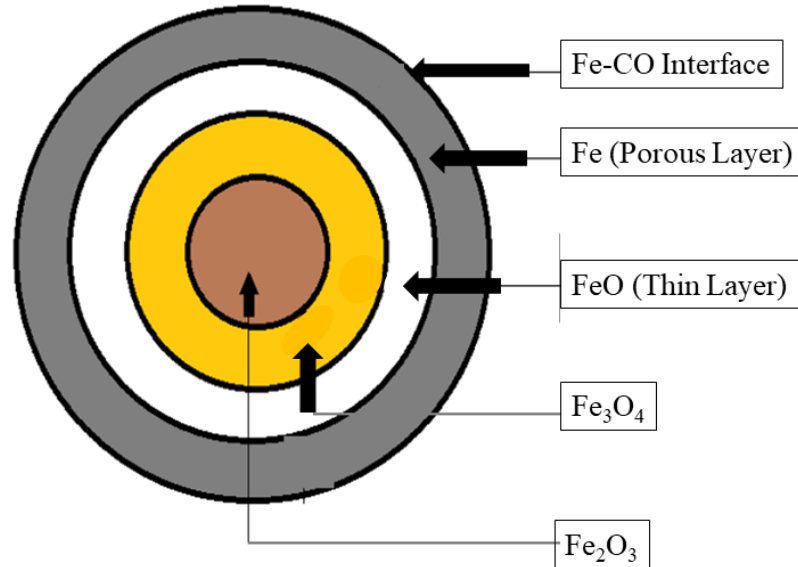


Figure-4.8 Topographical representation of reduction behavior of iron ore pellet.

The reduction of iron ore takes place in different steps as $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$ and $\text{FeO} \rightarrow \text{Fe}$. The reduction of Fe_2O_3 to FeO is faster than FeO to Fe , so the rate of reduction in the initial stage is very high [81] [63].

4.3.5 EFFECT OF BASICITY AND TEMPERATURE ON THE METALLIZATION

When the reduction exceeds 30%, the metallic iron begins to form and its presence increases with degree of reduction. The extent of metallic iron formation is expressed as [3]:

$$\% \text{Metallization } (\% \text{Fe}_{\text{Met.}}) = (\text{Weight of metallic iron} / \text{Total iron weight in sample}) \times 100.$$

The **percent metallization** could be determined by chemical analysis. It has been observed that the degree of reduction (%R) and the degree of metallization (%Fe_{Met}) bear linear relationship and hence expressed as: $\% \text{Fe}_{\text{Met.}} = 1.4294 \times \%R - 42.3$. This relationship could be useful in calculating % Fe_{Met} from %R value [3].

It can be easily correlated from the formula that iron metallization is directly proportional to the value of percentage reduction. On increasing the amount of reduction inside the material, metal value will definitely increase.

Figure-4.9 shows the effect of basicity and temperature on the metallization. It is evident from the figure that metallization increases on increasing the value of temperature of the process or value of basicity of the pellets. Metallization value is derived from the value of percentage reduction, effect of temperature and basicity on the value of percentage reduction is already discussed in the earlier sections.

