

## **Effect of mineralogy on reduction behaviour of iron ore pellets**

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### **Abstract**

The present study deals with influence of gangue content ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) in iron ores on reduction of its pellets for production of sponge iron. Iron ore pellets were reduced isothermally with noncoking coal fines in the range of 1123 - 1273 K with a time interval of 15, 30, 45, 60, 90 and 120 min. As the temperature rose from 1123 to 1223 K, the rate of reduction of all iron ore pellets increased and then decreased at temperature 1273 K. All iron ore pellets shows complete reduction at temperatures of 1173 and 1223 K within 120 minutes. The reduction results clearly show that the reducibility of the pellets depends on the initial mineralogy of the ore. It was also observed that the reducibility decreased as gangue content ( $\text{Al}_2\text{O}_3 + \text{SiO}_2$ ) increases. The activation energy of the pellets decreased from 46.54 and 49.13 kJ/mol when the gangue content increased. The pellets were analyzed with X-ray diffraction and scanning electron microscopy before and after reduction to identify phase transformations. Examination of the SEM microphotographs revealed that Whisker shape of iron grains were formed during the reduction process and clear porous structure was observed.

*Keywords:* Iron ore pellet, mineralogy, direct reduction, degree of reduction

### **1. Introduction**

Blast furnace (BF) iron making process is a traditional and significant iron making process, majority of the iron producing from this route. Sudden growth of iron consumption and deficiency of the high grade iron ores researchers concentrate on the alternative methods and utilization waste iron ores (low grade and iron ore fines). The fines are utilized by agglomeration technique such as pelletizing process. The pellets were used as a feed material for direct reduction (DRI) or sponge iron making process[1]. India is fifth largest producer of crude steel and number one producer in DRI production in the world. It is due to the rapid growth of coal-based sponge iron industries in the mineral-rich states (Orissa, Chhatisgarh and Jharkhand) of the country [2]. During the reduction process, oxygen can be removed from the iron oxides the by using the reduction media at below the fusion temperature of iron oxide while it is in solid state. It is also known as direct reduced iron (DRI). In DRI process, Reduction process was increased when non-cocking coal was used as a reactant because it contains a high amount of volatile matter, in the process of reduction the volatile matter was released and turns to reducing gases like CO and  $\text{H}_2$  [3]. Many numerous investigators were focused on the study true reduction reaction under the conditions of direct contact of iron oxide with carbon. It was observed that, the rate of reduction depending on the density, porosity, reducing temperature, time, and reducibility of iron oxide and reactivity of carbon[4–6]. Iron ore contains a variety of gangue oxides such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , and their presence can significantly affect the reduction process. The presence of gangue in the ore increases the requirement of flux consumption, slag volume and fuel consumption. Many numerous investigators were focused on the study true reduction reaction under the conditions of direct contact of iron oxide with carbon. It was observed that, the rate of reduction depending on the density, porosity, reducing temperature, time, and reducibility of iron oxide and reactivity of carbon. Many numerous investigators were focused on the study true reduction reaction under the conditions of direct contact of iron oxide with carbon. The kinetic behaviour of the iron ores are changing from ore to ore [7–10]. Very less amount of work is available for the effect of

gangaue content on the reduction behaviour of different iron ores and as well as reduction kinetics of the different iron ores.

The present study has focused on the effect of gangue minerals on the reduction behaviour of iron ore pellets prepared with five natural hematite iron ores. The influence of temperature and time on reduction behaviour was analyzed as well as XRD and SEM analysis was conducted to investigating the phase changes in the reduction process. And also determine the effect of gangue content on activation energy of the reduction reaction.

## 2. Materials and methods

### 2.1 Raw materials

In the present study, five different types of iron ore samples (Essel, PTA, OMC, Bacheli and Kirandul) were collected from across eastern region of India. The used raw materials (iron ore and bentonite) chemical compositions are shown in table1. Non-coking coal is used as a reductant and is collected from Basundhara-mines then proximate analysis was performed on the samples and its results are shown in Table 2.

