Chapter 5 Result and discussion of Reduction Studies and Smelting Reduction

5.1 Result and discussion of isothermal reduction

Important chemical constituents and stoichiometric calculated data of respective fractions are mentioned in Table 5.1. These data are required to calculate the degree of reduction. The chemical compositions of upgraded ore are mentioned in Table 3.17 and Table 3.18. Proximate analyses of coke and charcoal are reported in Table 3.6. The stoichiometric calculation is mentioned in section 4.2. Equations 4.2 to 4.6 were used to calculate of the degree of reduction and activation energy.

Table 5.1: Overall composition of composite briquette for reduction studies

Types	**Fe_2O_3 (pct)**	**Fixed Carbon (pct)**	**Ore required (gm)**	**Coke / charcoal required (gm)**	**Binder (gm)**	**Total**	**f_{coal}**	**f_{ore}**
AA	70.18	68.38	142.49	32.9	14.24	189.63	0.1735	0.7514
AB	70.18	75.37	142.49	29.85	14.24	186.58	0.1600	0.7637
BA	70.86	68.38	141.12	32.9	14.11	188.13	0.1749	0.7501
BB	70.86	75.37	141.12	29.85	14.11	185.08	0.1613	0.7625

5.1.1. Result of type-AA composite briquette

The overall composition of the type-AA composite briquette is shown in Table 5.1. Table 5.2 shows reduction data at different temperatures for composite briquette AA. Figures 5.1 to 5.3 show the reduction plots at different temperatures. Table 5.3 and Figure 5.4 show the activation energy value for composite briquette AA which was calculated from the rate of reduction at different temperatures.

Table 5.2: Reduction data for composite briquette - AA at different temperature

Holding time (s)	Initial weight (gm)W_i	Final weight (gm) W_f	Difference in weight ($W_i - W_f$) gm	Fractional weight loss, f_{wl}	Fraction of reduction, f	Average f
Temperature - 1223 K						
150	1.889	1.860	0.029	0.015	0.87	0.75
150	1.839	1.812	0.027	0.015	0.63	
300	1.841	1.790	0.051	0.028	5.33	6.30
300	1.846	1.785	0.061	0.033	7.26	
450	1.802	1.727	0.075	0.042	10.36	11.55
450	1.805	1.718	0.087	0.048	12.73	
600	1.911	1.797	0.114	0.060	16.87	16.07
600	1.830	1.729	0.101	0.055	15.26	
1200	1.890	1.770	0.120	0.063	18.26	19.39
1200	1.850	1.721	0.129	0.070	20.51	
Temperature - 1273 K						
150	1.629	1.470	0.159	0.098	30.58	33.76
150	1.380	1.221	0.159	0.115	36.94	
300	1.704	1.491	0.213	0.125	40.48	45.01
300	1.739	1.478	0.261	0.150	49.54	
450	1.597	1.338	0.259	0.162	53.91	54.20
450	1.709	1.429	0.280	0.164	54.50	
600	1.687	1.395	0.292	0.173	57.85	58.16
600	1.653	1.364	0.289	0.175	58.48	
1200	1.730	1.392	0.338	0.195	65.90	62.47
1200	1.661	1.368	0.293	0.176	59.04	
Temperature - 1323 K						
150	1.677	1.331	0.346	0.206	69.85	58.28
150	1.680	1.441	0.239	0.142	46.71	
300	1.521	1.264	0.257	0.169	56.36	54.84
300	1.613	1.354	0.259	0.161	53.32	
450	1.722	1.415	0.307	0.178	59.72	60.70
450	1.693	1.382	0.311	0.184	61.68	
600	1.622	1.326	0.296	0.182	61.24	64.45
600	1.648	1.318	0.330	0.200	67.65	
1200	1.668	1.301	0.367	0.220	74.80	75.36
1200	1.685	1.309	0.376	0.223	75.93	

Calculation of degree of reduction (α):

According to Eq. 4.2,

$$\alpha = \left[\frac{4 \times \{f_{wl} - (f_{coal} \times f_{vm})\}}{7 \times \{f_{ore} \times \rho_{ore} \times f_O\}}\right] \times 100$$

For AA composite briquette at 150 s, 1223 K:

f_{wl} = 0.01535; f_{coal}= 0.1735; f_{vm} = 0.0746; f_{ore} = 0.7514; ρ_{ore} = 0.7018; f_O = 0.3

Sources of mentioned data are in Table 5.1, 3.17 and 3.18.

$$\alpha = \left[\frac{4 \times \{0.01535 - (0.1735 \times 0.0746)\}}{7 \times \{0.7514 \times 0.7018 \times 0.3\}}\right] \times 100$$

$$\alpha = \left[\frac{4 \times \{0.01535 - 0.01294\}}{7 \times \{0.1582\}}\right] \times 100$$

$$\alpha = \left[\frac{4 \times \{0.00241\}}{7 \times \{0.1582\}}\right] \times 100 = \mathbf{0.87}$$

Similarly, degree/fraction of reduction is calculated for isothermal and non isothermal studies.