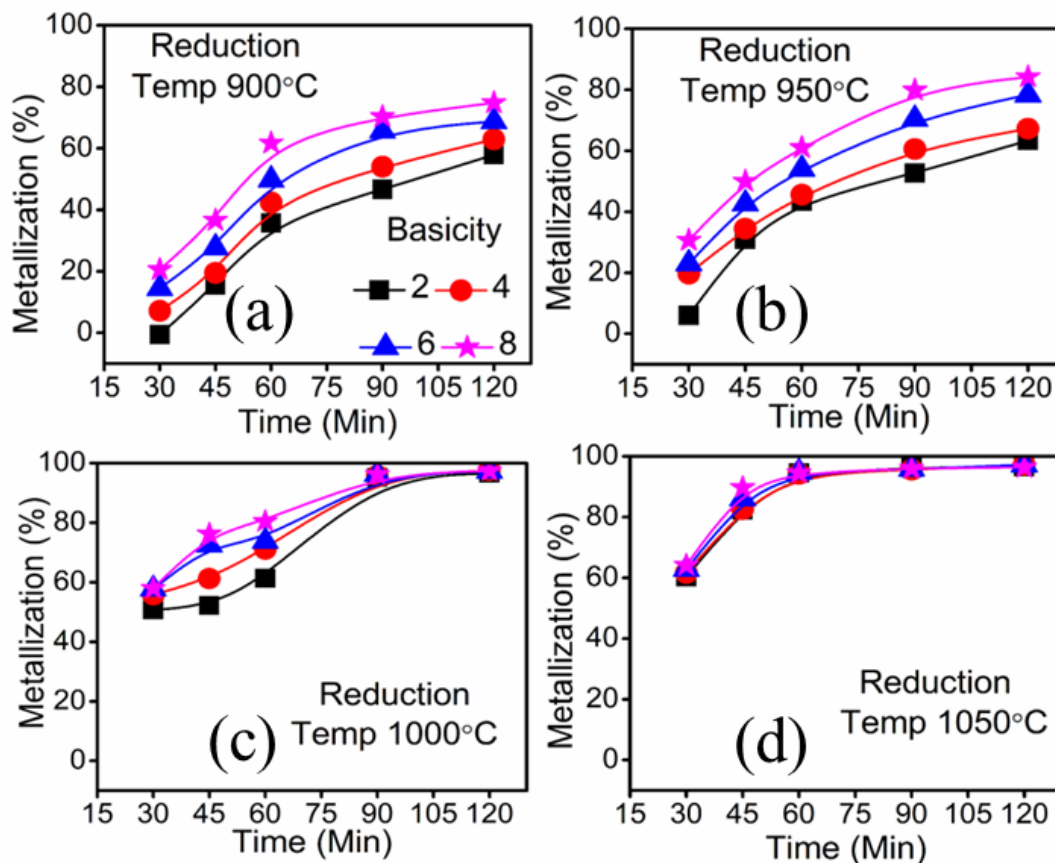


Figure-4.9 Effect of Temperature and Basicity on the Metallization;
a) 900°C, b) 950°C, c) 1000°C, d) 1050°C

4.3.6 XRD (PHASE ANALYSIS) OF THE HIGHLY FLUX REDUCED IRON ORE PELLETS (DRI)

From the above data it is observed that for one hour holding reduction time at 1000°C reduction temperature provides sufficient percentage reduction value which is desirable for further application in steelmaking. Further to know the formation of the phases during reduction process of optimized samples, XRD (phase analysis) was performed. **Figure-4.10** shows the presence of different phases in the flux iron ore pellet before and after one hour reduction time at 1000°C temperature.

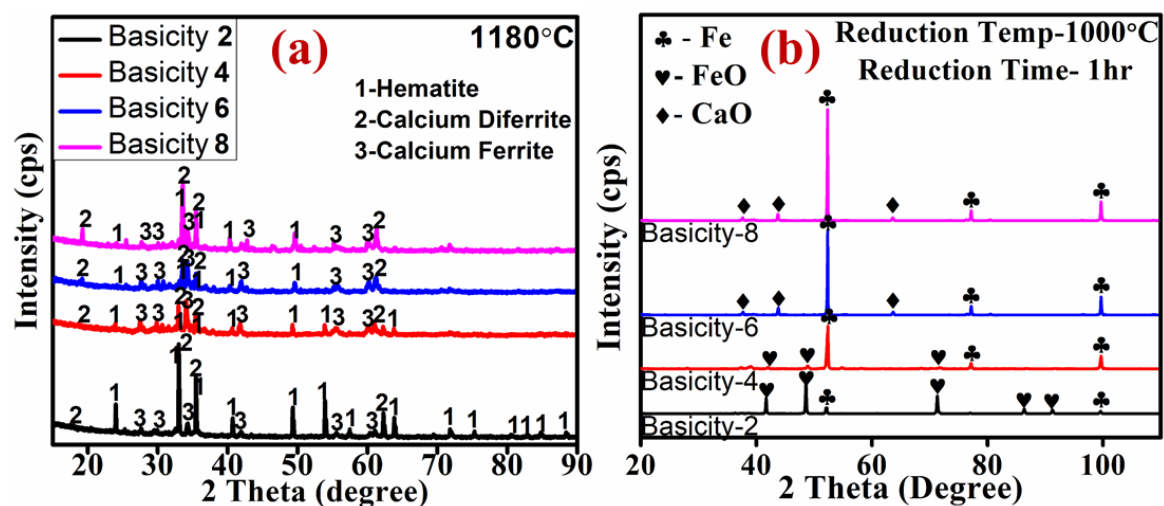


Figure-4.10 Comparative study of the phases; a) phase analysis of pellets (before reduction) X-ray source Cu-K α ; b) phase analysis of pellet (after reduction) X-ray source Co-K α