**Table 1:** Nominal chemical composition (%) of iron ores from different mines

S. NO	Iron ore	Fe	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P	S	LOI
1	Essel	56.50	7.53	4.54	0.065	0.016	7.54
2	OMC	62.63	3.79	3.92	0.063	0.015	2.43
3	PTA	64.06	2.52	2.61	0.061	0.015	2.31
4	Kirandul	65.79	2.12	2.86	0.062	0.014	2.25
5	Bacheli	67.00	1.50	2.10	0.040	0.012	2.12
6	Bentonite	3.96	58.36	21.14	-	-	6.75

**Table 2:** Proximate analysis of non-coking coal collected from Basundhara Mines Ltd.

Non-coking Coal	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)	Sulfur content (%)	Caking -Index	Ash Fusion Temperature (K)			
						IDT	ST	HT	FT
Basundhara Mine	25.26	39	35	0.48	2.0	1526	1701	1797	1873

### 2.2 Experimental methods

The pellet feed was prepared by mixing of iron ore fines (-75 μm) and bentonite binder (1 wt %). Then mixture was transferred to disc-pelletizer and operated at 25 rpm, and moisture was added to the mixture. The obtained green pellets were dried in oven at 105 K, and then pellets were fired at different temperatures i.e., 1173, 1273, 1373, 1473 and 1573 K. Compressive strength test was performed as per ISO 4700 on fired pellets to study weather prepared pellets can withstand operating conditions. Meanwhile, porosity was also measured by using Archimedes principle. The fired pellets were reduced with non-coking coal fines at different reduction temperatures (1123, 1173, 1223 and 1273 K) and time (15, 30, 45, 60, 90 and 120 min). The weight difference of the samples were measured as a degree of reduction [11]. The kinetics of reduction behaviour of a reduced iron ore pellets was also investigated to study the effect of chemical composition and reduction temperature. The Xrd analysis was performed using Panalytical PW3040 X'Pert MPD on reduced pellets to observe phase transformation. The SEM (JEOL-xxx) analysis was used to study the morphology of reduced iron-ore pellets

### 3. Results and discussion

#### 3.1 Compressive strength

Fig.1 shows the influence of temperature on porosity and compressive strength of the different iron ore pellets. From the Fig.1(a) it can be observed with increasing firing temperature from 1173-1573 K, porosity of the sample has reduced from 30-20 %. At higher temperatures the bentonite present in the inter-particles melts and fills the voids thus reduces the gap between the iron-ore particles. Fig.1 (b) shows the effect of temperature on the compressive strengths of different iron ore pellets. Initial samples were fired at 1173 K, and evaluated its compressive strength. From the results (Fig. 1(b)) it can be observed that strength of the different pellets are in the range of 870-994 N/pellet. The obtained strength values are not in the required industrial limit 2500 N/pellet[12]. To improve the strength of iron-ore pellets, samples were further fired from 1273 to 1573 K. From the Fig.1(b), it can be observed that with increasing firing temperature strength of the pellets has increased and its maximum compressive strength values are range of 2630-2985 N/pellet at 1573 K, and the obtained strength values are above the industrial limit. Increase in strength could attributed to reduced porosity and which improved the bonding between the particles. The compressive strength results are in good agreement with the porosity results and same can be observed in the Fig.1.

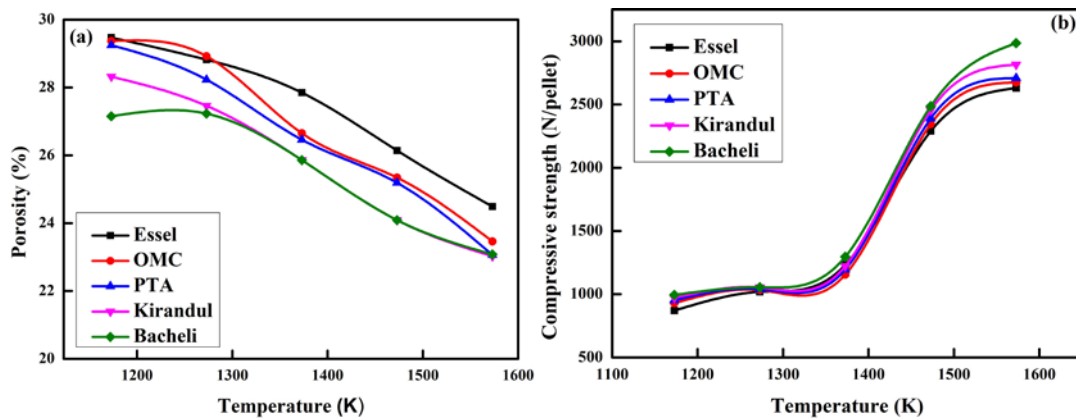


Fig.1 Effect of temperatures on (a) porosity and (b) compressive strength of different iron ore pellets

#### 3.2 Reduction behaviour of iron ore pellets

Fig.2 illustrates the influence of reduction temperatures and time on reducibility of different iron-ore pellets. From the reduction results, it can be observed that with increasing temperature reduction rate has increased. Based on the results the reduction can be classified into three stages, it was shown in Fig.2 (a). Initial stages the reduction rate is very rapid up to 40%, due to release of volatile matter from the non-coking coal and reducing gases did not obstruct the flow inside the pellet. At the second stage reduction rate has reduced compared to the first stage. Whereas, at the stage three difference in reduction rate is negligible and further increasing in temperature there will not be any improvement in the reduction rate, this effect may be due to absence of volatile matters.