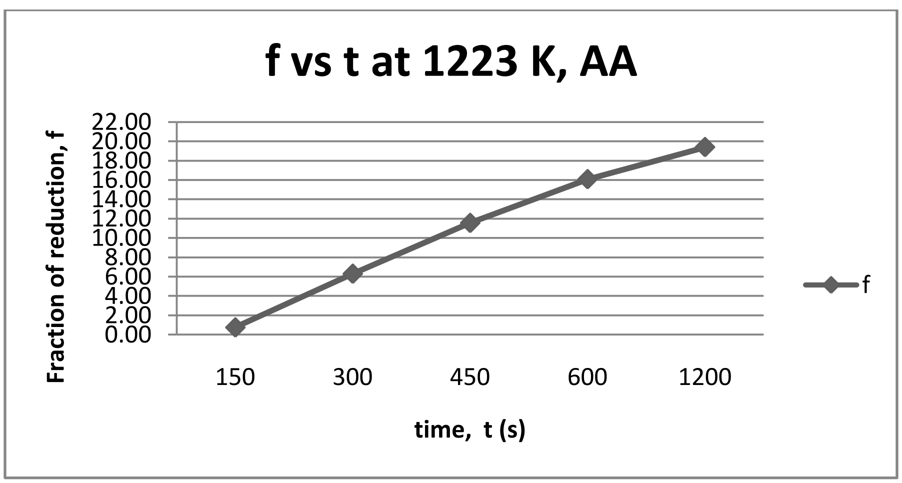


Figure 5.1: fraction of reduction *vs* time plot at 1223 K, AA

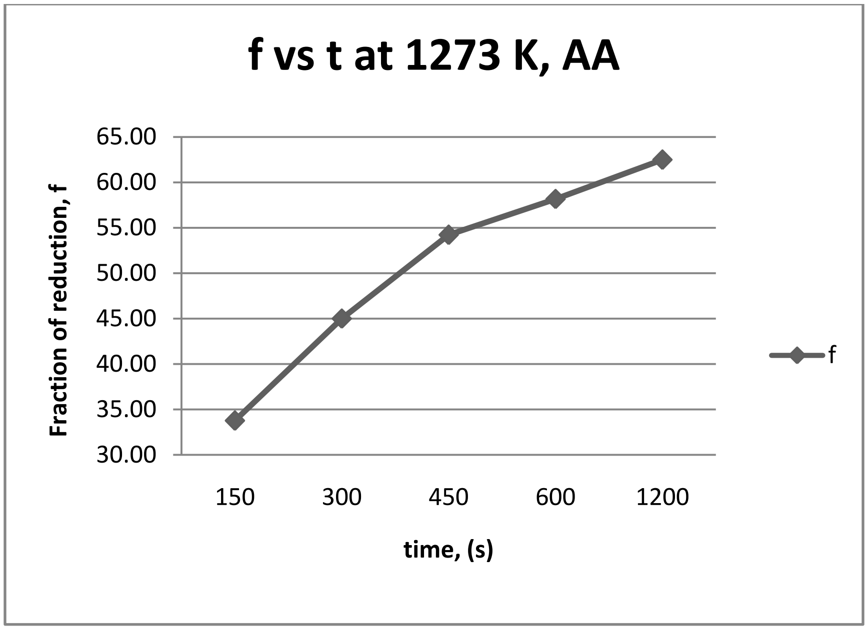


Figure 5.2: fraction of reduction vs time plot at 1273 K, AA

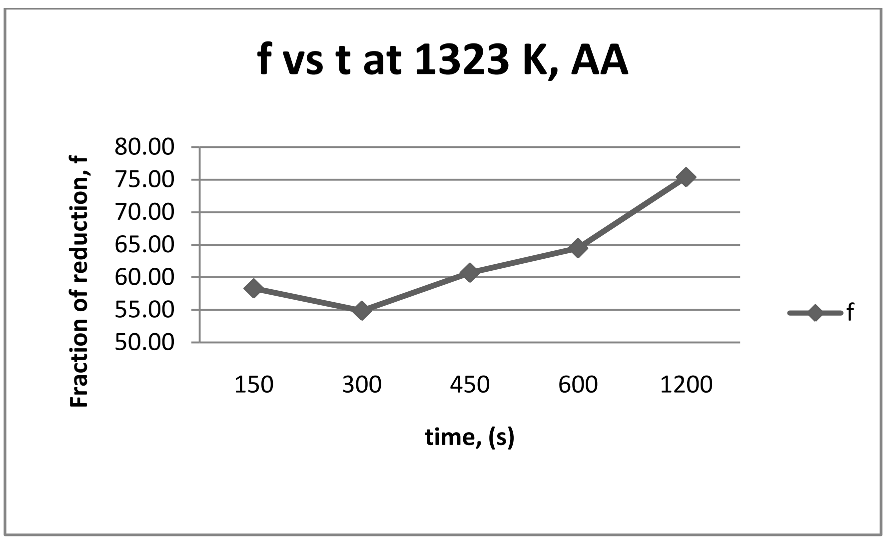


Figure 5.3: fraction of reduction vs time plot at 1323 K, AA

Table 5.3: Rate of reduction and activation energy for composite briquette - AA

Temperature T, K	**1/T**	**Rate of reduction, k**	**ln k**	**Activation energy (kJ/mol)**
1223	0.000818	0.030	-3.502	36.93
1273	0.000786	0.061	-2.791	
1323	0.000756	0.039	-3.242	

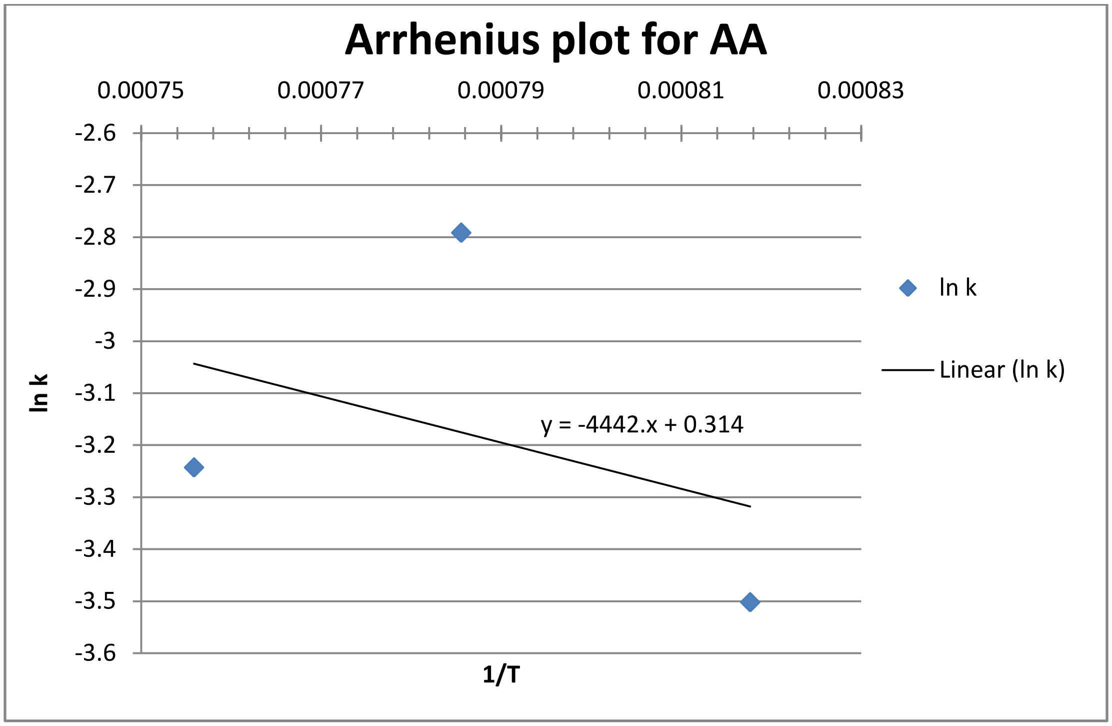


Figure 5.4: Arrhenius plot for Composite briquette AA

For AA composite briquette, a fraction of reduction value increases with an increase in temperature. The rate of reduction is observed maximum at 1273 K. Values of the rate of reduction are scattered on a graph. So, a linear line is drawn from the calculation of activation energy.

5.1.2 Result of type-AB composite briquette

The overall composition of type-AB composite briquette is shown in Table 5.1.

Table 5.4: Reduction data for composite briquette - AB at different temperature

Holding time (s)	**Initial weight (gm) W_i**	**Final weight (gm) W_f**	**Difference in weight $(W_i - W_f)$ gm**	**Fractional weight loss, f_{wl}**	**Fraction of reduction, f**	**Average f**
Temperature - 1223 K						
150	1.668	1.569	0.099	0.059	10.74	
150	1.638	1.521	0.117	0.071	15.03	12.88
300	1.579	1.383	0.196	0.124	33.76	33.31

300	1.587	1.394	0.193	0.122	32.87	
450	1.601	1.422	0.179	0.112	29.38	
450	1.602	1.383	0.219	0.137	38.23	33.80
600	1.709	1.410	0.299	0.175	51.82	
600	1.647	1.357	0.290	0.176	52.22	52.02
1200	1.729	1.365	0.364	0.211	64.46	
1200	1.589	1.260	0.329	0.207	63.23	63.85
Temperature - 1273 K						
150	2.686	2.501	0.185	0.069	14.12	14.12
300	2.828	2.401	0.427	0.151	43.31	43.31
450	2.734	2.276	0.458	0.168	49.18	49.18
600	2.826	2.407	0.419	0.148	42.34	42.34
1200	3.372	2.704	0.668	0.198	60.05	60.05
Temperature - 1323 K						
150	2.940	2.674	0.266	0.090	21.80	21.80
300	2.749	2.233	0.516	0.188	56.31	56.31
450	2.955	2.265	0.690	0.234	72.63	72.63
600	2.991	2.345	0.646	0.216	66.40	66.40
1200	2.736	2.019	0.717	0.262	82.78	82.78