This figure is used to explain the phase changes during reduction with different basicity at constant time and temperature. It is clear from the figure that phases present before the reduction changes after reduction. During reduction process calcium ferrite and calcium diferrite phases may dissociate in the iron oxides and lime. After dissociation iron oxide get reduced in the iron because reducibility of calcium ferrite is 80.3 compare to hematite [3]. It means calcium ferrite may also reduce easily with iron ore during reduction process. Phases formed during hardening disappear after reduction. It can be seen from the figure as the

percentage of lime (basicity) increases the intensity of iron peak increases sharply. In the case of lower basicity (2 & 4), no peaks of free lime observed it may be due to the presence of lesser amount of lime which cannot be detected with the help of XRD. For the 2 basicity FeO peaks are highest with small amount of iron peaks, which indicates the major presence of iron oxide phase. For basicity 4 intensity of iron phase increases with few small peaks of FeO. At higher basicity (6 & 8) some peaks of free lime were observed, which indicates the presence of free lime at higher basicity. It may be due to the higher reduction of calcium ferrite phases compare to the low basicity pellets.

The presence of free lime provides the more porous media for gas diffusion which promotes the reduction of hematite into iron.

4.3.7 SCANNING ELECTRON MICROSCOPY ANALYSIS OF HIGHLY FLUX REDUCED IRON ORE PELLETS

SEM tests were performed on the reduced flux iron ore pellets to determine the morphological changes and to know the chemical analysis SEM/EDS test performed. **Figure-4.11** shows the SEM images of highly flux hardened iron ore pellets reduced at 1000°C for 1hr. The cause of morphology change was found due to iron nucleation and growth in the form of whiskers. The iron whiskers nucleated (**Figure-4.11a**) due to reduction of iron oxide at a given site which then grows into long whiskers (**Figure-4.11b**). The increase in growth could be noted up to 8 basicity. These growing whiskers push each other and result in shape change. With further reduction, the fusion of whiskers resulted in shrinkage **Figure-4.11c & 4.11d** [3].