##### 3.2.1. Effect of time and temperature on reduction behaviour

From the results it can be observed that reduction temperature has a pronounced effect on degree of reduction rate. When samples reduced at particular temperature with increasing time, the amount of mass loss has elevated i.e removing of oxygen has increases. At a temperature 1123K the iron-ore samples have reduced to only 70.0 %, when the temperature raised to 1173K reduction about 90.0 % after 120 minutes. The reason for not improving the reduction rate is due to the combination of effects at first due to deficient breaking of hydrocarbons, and formation of unstable CO gas which lead to insufficient amount of reducibility gases. The reduction rate gradually increases with time up to a certain limit and then decreases due to the formation of a dense iron layer and formation of viscous

slag over the periphery of pellets, and core portion will be un-reduced. At higher reduction temperatures 1223 and 1273 K, reduction reaches more than 95% within 60-45 minutes of time due to the rapid heating of coal. From the Fig.2 (a-d) it can also be observed that the composition of iron-ore also plays an important role in reduction of those pellets. The Bachelu and Kirandul iron ore pellets have shown higher reduction values followed by OMC, PTA and Essel iron ore pellets. This could be attributed to higher percentage of gangue ( $Al_2O_3$ ,  $SiO_2$ , etc.) content in the iron-ore. These gangue minerals create a hindrance to the diffusion of reducing gases at reaction sites this results in less reduction of iron ore pellets.