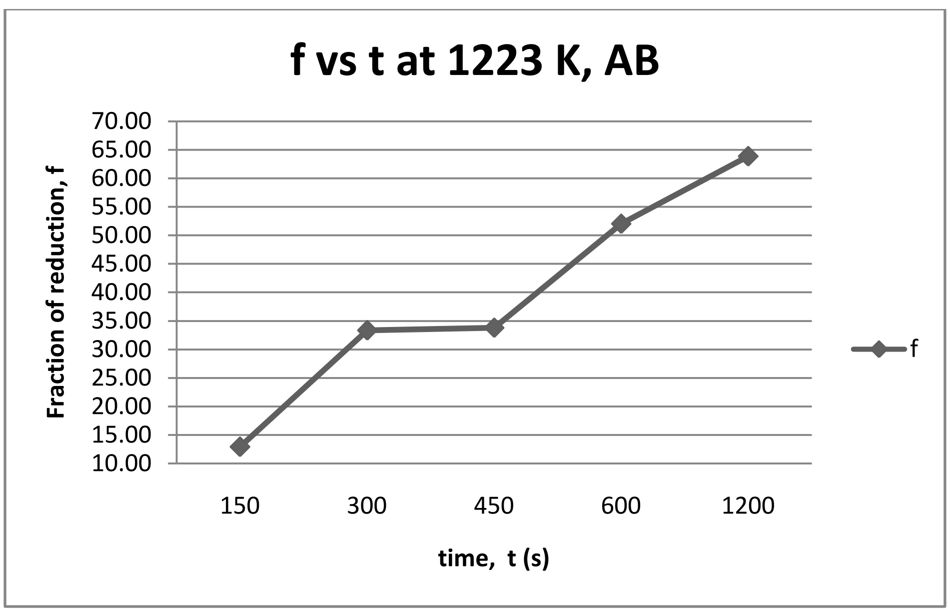


Figure 5.5: fraction of reduction vs time plot at 1223 K, AB

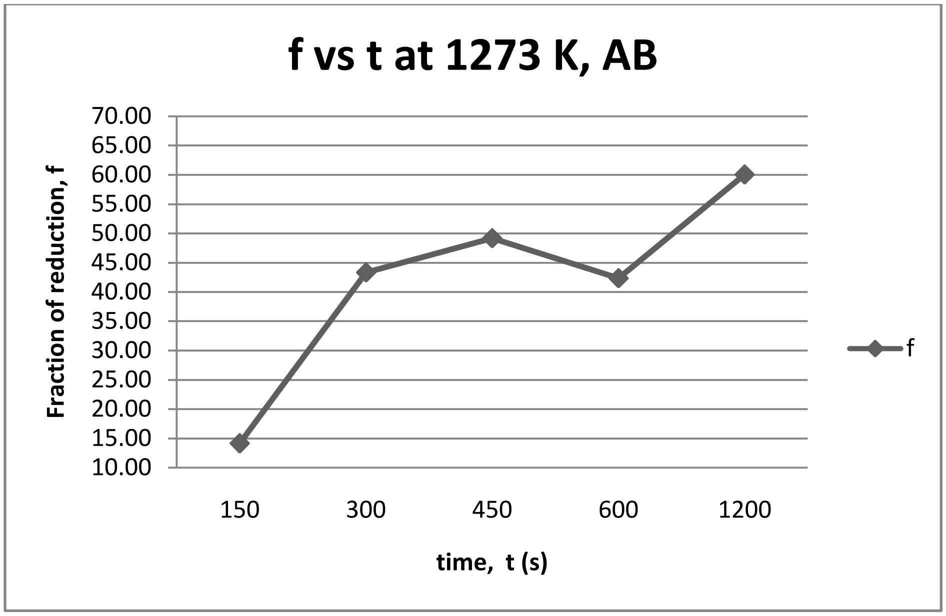


Figure 5.6: fraction of reduction vs time plot at 1273 K, AB

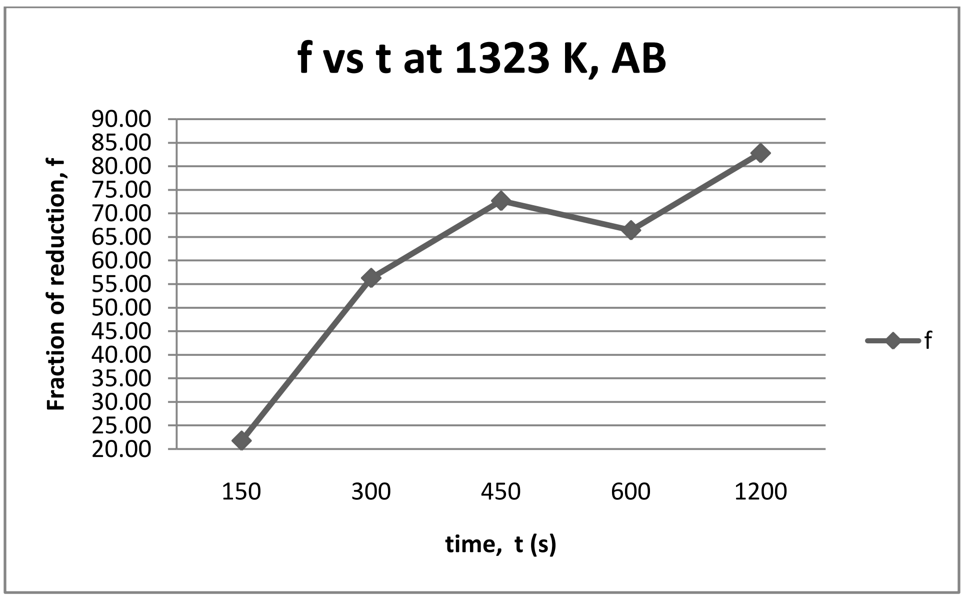


Figure 5.7: fraction of reduction vs time plot at 1323 K, AB

Table 5.5: Rate of reduction and activation energy for composite briquette - AB

Temperature T, K	1/T	Rate of reduction, k	ln k	Activation energy (kJ/mol)
1223	0.000818	0.121454	-2.10822	28.16
1273	0.000786	0.039164	-0.00323	
1323	0.000756	0.108766	-0.04151	

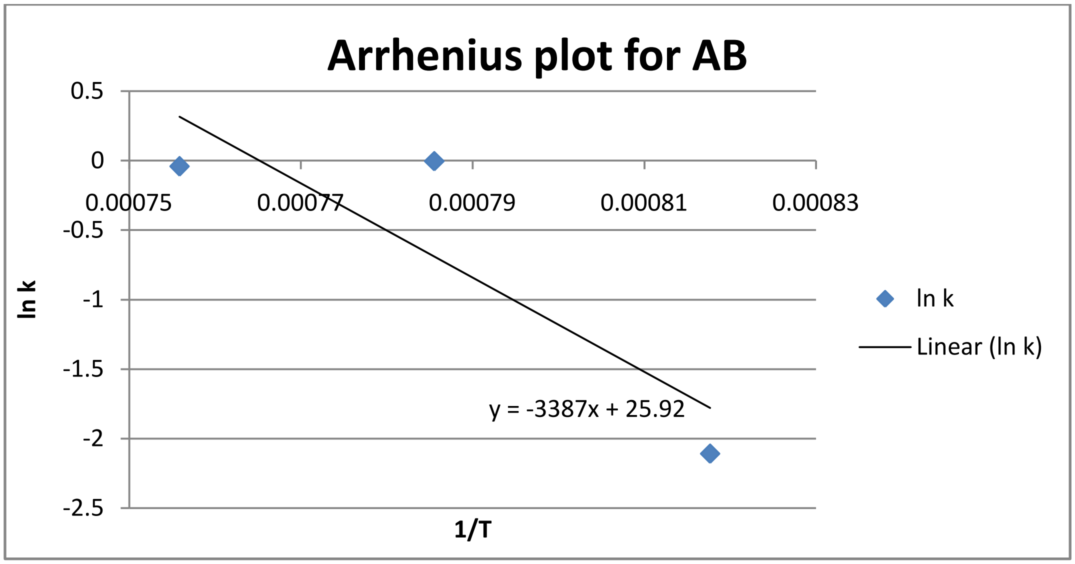


Figure 5.8: Arrhenius plot for Composite briquette AB

Table 5.4 shows reduction data at different temperatures for composite briquette AB. Figures 5.5 to 5.7 show reduction plots at different temperatures. Table 5.5 and Figure 5.8 show the activation energy value for composite briquette AB which was calculated from the rate of reduction at different temperatures. For 1273 K and 1323 K briquettes were powdered during the reduction study. So, Average of two briquettes was considered for reduction study calculation. In between of 300 to 600 s, a fraction of the reduction values are not linear due to liberation of volatile matters. AB Composite briquette has charcoal as raw material and has18.21 pct.

5.1.3 Result of type-BA composite briquette

The overall composition of type-BA composite briquette is shown in Table 5.1.

Table 5.6: Reduction data for composite briquette - BA at different temperature

Holding time (s)	**Initial weight (gm) W_i**	**Final weight (gm) W_f**	**Difference in weight ($W_i - W_f$) gm**	**Fractional weight loss, f_{wl}**	**Fraction of reduction, f**	**Average f**
Temperature - 1223 K						
150	1.632	1.495	0.137	0.084	25.41	24.46
150	1.615	1.488	0.127	0.079	23.50	
300	1.584	1.412	0.172	0.109	34.24	38.94
300	1.528	1.322	0.206	0.135	43.64	
450	1.602	1.388	0.214	0.134	43.20	44.58
450	1.592	1.367	0.225	0.141	45.97	
600	1.618	1.398	0.220	0.136	44.05	43.54
600	1.630	1.413	0.217	0.133	43.03	
1200	1.672	1.397	0.275	0.164	54.27	54.13
1200	1.570	1.313	0.257	0.164	53.99	
Temperature - 1273 K						
150	1.743	1.535	0.208	0.119	38.09	30.82
150	1.612	1.485	0.127	0.079	23.56	
300	1.579	1.338	0.241	0.153	50.02	49.63
300	1.575	1.338	0.237	0.150	49.25	
450	1.595	1.330	0.265	0.166	54.86	58.37
450	1.594	1.298	0.296	0.186	61.87	
600	1.649	1.320	0.329	0.200	66.82	62.39
600	1.665	1.374	0.291	0.175	57.96	
1200	1.551	1.215	0.336	0.217	72.96	73.38
1200	1.589	1.241	0.348	0.219	73.81	
Temperature - 1323 K						
150	1.663	1.421	0.242	0.146	47.47	46.22
150	1.826	1.573	0.253	0.139	44.98	
300	1.613	1.277	0.336	0.208	69.97	63.08
300	1.572	1.305	0.267	0.170	56.19	
450	1.584	1.289	0.295	0.186	62.06	66.03
450	1.598	1.265	0.333	0.208	70.00	
600	1.583	1.283	0.300	0.190	63.24	66.14
600	1.614	1.282	0.332	0.206	69.04	
1200	1.660	1.296	0.364	0.219	73.90	74.86
1200	1.554	1.205	0.349	0.225	75.81	