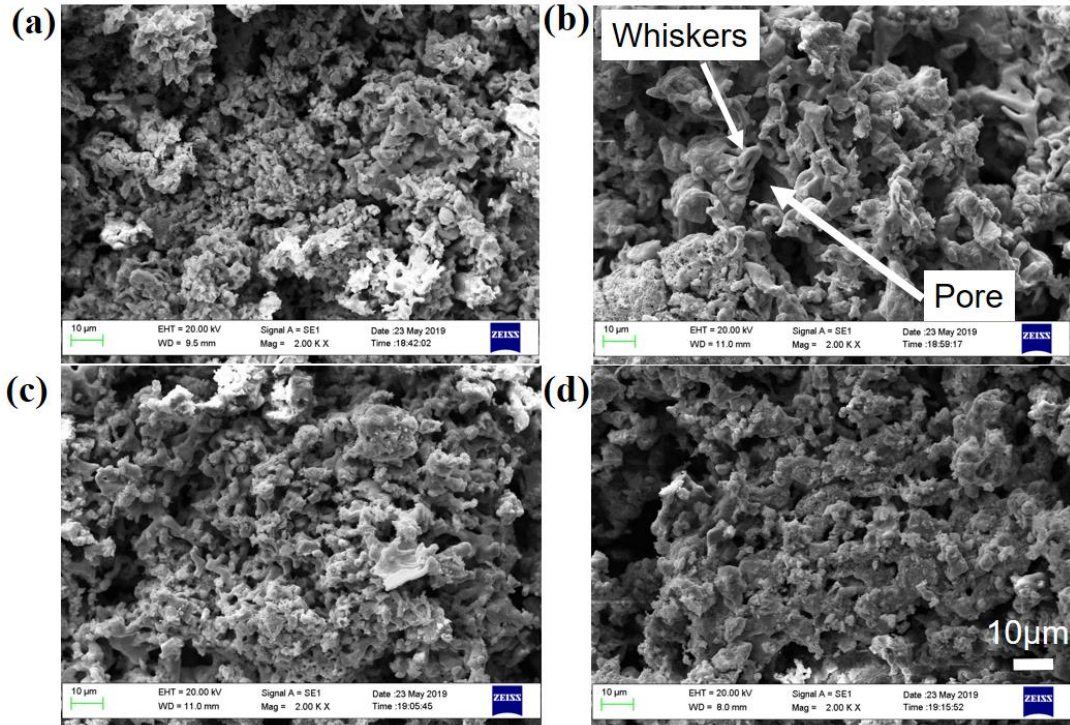


Figure-4.11 SEM images of highly flux hardened iron ore pellets reduced at 1000°C for 1 hour at 2000 X Magnification: For a) 2Basicity; b) 4Basicity; c) 6Basicity; d) 8Basicity

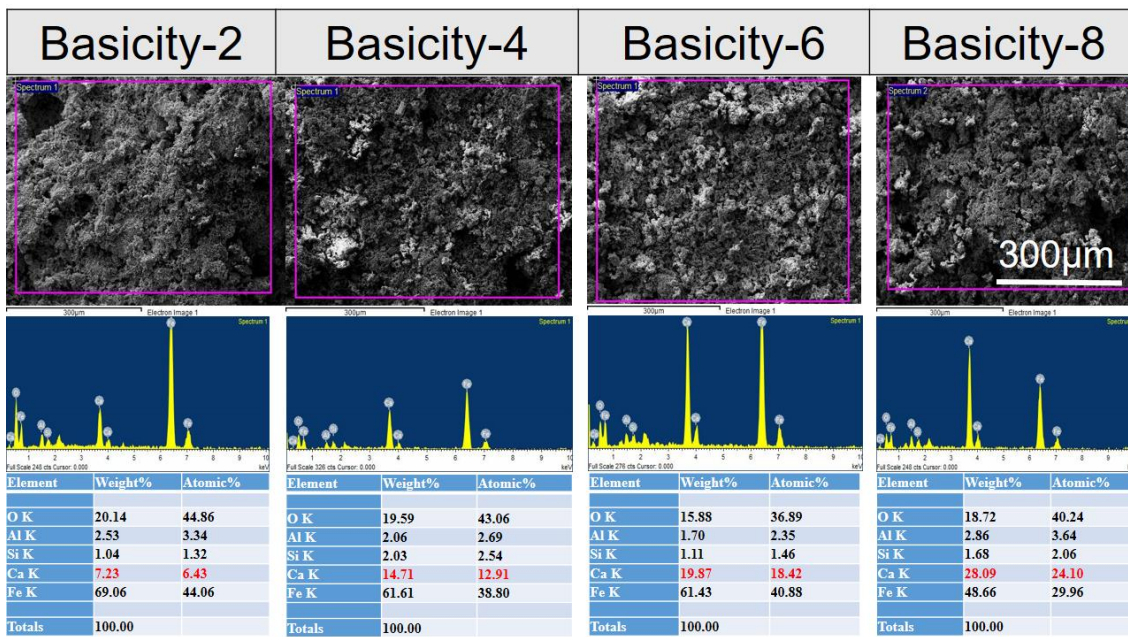


Figure-4.12 SEM/EDS images of highly flux reduced iron ore pellets at 1000°C for 1 hour.

From the SEM/EDS analysis (Figure-4.12), it can be perceived that with increasing the lime (basicity) the amount of free lime increases inside the pellets, which was confirmed by the XRD analysis. The value of calcium is approximately equivalent to the value added in the starting to make the pellets.