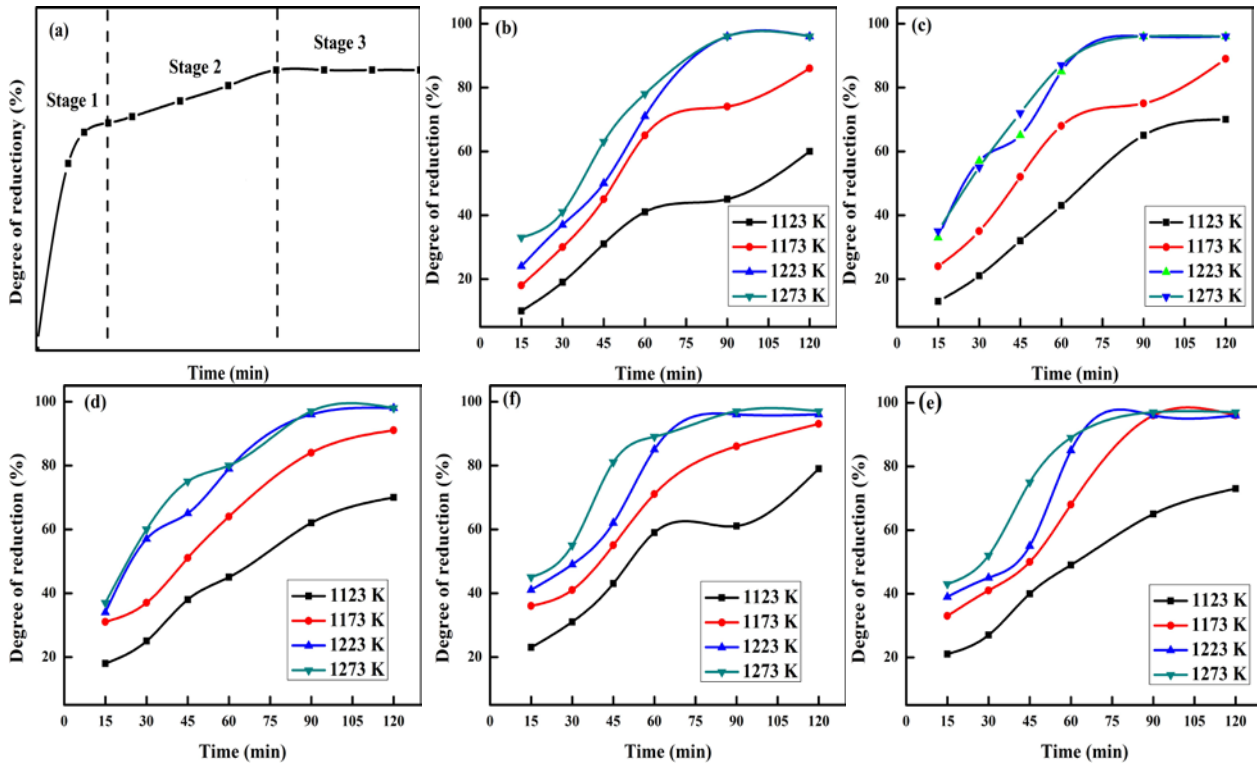


Fig. 2 Effect of temperature and time on reduction of iron ore pellets a) Reduction steps b) Essel c) OMC d) PTA e) Kirandul f) Bachelu

### 3.3. XRD analysis

XRD analysis was performed on reduced iron ore pellets from the results all the mines shows similar phases were identified, from the results Essel iron ore results were displayed in Fig.3. Fig.3 show the XRD results of ESSEL iron at 1123 K and 1273 K at different time intervals. Initially the ore consist of  $Fe_2O_3$  and minor peaks of  $Fe_3O_4$ . At 1123 K,  $Fe_2O_3$  transforms to  $Fe_3O_4$  within 45 minutes of time, with further increasing the holding time to 60 minutes it transforms to FeO and at 120 minutes the Fe peaks were noticed majorly. At temperature 1173 K,  $Fe_3O_4$  transforms to FeO within 60 minutes and in earlier Fe phase was observed. At 1223 and 1273 K rapid reduction rate was observed and phase transformations were not strictly follow the series of Hematite ( $Fe_2O_3$ )→Magnetite ( $Fe_3O_4$ )→wustite (FeO)→iron(Fe), and they are dominantly occupied by FeO and finally Fe phase was observed in earlier time.

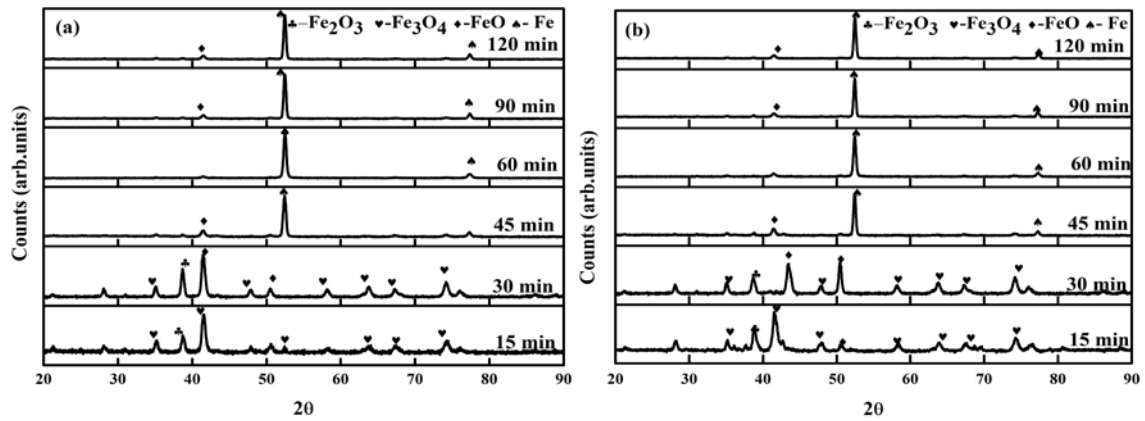


Fig.3 XRD analysis of reduced iron ore pellet (Essel iron ore) at a temperature a) 1123 K b) 1273 K

### 3.4. Microstructure analysis of reduced pellets

The SEM images of the pellets were examined after reduction to identify any change in morphology at different temperatures, and same can be observed in Fig.4. From the microstructures, it can be observed that the iron whiskers area increases with increasing the temperature, while the unreduced hematite portion was decreased. The pore size distribution of the pellet increases with increasing the temperature from 1123 to 1273K. As can be seen from the Fig.4, the periphery region is more porous than the core region. During reduction process hematite will transform to magnetite but it is difficult to identify in the morphology. The final transformation iron-ore pellet is continuous and more porous structure is present.