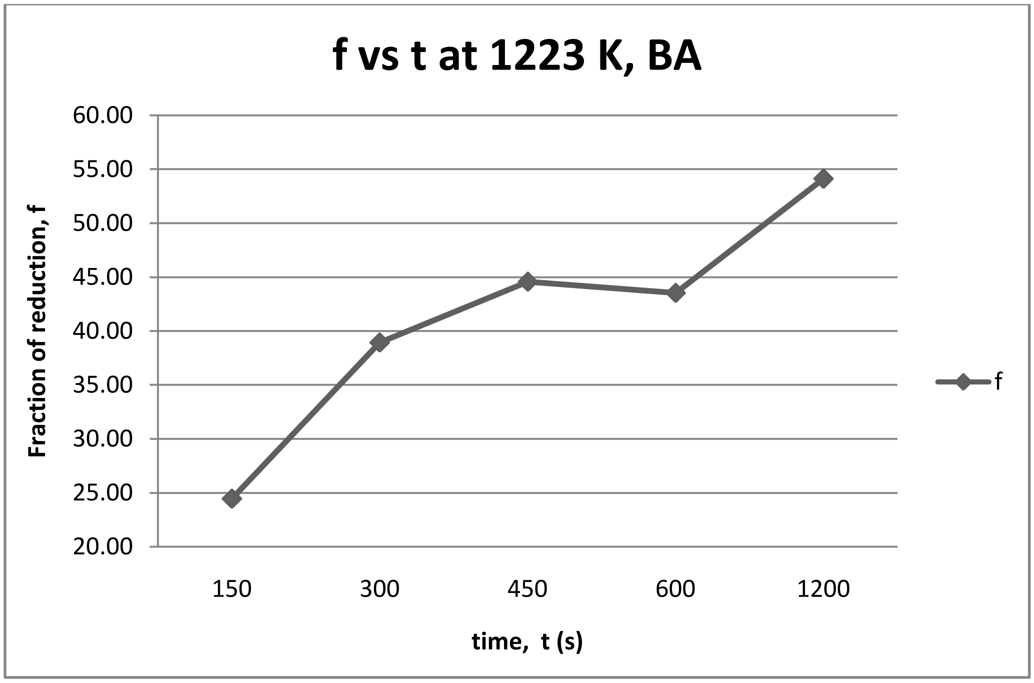


Figure 5.9: fraction of reduction vs time plot at 1223 K, BA

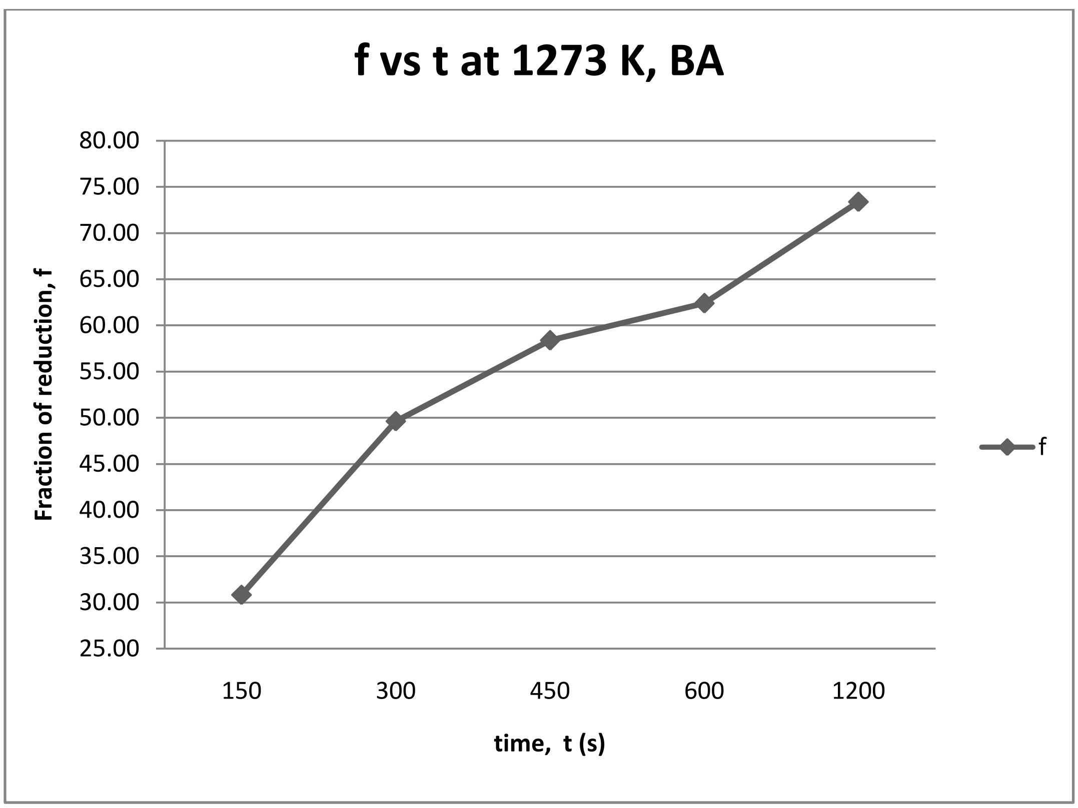


Figure 5.10: fraction of reduction vs time plot at 1273 K, BA

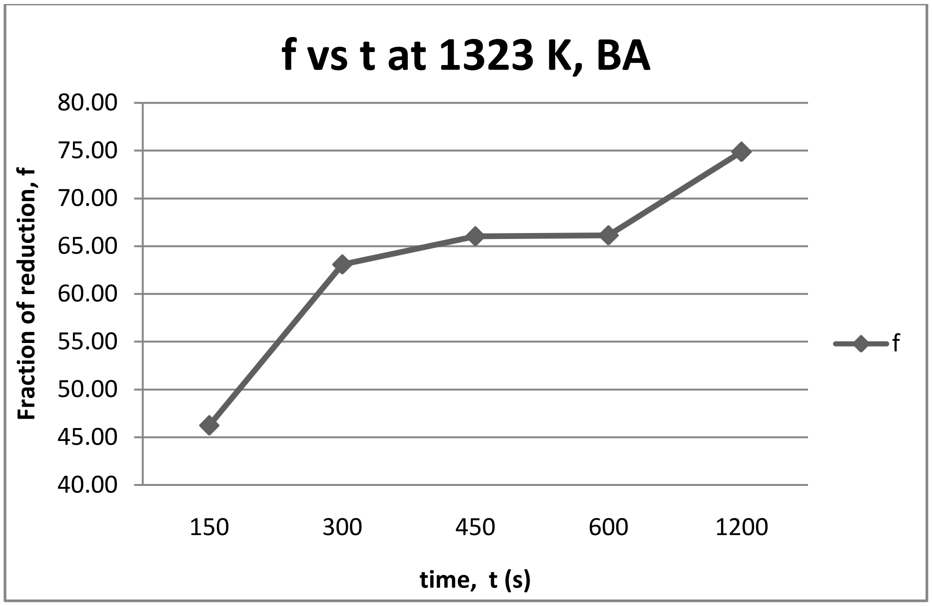


Figure 5.11: fraction of reduction vs time plot at 1323 K, BA

Table 5.7: Rate of reduction and activation energy for composite briquette - BA

Temperature T, K	1/T	Rate of reduction, k	ln k	Activation energy (kJ/mol)
1223	0.000818	0.037642	-3.27963	-84.58
1273	0.000786	0.058217	-2.84358	
1323	0.000756	0.019672	-3.92858	