4.3.8 ACTIVATION ENERGY CALCULATION FOR THE REDUCTION OF HIGHLY FLUXED IRON ORE PELLETS

For calculating the activation energy, constant k values are required. There are well known five models used to calculate the value of constant k given in **Table -4.3**. For calculating the values of models, (α -percentage reduction) values chosen from the **Table-4.2** and the calculated values of models are given in **Table- 4.4**. Plots of model v/s time provide the R-square values which are given in the **Table-4.5**. On the behalf of R-square value, (which is most close to one) best fit model was chosen to calculate the value of constant k. The values of constant k and activation energy is given in **Table-4.6**.

Table 4.3 Models used to calculate the Activation Energy [90][63],[81]

Models		
S.No.	Equation	Model Name
1	$-\ln(1-\alpha) = kt$	Chemical: first order phase boundary reaction control model equation
2	$1-(1-\alpha)^{1/3} = kt$	Chemical: contracting spherical reaction control model equation
3	$[1-(1-\alpha)^{1/3}]^2 = kt$	Diffusion: Jander's equation
4	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	Diffusion: Ginstling-Brounshtein (GB) diffusion control model equation
5	$[(1-\alpha)^{-1/3}-1]^2 = kt$	Diffusion: Zhuravlev-Lesokhin-Tempel'man (ZLT) diffusion control model equation

Table 4.4 Calculation based on different Model values with respect to time for reduction

		Model Values					
Basicity	Model	Temp (°C)	Time (Min)				
			30	45	60	90	120
2	$-\ln(1-\alpha) = kt$	900	0.345	0.517	0.788	0.972	1.207
		950	0.412	0.717	0.914	1.091	1.344
		1000	1.051	1.081	1.291	3.261	3.556
		1050	1.266	2.058	3.136	3.491	3.571
	$1-(1-\alpha)^{1/3} = kt$	900	0.108	0.158	0.231	0.276	0.331
		950	0.128	0.212	0.262	0.304	0.361
		1000	0.295	0.302	0.349	0.662	0.694
		1050	0.344	0.496	0.648	0.687	0.695
	$[1-(1-\alpha)^{1/3}]^2 = kt$	900	0.011	0.025	0.053	0.076	0.109
		950	0.016	0.045	0.069	0.092	0.131
		1000	0.087	0.091	0.122	0.439	0.482
		1050	0.118	0.246	0.421	0.472	0.484
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	900	0.011	0.022	0.045	0.062	0.085
		950	0.015	0.038	0.056	0.074	0.099
		1000	0.071	0.073	0.093	0.245	0.258
		1050	0.091	0.164	0.238	0.256	0.259
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	900	0.014	0.035	0.091	0.146	0.245
		950	0.021	0.073	0.126	0.192	0.319
		1000	0.176	0.188	0.289	3.862	5.163
		1050	0.275	0.972	3.402	4.851	5.235
	$-\ln(1-\alpha) = kt$	900	0.424	0.566	0.897	1.121	1.332
		950	0.569	0.769	0.954	1.271	1.453
		1000	1.158	1.288	1.575	3.394	3.837
		1050	1.297	2.069	3.103	3.341	3.732
	$1-(1-\alpha)^{1/3} = kt$	900	0.131	0.171	0.258	0.311	0.358
		950	0.172	0.226	0.272	0.345	0.383
		1000	0.321	0.349	0.408	0.677	0.721
		1050	0.351	0.498	0.644	0.671	0.711
	$[1-(1-\alpha)^{1/3}]^2 = kt$	900	0.017	0.029	0.066	0.097	0.128
		950	0.029	0.051	0.074	0.119	0.147
		1000	0.103	0.122	0.167	0.459	0.521
		1050	0.123	0.248	0.415	0.451	0.506
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	900	0.015	0.026	0.051	0.076	0.097
		950	0.026	0.043	0.06	0.091	0.109
		1000	0.080	0.093	0.121	0.251	0.270
		1050	0.094	0.165	0.236	0.249	0.266
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	900	0.023	0.043	0.121	0.205	0.312
		950	0.043	0.085	0.141	0.278	0.388
		1000	0.222	0.287	0.477	4.409	6.729
		1050	0.293	0.986	3.291	4.186	6.101