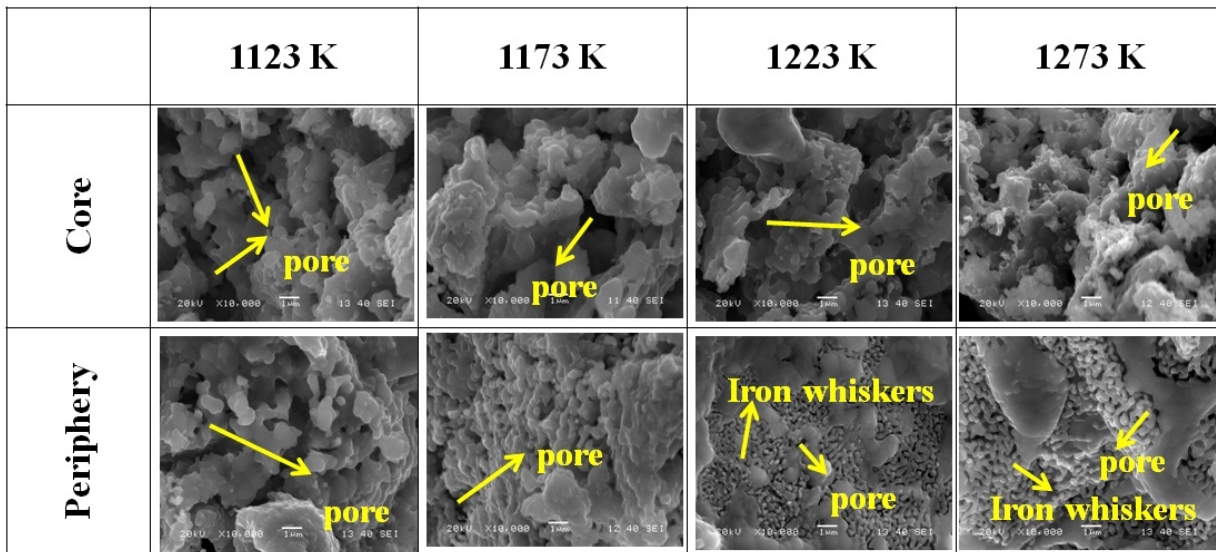


Fig. 4 SEM microstructure of the iron ore pellets after reduction at different temperatures

### 3.5 Activation energy

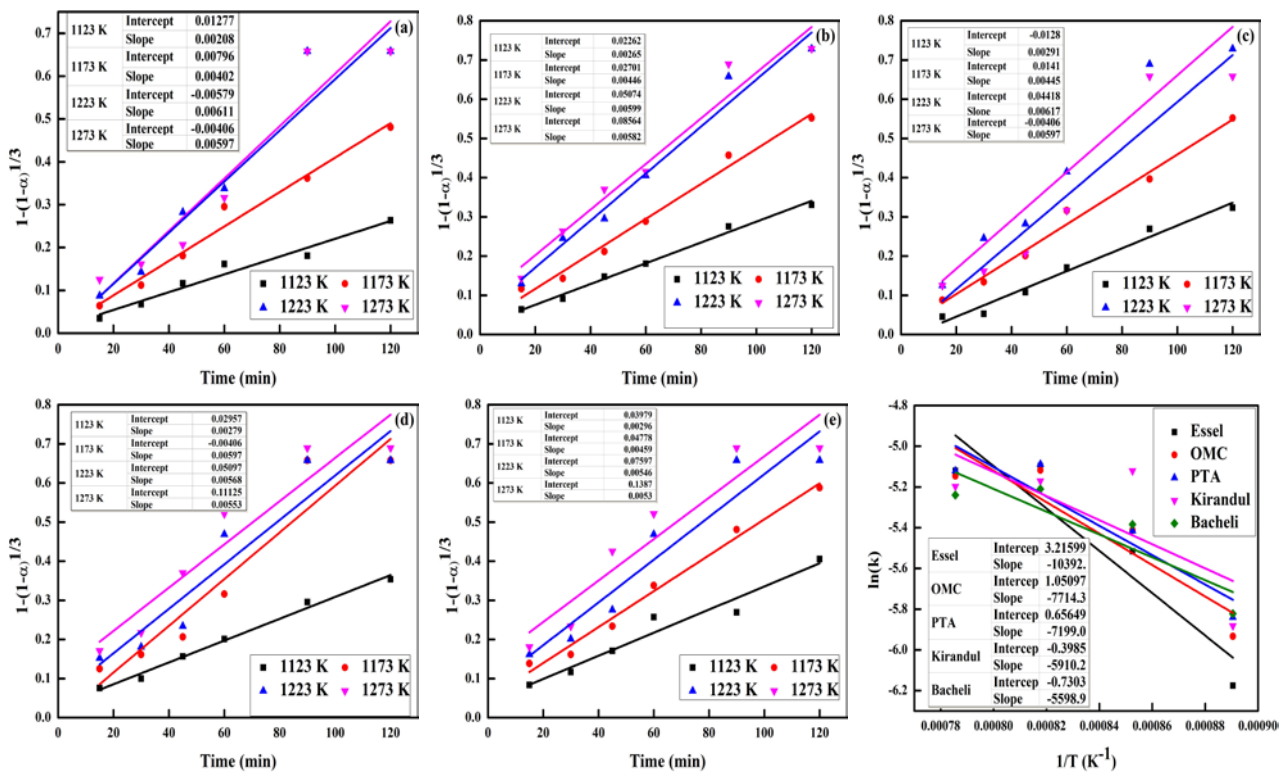
The kinetics of direct reduction process is complex and many models have been developed in this regard. Table 3 shows the different solid state kinetic equations used to study the kinetic reduction behavior. The kinetic models were examined by using experimental data. It was found that the experimental data would fit perfectly with the Mckewan interface chemical reaction  $(1-(1-\alpha)^{1/3} = kt)$ . The values of rate constant  $k$  at temperatures of 1123, 1173, 1223 and 1273 K were determined from the slope of respective lines.