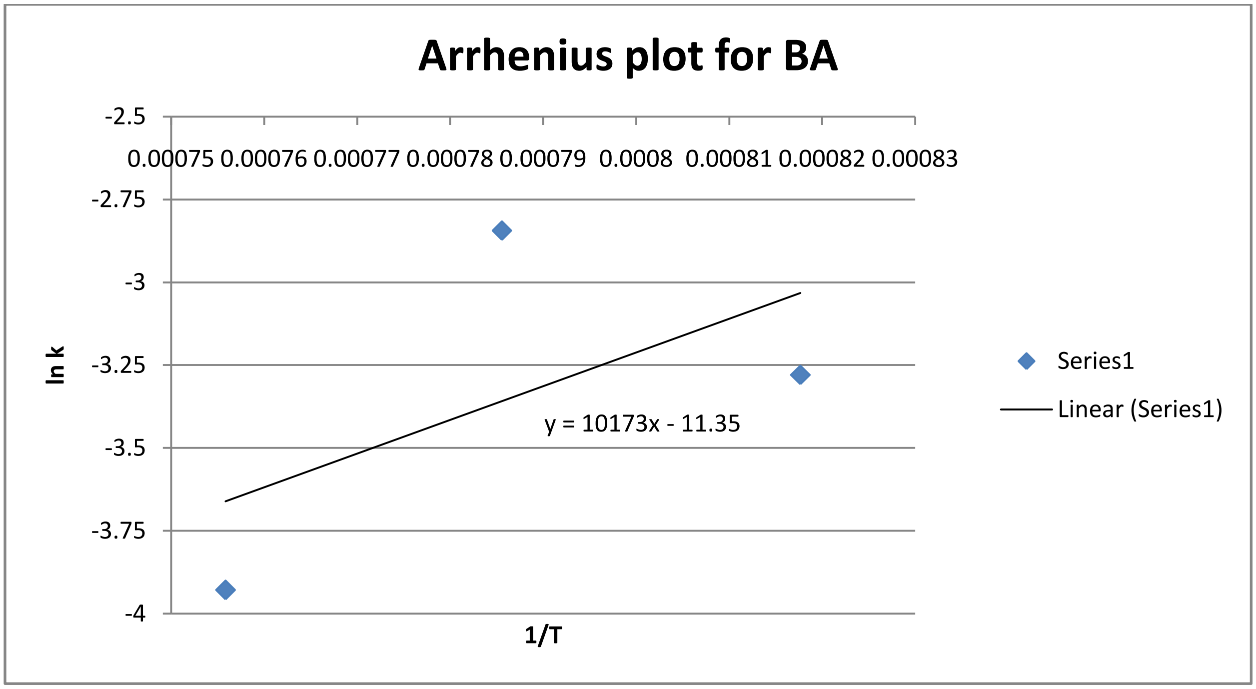


Figure 5.12: Arrhenius plot for Composite briquette BA

Table 5.6 shows reduction data at different temperature for composite briquette BA. Figures 5.9 to 5.11 show the reduction plots at different temperatures. Table 5.7 and Figure 5.12 show the activation energy value for composite briquette BA which was calculated from the rate of reduction at different temperatures. In between 300 to 600 s, briquette BA has a similar type of behavior which was observed in briquette AB.

5.1.4 Result of type-BB composite briquette

The overall composition of type-BB composite briquette is shown in Table 5.1.

Table 5.8: Reduction data for composite briquette - BB at different temperature

Holding time (s)	Initial weight (gm) W_i	Final weight (gm) W_f	Difference in weight $(W_i - W_f)$ gm	Fractional weight loss, f_{wl}	Fraction of reduction, f	Average f
Temperature - 1223 K						
150	1.749	1.507	0.242	0.138	38.42	
150	1.611	1.478	0.133	0.083	18.75	28.59
300	1.665	1.494	0.171	0.103	25.85	
300	1.721	1.541	0.180	0.105	26.52	26.18
450	1.775	1.524	0.251	0.141	39.50	
450	1.884	1.632	0.252	0.134	36.80	38.15
600	1.676	1.446	0.230	0.137	38.02	
600	1.732	1.478	0.254	0.147	41.34	39.68
1200	1.727	1.411	0.316	0.183	54.15	
1200	1.635	1.330	0.305	0.187	55.41	54.78
Temperature - 1273 K						
150	1.756	1.611	0.145	0.083	18.76	
150	1.780	1.584	0.196	0.110	28.46	23.61
300	1.755	1.493	0.262	0.149	42.27	
300	1.749	1.479	0.270	0.154	44.07	43.17
450	1.792	1.477	0.315	0.176	51.61	
450	1.823	1.512	0.311	0.171	49.79	50.70
600	1.679	1.384	0.295	0.176	51.59	
600	1.570	1.278	0.292	0.186	55.21	53.40
1200	1.582	1.263	0.319	0.202	60.73	
1200	1.709	1.353	0.356	0.208	63.08	61.91
Temperature - 1323 K						
150	1.686	1.464	0.222	0.132	36.06	
150	1.760	1.502	0.258	0.147	41.32	38.69
300	1.783	1.464	0.319	0.179	52.72	
300	1.730	1.417	0.313	0.181	53.43	53.07
450	1.629	1.286	0.343	0.211	63.87	
450	1.757	1.394	0.363	0.207	62.48	63.18
600	1.764	1.358	0.406	0.230	70.78	
600	1.570	1.338	0.232	0.148	41.74	56.26