		Model Values					
Basicity	Model	Temp (°C)	Time (Min)				
			30	45	60	90	120
6	$-\ln(1-\alpha) = kt$	900	0.506	0.671	1.033	1.408	1.499
		950	0.610	0.901	1.121	1.551	1.858
		1000	1.202	1.626	1.669	3.474	3.732
		1050	1.328	2.281	3.193	3.377	3.740
	$1-(1-\alpha)^{1/3} = kt$	900	0.155	0.200	0.291	0.374	0.393
		950	0.184	0.259	0.311	0.403	0.461
		1000	0.330	0.418	0.426	0.685	0.711
		1050	0.357	0.532	0.655	0.675	0.712
	$[1-(1-\alpha)^{1/3}]^2 = kt$	900	0.024	0.040	0.084	0.141	0.154
		950	0.033	0.067	0.097	0.163	0.213
		1000	0.109	0.175	0.182	0.471	0.506
		1050	0.127	0.283	0.429	0.456	0.507
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	900	0.021	0.034	0.068	0.105	0.114
		950	0.029	0.055	0.076	0.119	0.147
		1000	0.085	0.126	0.131	0.255	0.266
		1050	0.097	0.182	0.241	0.251	0.266
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	900	0.033	0.063	0.169	0.359	0.420
		950	0.051	0.122	0.205	0.459	0.736
		1000	0.243	0.518	0.554	4.768	6.101
		1050	0.310	1.297	3.606	4.339	6.145
8	$-\ln(1-\alpha) = kt$	900	0.579	0.803	1.301	1.551	1.710
		950	0.713	1.036	1.283	1.931	2.164
		1000	1.208	1.769	1.954	3.481	3.784
		1050	1.364	2.573	3.155	3.432	3.517
	$1-(1-\alpha)^{1/3} = kt$	900	0.175	0.234	0.351	0.403	0.434
		950	0.211	0.292	0.348	0.474	0.513
		1000	0.331	0.445	0.478	0.686	0.716
		1050	0.365	0.575	0.651	0.681	0.690
	$[1-(1-\alpha)^{1/3}]^2 = kt$	900	0.030	0.055	0.123	0.162	0.188
		950	0.044	0.085	0.121	0.225	0.264
		1000	0.109	0.198	0.229	0.471	0.513
		1050	0.133	0.331	0.423	0.464	0.476
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	900	0.027	0.046	0.094	0.119	0.134
		950	0.038	0.068	0.093	0.154	0.173
		1000	0.085	0.139	0.156	0.255	0.268
		1050	0.101	0.204	0.239	0.253	0.257
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	900	0.045	0.094	0.294	0.457	0.591
		950	0.072	0.170	0.285	0.817	1.118
		1000	0.246	0.645	0.843	4.798	6.404
		1050	0.331	1.843	3.471	4.578	4.972

Table 4.5 R² Values for different models used to calculate activation energy

Basicity	Model	R ² Values			
		Temp (°C)			
		900	950	1000	1050
2	$-\ln(1-\alpha) = kt$	0.954	0.928	0.866	0.709
	$1-(1-\alpha)^{1/3} = kt$	0.935	0.897	0.865	0.642
	$[1-(1-\alpha)^{1/3}]^2 = kt$	0.982	0.972	0.859	0.695
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0.974	0.956	0.858	0.631
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	0.982	0.984	0.880	0.842
4	$-\ln(1-\alpha) = kt$	0.942	0.973	0.913	0.784
	$1-(1-\alpha)^{1/3} = kt$	0.922	0.957	0.912	0.699
	$[1-(1-\alpha)^{1/3}]^2 = kt$	0.970	0.988	0.905	0.762
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0.957	0.979	0.904	0.682
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	0.986	0.994	0.905	0.937
6	$-\ln(1-\alpha) = kt$	0.902	0.985	0.896	0.739
	$1-(1-\alpha)^{1/3} = kt$	0.883	0.965	0.895	0.644
	$[1-(1-\alpha)^{1/3}]^2 = kt$	0.923	0.996	0.890	0.717
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0.909	0.986	0.891	0.624
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	0.949	0.983	0.888	0.917
8	$-\ln(1-\alpha) = kt$	0.863	0.963	0.933	0.613
	$1-(1-\alpha)^{1/3} = kt$	0.832	0.943	0.916	0.521
	$[1-(1-\alpha)^{1/3}]^2 = kt$	0.892	0.970	0.928	0.593
	$1-(2/3)\alpha-(1-\alpha)^{2/3} = kt$	0.865	0.957	0.912	0.503
	$[(1-\alpha)^{-1/3}-1]^2 = kt$	0.955	0.971	0.920	0.826