**Table 3:** Solid state kinetic equations for reduction of iron oxide with carbon

S. No	Description	Kinetic Model Equations
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K.E 1	First order pseudo-homogeneous model[13]	$-\ln(1-\alpha) = Kt$
K.E 2	Mckewan interface chemical reaction[14]	$1-(1-\alpha)^{1/3} = Kt$
K.E 3	Three dimensional diffusion[14]	$(1-(1-\alpha)^{1/3})^2 = Kt$
K.E 4	one dimensional diffusion equation[14]	$\alpha^2 = Kt$

The slope values of different iron ore pellets at different temperatures were shown in Fig.5 (a-d). Based on the Arrhenius equation, activation energy for the reduction of iron ore pellets was calculated based on those results  $\ln(k)$  vs. reciprocal temperature ( $T^{-1}$ ) were plotted and same can be observed in Fig.5 (f). The activation energy was measured from slope of the Fig.and its results are tabulated in table 4. As can be seen from the figure, that the activation energy increases sharply which is indicated by a sharp change of slope. The reduction of Bacheli and Kirandul iron ore pellets were accompanied by lower activation energies (46.54 and 49.13 kJ mol<sup>-1</sup>) than OMC, PTA and Essel iron ore pellets. The difference in the activation energy values is due to the presence of gangue content. It was decreased with increase of gangue content and results are in good agreement with the reducibility values. Lower activation energy values indicates that the reduction of iron ore with non-coking coal was highly sensitive[2], and the relatively lower activation energies obtained in the present study with coal attributed to its higher reactivity.



**Fig.5**  $(1 - (1 - \alpha) / 3)$  vs. time at different temperatures for reduction of iron ore pellets a)Essel b) OMC b) PTA d) Kirandul e) Bacheli f)  $\ln(k)$  vs.  $1/T$  for different iron ores

**Table 4:** Activation energy values for different hematite iron ore pellet with coal at a temperature range of 1123-1273K

Iron ore	Essel	OMC	PTA	Kirandul	Bacheli
Activation energy (KJmol <sup>-1</sup> )	86.40	64.13	59.85	49.13	46.54

#### 4. Conclusions:

- The compressive strength of the fired pellets has increased with increasing temperature and porosity has decreased. At 1573 K highest compressive strength (>2500 N/pellet) with least porosity was achieved.
- Reduction temperature and time has pronounced effect on reduction behaviour of iron ore pellets. At temperature 1223, and 1273 K have exhibited high reduction % within 60 to 45 mins
- The reduction values decreased with increase of gangue content ( $Al_2O_3+SiO_2$ ).
- The Fe peaks were observed at all the temperature but at higher temperatures the Fe peaks were observed within 60 mins and it didn't follow the convention process  $Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$
- The activation energy values were calculated using Mckewan interface chemical reaction for different iron ore pellets which are in the range of 46.54 to 86.40  $kJ\ mol^{-1}$ . Bachel and Kirandul iron ore pellets have exhibited lower activation energies (46.54 and 49.13  $kJ\ mol^{-1}$ ) i.e., they are more sensitive to reduction process.

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