1200	1.801	1.378	0.423	0.235	72.44	
1200	1.826	1.390	0.436	0.239	73.82	73.13

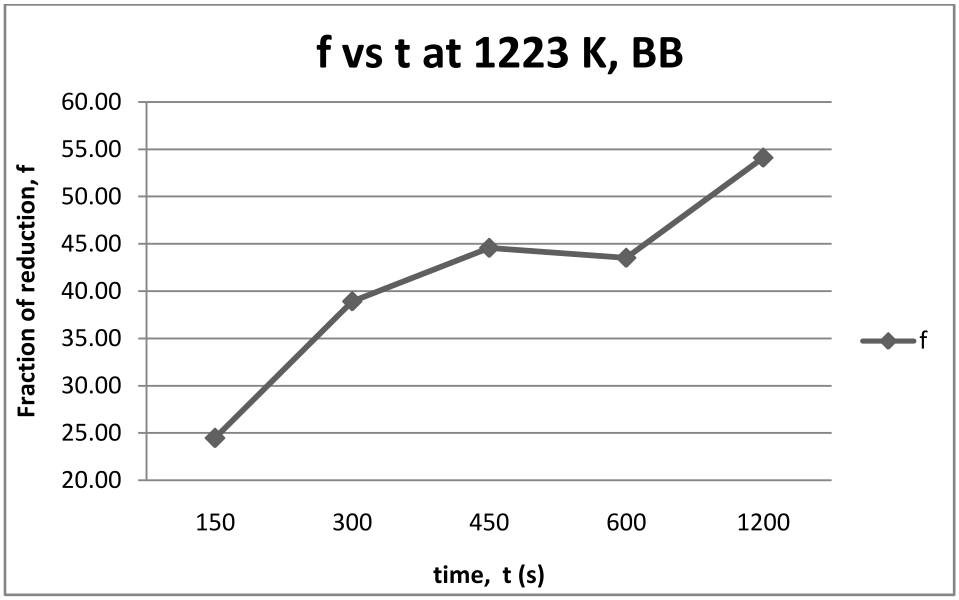


Figure 5.13: fraction of reduction vs time plot at 1223 K, BB

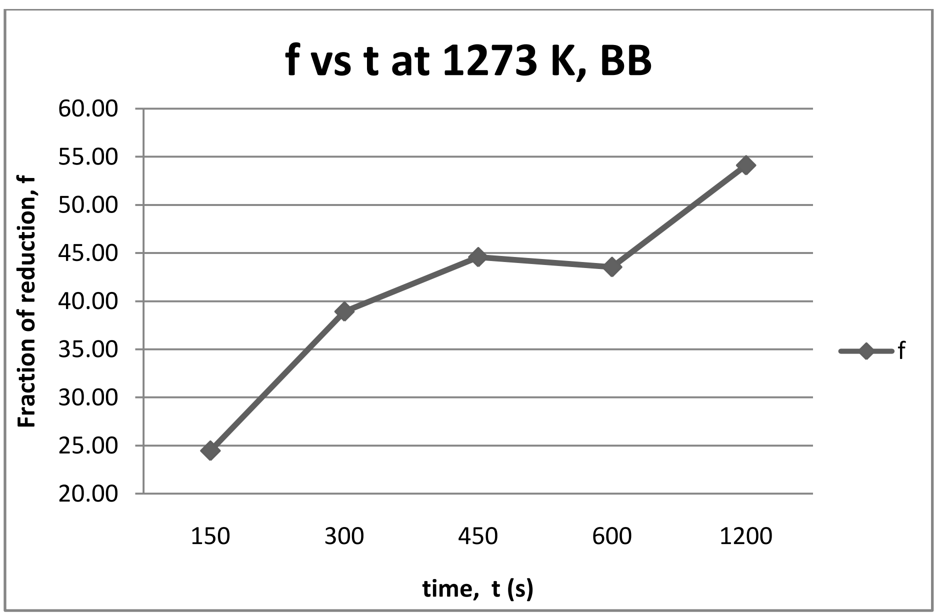


Figure 5.14: fraction of reduction vs time plot at 1273 K, BB

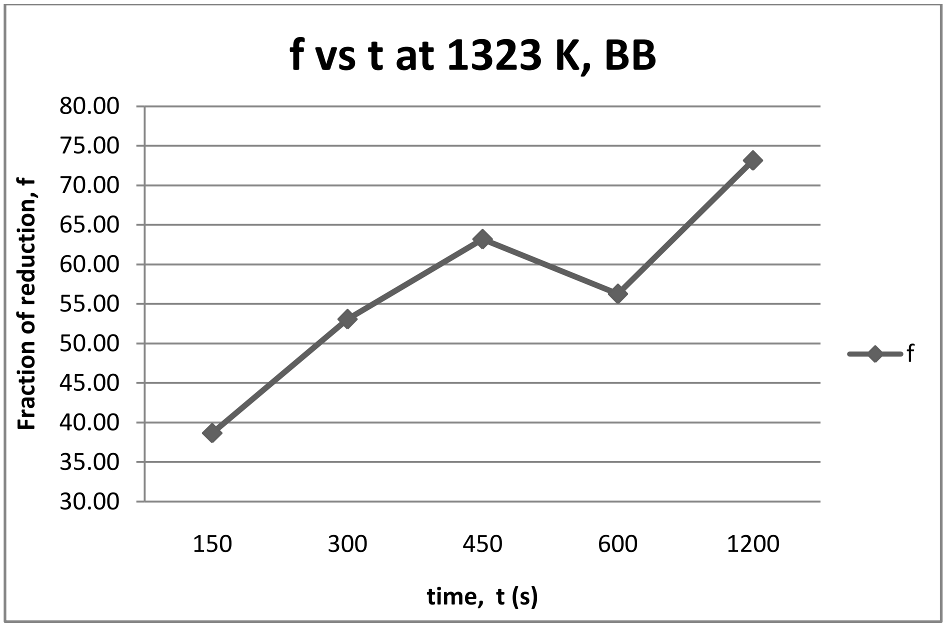


Figure 5.15: fraction of reduction vs time plot at 1323 K, BB

Table 5.9: Rate of reduction and activation energy for composite briquette - BB

Temperature T, K	1/T	Rate of reduction, k	ln k	Activation energy (kJ/mol)
1223	0.000818	0.079759	-2.52875	-24.04
1273	0.000786	0.050198	-2.99179	
1323	0.000756	0.067362	-2.69767	

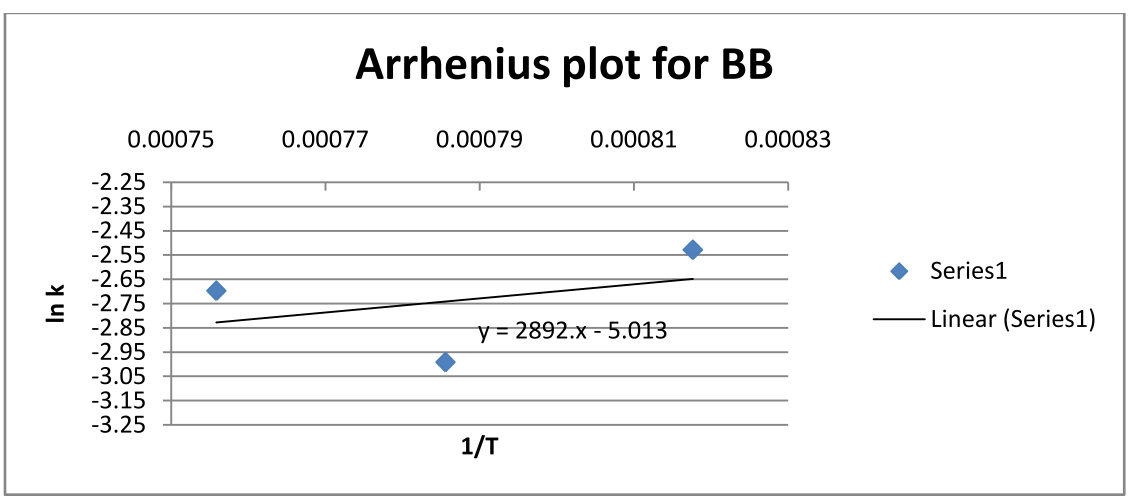


Figure 5.16: Arrhenius plot for Composite briquette BB

Table 5.8 shows reduction data at different temperatures for composite briquette BA. Figures 5.13 to 5.15 show the reduction plots at different temperatures. Table 5.9 and Figure 5.16 show the activation energy value for composite briquette BA which was calculated from the rate of reduction at different temperatures. From 300 to 600 s, a fraction of reduction is varied in all three temperatures due to volatile matters and gangue compounds present in ore.

Table 5.10: Activation energy of isothermal reduction of composite briquettes

Sr. No.	**Composite briquette**	**Activation Energy, kJ/mol**
1	AA	36.93
2	AB	28.16
3	BA	-84.58
4	BB	-24.04

Activation energies are calculated and found to be lower value (24 to 85 kJ/mol) due to the presence of volatile matters, gasification reactions, and metallization of iron by in situ carbothermic reduction. Overall reactions of the isothermal reduction process are controlled by following gasification reactions:

$C_{(s)} + CO_{2\,(g)} \rightarrow 2CO_{(g)}$ and $C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2\,(g)}$.

Similar results were found by the other research workers. Goswami et al [129] studied on fluxed composite pellets and obtained an activation energy of 60.75 kJ/mol. A mixed kinetic model is observed where reduction is initially diffusion controlled and later on by chemical reaction controlled.

Sarkar et al[2–4] studied isothermal reduction kinetics on cold bonded composite briquette of titaniferous magnetite ore with two different reductants - coke dust and lean grade coal. Lean grade coal took less time to reduce as compared to coke. Coal contains more than 25 pct volatile matter which liberates H_2 and CO gases during the reduction process. These gases take part in actively in reduction which results in the maximum yield value of iron. Out of the several gas–solid reaction mechanisms, a spherical mechanism used for activation energy was calculated as 59.52 KJ/mol for coke dust and 93.42 KJ/mol for lean grade coal.

Lyu et al[130] investigated the isothermal and non-isothermal reduction of iron ore by H_2 gas. They have observed that temperature plays a vital role in the reduction process for isothermal conditions. The activation energy was obtained from 27 to 93 kJ/mol. The rate-controlling step was gaseous diffusion and interfacial chemical reaction mixed control in the initial stages, and interfacial chemical reaction and solid diffusion in the final stages. In the non-isothermal reduction experiment, the heating rate significantly affected the reaction rate. The calculated activation energy was obtained 26 kJ/mol. The reaction mechanism for the non-isothermal kinetics of the reduction of iron ore fines includes mixed control, two-dimensional diffusion, and three-dimensional diffusion, depending on the stage of the reduction process.

Overall fraction of reduction (i.e. degree of reduction) values increase with time. The time dependent reduction curve shows three stages of reduction. The reduction at initial stage proceeds relatively slower (150-450 s), at intermediate stage much faster (450-600 s), and at final stage again become slower (600-1200 s). This is due to the incubation period at earlier stage. At intermediate stage gases (mainly hydrogen released from volatile matters in coal) diffuse through the porous solids and finally the fraction of reduction decreases due to the sintering and densification of product iron before melting.[59] El-Geassy et al.[108] observed that the diffusivity of hydrogen gas is about 4 times as fast as that of CO gas the reduction rate at inter mediate stage is faster than the final stage.

Initially, the reduction rate is very fast for all type of composite briquettes and later on the rate decreases with the time. This is due to release of volatiles at a time from the coal in the composite briquettes which causes rapid gas solid reactions. At higher temperature in densification of the product particles occur and has the rate of reduction decreases going to over diffusivity of gases and slower diffusion of carbon at final stage.[63], [108]

5.2 Phase identification of composite briquette by XRD

To identify final phases remained in reduced briquettes; characterized by XRD. All type of reduced briquettes is heated at 1323 K and 1200 s.