Figure-4.13 shows best fit model for the reduction of highly fluxed (2, 4, 6 & 8 basicity) harden iron ore pellets. “ $[(1 - \alpha)^{-1/3} - 1]^2 = kt$ ” (α is the fraction of reduction and t is the time consumed in reduction) was found best fit model for reduction of fluxed iron ore pellets in coal bed. **Figure-4.13** is used to find out the value of constant k for calculating the activation energy. The activation energy of the reduction for pellets of different basicity was calculated from the Arrhenius plots. The values of $\ln k$ and activation energy for different basicity are given in **Table 4.6**.

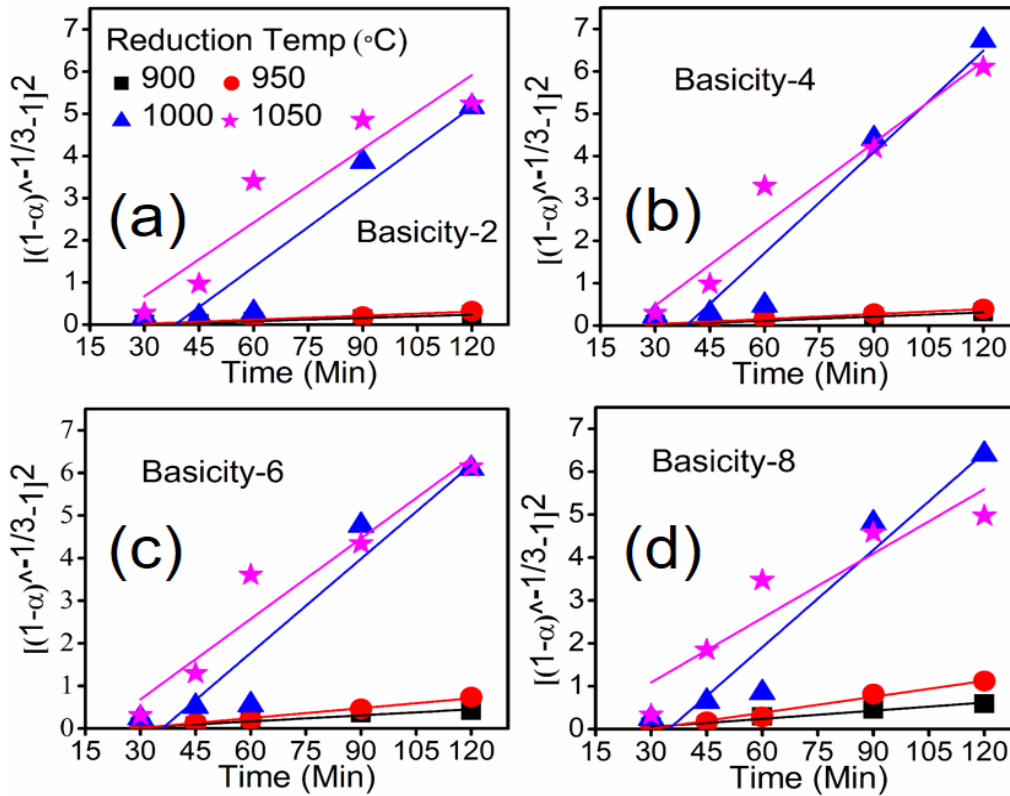


Figure-4.13 Model fitting curve for activation energy calculation:
a) 2 basicity; b) 4 basicity; c) 6 basicity; d) 8 basicity

The activation energies of reduction for fluxed iron ore pellets are calculated by using Arrhenius Equation.

$$k = A \cdot e^{-E_a / RT}$$

Where, k = rate constant
A = frequency factor (or) pre-exponential factor
E_a = Activation Energy,
R = Gas constant,
T = Temperature (kelvin)