Composite briqeutte - AA:

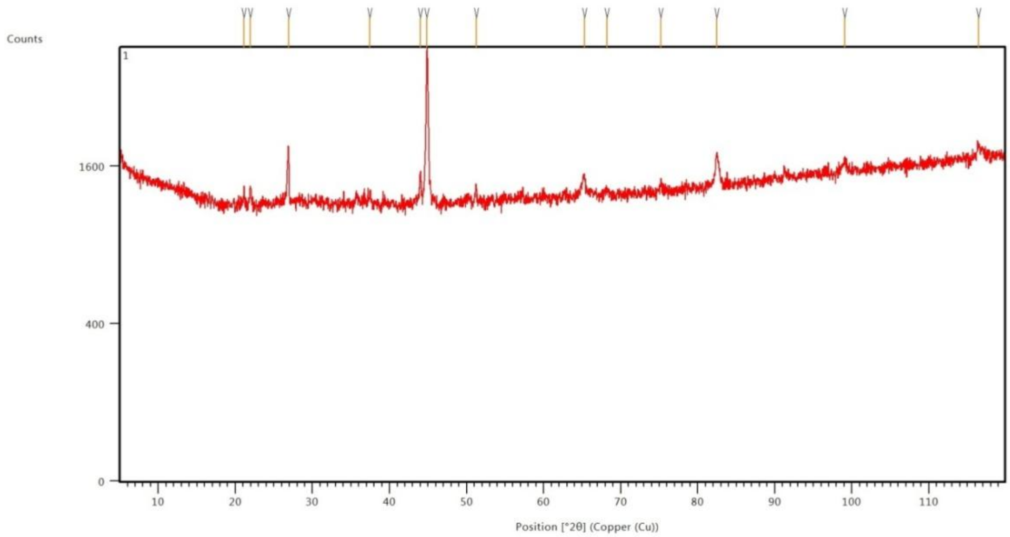


Figure 5.17: XRD graph of composite briqeutte AA

Table 5.11: XRD analysis of composite briquette AA

2θ	d spacing(Å)	I/I_0 (pct)	Phases present
21.1257	4.20556	5.10	Maghemite
21.9644	4.04684	9.44	Cristobalite, stable
26.8988	3.31463	28.58	Silica
37.4320	2.40259	4.86	Titanomaghemite
44.0089	2.05760	16.72	Pervoksite
44.8717	2.02001	100.00	Iron
51.2470	1.78269	8.85	Pervoksite
65.3315	1.42836	9.99	Iron
68.1897	1.37529	3.29	Silica
75.1942	1.26361	3.28	Pervoksite
82.4395	1.16995	17.25	Iron
99.0533	1.01345	5.52	Iron
116.4232	0.90699	7.51	Iron

Composite briqeutte - AB:

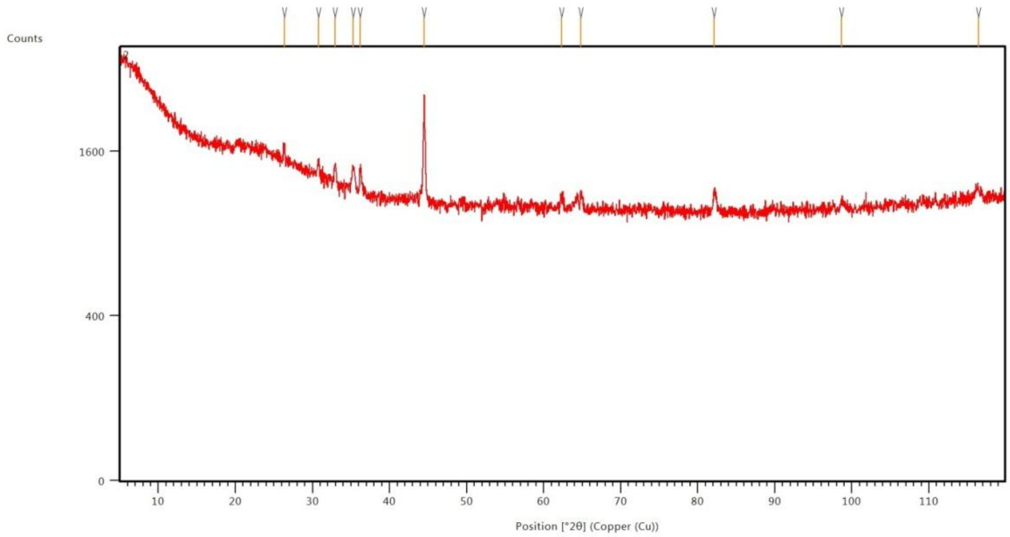


Figure 5.18: XRD plot of composite briquette AB

Table 5.12: XRD analysis of composite briquette AB

2θ	d spacing(Å)	I/I_0 (pct)	Phases present
26.3492	3.38250	9.10	Maghemite
30.7803	2.90492	11.32	Lime
32.9363	2.71952	16.63	Maghemite
35.2603	2.54543	21.30	Goethite
36.2143	2.48053	22.09	Cristobalite, stable
44.4921	2.03637	100.00	Iron
62.3655	1.48896	9.09	Goethite
64.8294	1.43820	14.02	Iron
82.1374	1.17349	15.61	Iron
98.6525	1.01649	5.79	Iron
116.4244	0.90698	7.36	Iron

Composite briqeutte - BA:

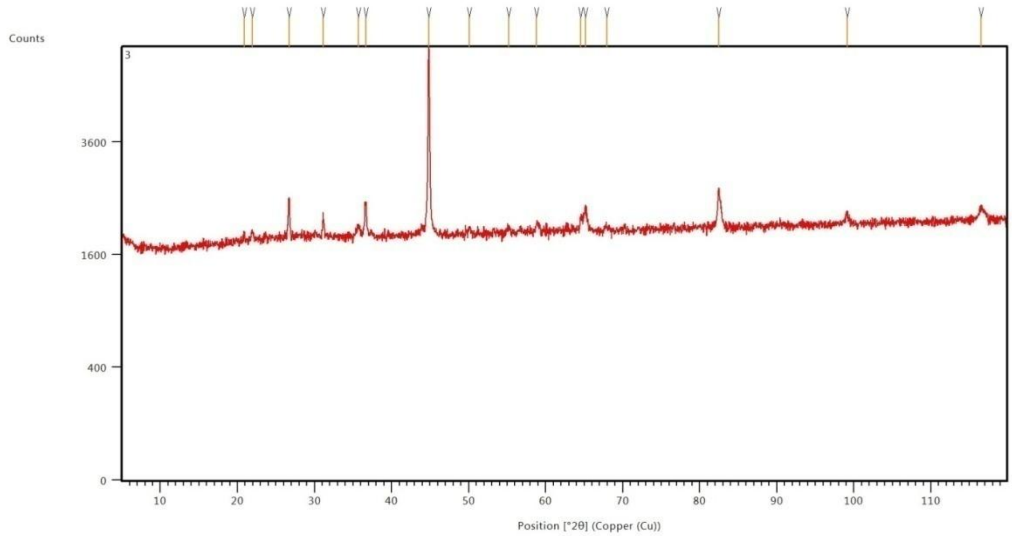


Figure 5.19: XRD plot of Composite briquette BA

Table 5.13: XRD analysis of composite briquette of BA

2θ	d spacing(Å)	I/I_0 (pct)	Phases present
20.8799	4.25451	2.76	Silica
21.9479	4.04984	3.35	Cristobalite, stable
26.7176	3.33669	13.99	Silica
31.1151	2.87442	9.38	Aluminium oxide
35.6753	2.51676	3.97	Hematite
36.6581	2.45151	14.41	Silica
44.8193	2.02225	100.00	Iron
50.0848	1.82130	2.19	Maghemite
55.1982	1.66408	2.29	Titanomaghemite
58.8407	1.56946	3.56	Titanomaghemite
64.5659	1.44343	5.01	Silica
65.1499	1.43190	9.70	Iron
67.9263	1.37998	1.68	Silica
82.4732	1.16956	16.67	Iron
99.1071	1.01304	4.44	Iron
116.4973	0.90662	4.69	Iron

Composite briqeutte - BB:

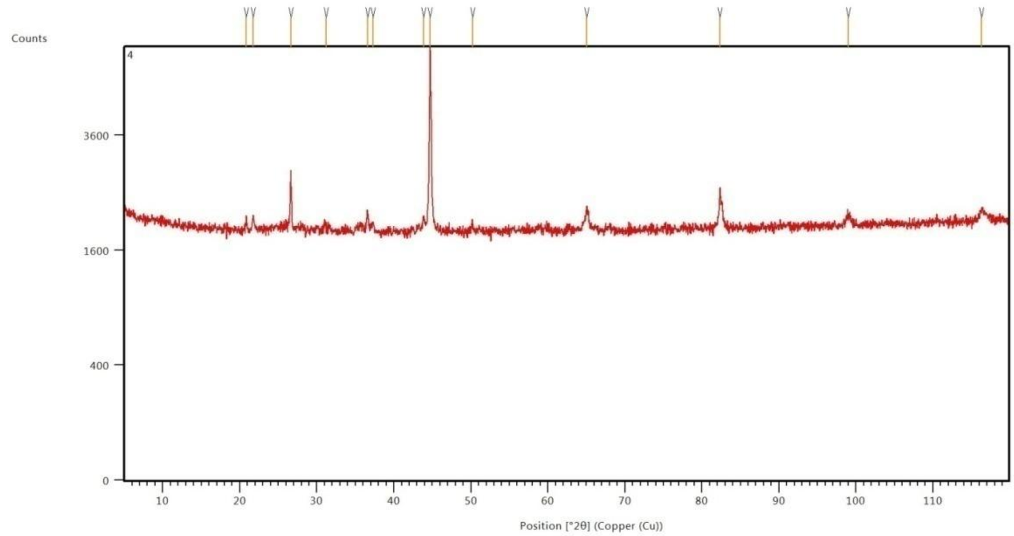


Figure 5.20: XRD plot of composite briquette BB

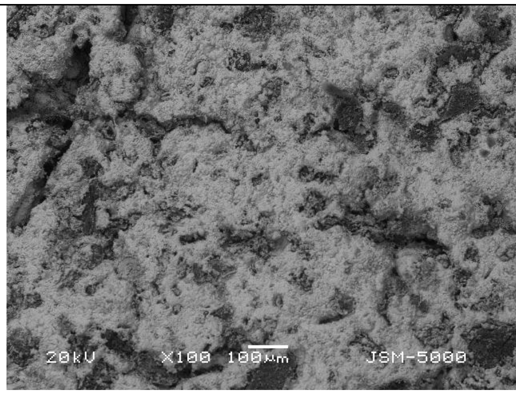
Table 5.14: XRD analysis of composite briquette BB