Table-4.6 k values and Activation Energy for different basicity

Activation Energy Calculation					
Basicity	Temperature (Kelvin)	k values (from the graphs)	ln k	Slope Value	Activation Energy (KJ/mol)
2	1173	0.0026	-5.968	-3.840	31.927
	1223	0.0032	-5.751		
	1273	0.0633	-2.760		
	1323	0.0583	-2.843		
4	1173	0.0033	-5.714	-3.699	30.750
	1223	0.0040	-5.534		
	1273	0.0797	-2.530		
	1323	0.0641	-2.748		
6	1173	0.0047	-5.356	-3.124	25.972
	1223	0.0077	-4.861		
	1273	0.0736	-2.609		
	1323	0.0630	-2.765		
8	1173	0.0063	-5.063	-2.510	20.870
	1223	0.0124	-4.391		
	1273	0.0756	-2.582		
	1323	0.0501	-2.995		

Figure-4.14 is the Arrhenius plot which is used to calculate the activation energy of reduction for different basicity hardened flux pellets. Arrhenius plot is drawn between $[\ln k \text{ v/s } (1/T)]$, k is the rate constant and T is the temperature in kelvin). From the figure-4.14 it is depicted that as the basicity of hardened flux iron ore pellets increases the amount of activation energy was found to decrease. Presence of CaO and MgO enhances the catalytic effect of coal which in turn increases the reactivity of coal [91]. Catalytic enhancement of carbon gasification by

metallic iron and higher amount of reduction for high basicity could be responsible for lower activation energy at higher basicity [63].

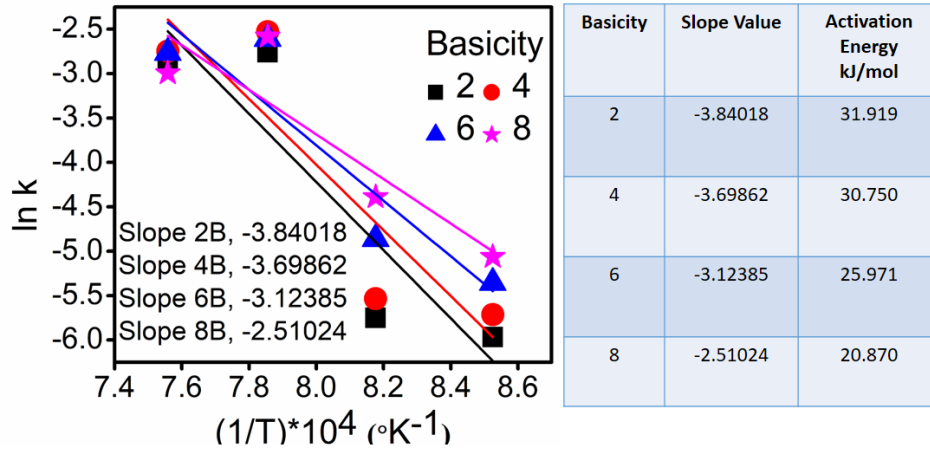


Figure-4.14 Arrhenius Plot and Activation energy values for basicity 2, 4, 6 and 8 Iron ore pellets reduced at temperature 900, 950, 1000 and 1050°C

The values of activation energy were 31.92, 30.75, 25.97, 20.87 kJ/mol for the pellets of basicity 2, 4, 6 and 8 respectively. Similar type of energy values were observed by Mandal et al. 9.97-14.65 kJ/mol for iron oxide and carbon monoxide combination [66] and Sah et al. 12.37-38.32 kJ/mol for iron ore coal composite pellets [59].

4.4 FINDINGS

This study resulted following conclusions:

- It is possible to prepare iron ore pellets of highly fluxed (8 Basicity) and reduced DRI (>80%R) when heated in coal bed at 1000°C reduction temperature for 60 minute time.

- Reduction temperature and iron ore pellet basicity both affect the reduction process. Higher reduction percent could be achieved by increasing the temperature (900-1050°C) with required reduction time for iron ore pellets having basicity (from 2 to 8).
- The kinetic model " $[(1 - \alpha)^{-1/3} - 1]^2 = kt$ " is the best fit model for reduction of highly fluxed iron ore pellets in coal bed. The activation energy of the reduction decreases with increasing basicity. The values of activation energy are 31.92, 30.75, 25.97, 20.87 kJ/mol for the reduction of iron ore pellets having basicity 2, 4, 6 and 8 respectively.