2θ	**d spacing(Å)**	**I/I_0 (pct)**	**Phases present**
20.8649	4.25753	4.32	Silica
21.7223	4.09138	5.04	Maghemite
26.6294	3.34754	25.40	Silica
31.1906	2.86763	1.90	Magnetite
36.5897	2.45594	7.34	Silica
37.2694	2.41270	2.78	Maghemite
43.8611	2.06418	5.74	Aluminium oxide
44.7005	2.02736	100.00	Iron
50.2290	1.81641	3.04	Maghemite
65.0274	1.43430	9.85	Iron
82.3623	1.17085	16.98	Iron
98.9964	1.01388	4.63	Iron
116.3178	0.90750	3.89	Iron

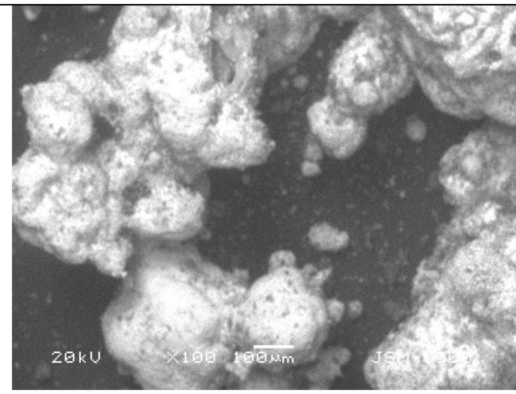
XRD analysis of reduced composite briquette, at 1200 s at 1323 K, was carried out for phase identification after reduction. In all briquettes, iron is identified as a major phase while silica and its forms - Cristobalite (*stable*) are identified as a second major phase. The presence of iron confirms the reduction process and topochemical pattern ($Fe_2O_3 \rightarrow$

Fe_3O_4 → FeO → Fe). Fe_2O_3 or Fe_3O_4 is also observed as minor phases. These are unreduced or partially transformed phases. In the AA composite briquette, pervoskite (*oxide of Ca and Si*) is also observed. This is formed as a slag phase during the reduction process.

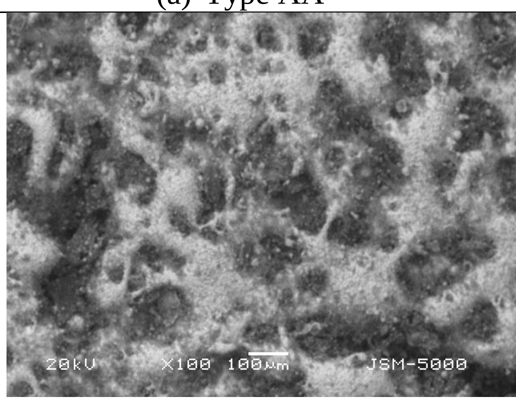
5.3 SEM analysis



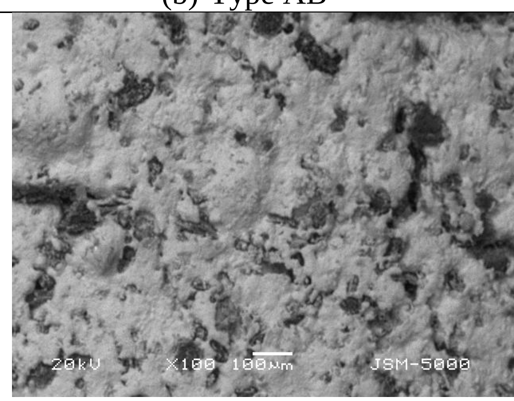
(a) Type AA



(b) Type AB



(c) Type BA



(d) Type BB

Reduction conditions- 1200 s at 1323 K

Figure 5.21: SEM images of reduced composite briquette

In a Figure 5.21, SEM images are shown for all four types of reduced composite briquette at 1323 K and 1200 s. In SEM images, white phases confirm freshly reduced iron while grey-coloured portions indicate slag phases or gangue phases like silica or alumina. All the SEM image is taken at 100X. So, the segregation of reduced iron is clearly shown in each type while the maximum segregation is formed as a lump in type AB reduced briquette. Except in AB type, all three have a uniform distribution of reduced iron which signifies effective reduction.

5.4 Non isothermal reduction studies of composite briquettes (TG-DTA)

The variables and procedures for non isothermal reduction studies for composite briquettes are similar to isothermal reduction studies. In section 5.1, detailed analysis and calculation are mentioned for isothermal studies. The degree of reduction is calculated by weight loss method and by using eq. 4.2. Weight loss and fraction of reduction are calculated from the TG-DTA curve and data (Figures 5.22 to 5.25). Testing parameters, results of TG and fraction of reduction of all four composite briquettes are mentioned in Table 5.15.

After 423 K, the fraction of reduction is increased due to the removal of moisture and release of primary volatile matters of charcoal or coke. AA and AB types have significant endoderm between 873 to 1073 K which indicates the release of coal volatiles and reduction of iron oxide by CO. BA and BB types have noticeable endoderm after 1273 K which indicates reduction reactions take place at higher temperature. So, a considerable amount of reduction occurs after 1273 K.

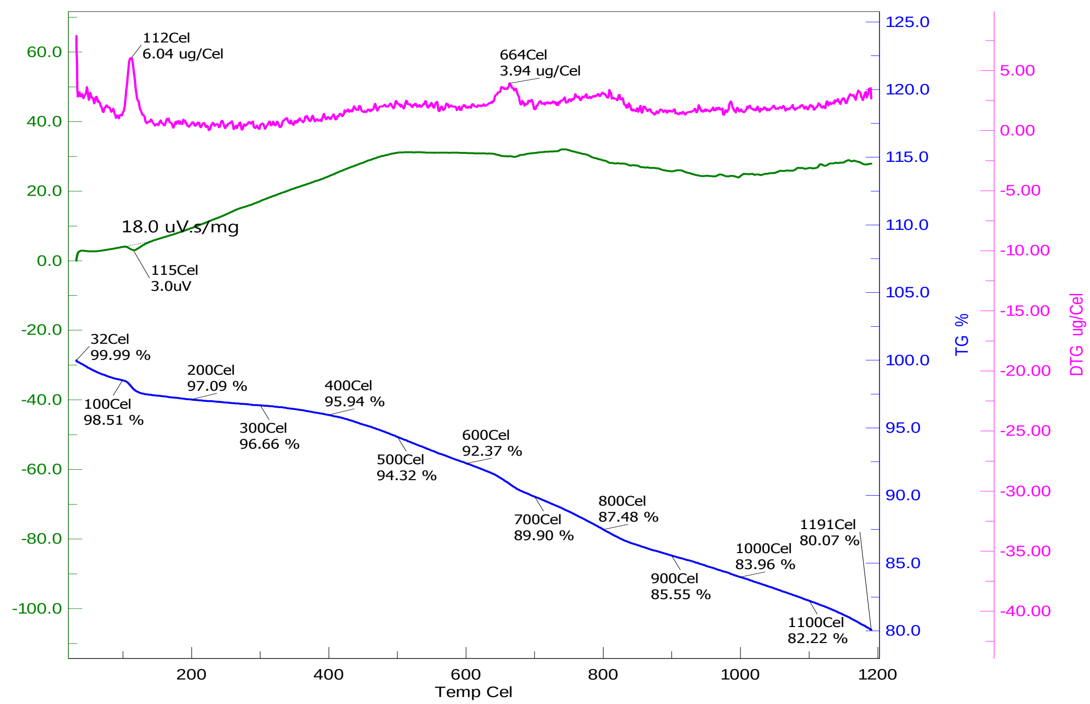


Figure 5.22: Simultaneous thermal analysis of AA composite briquette

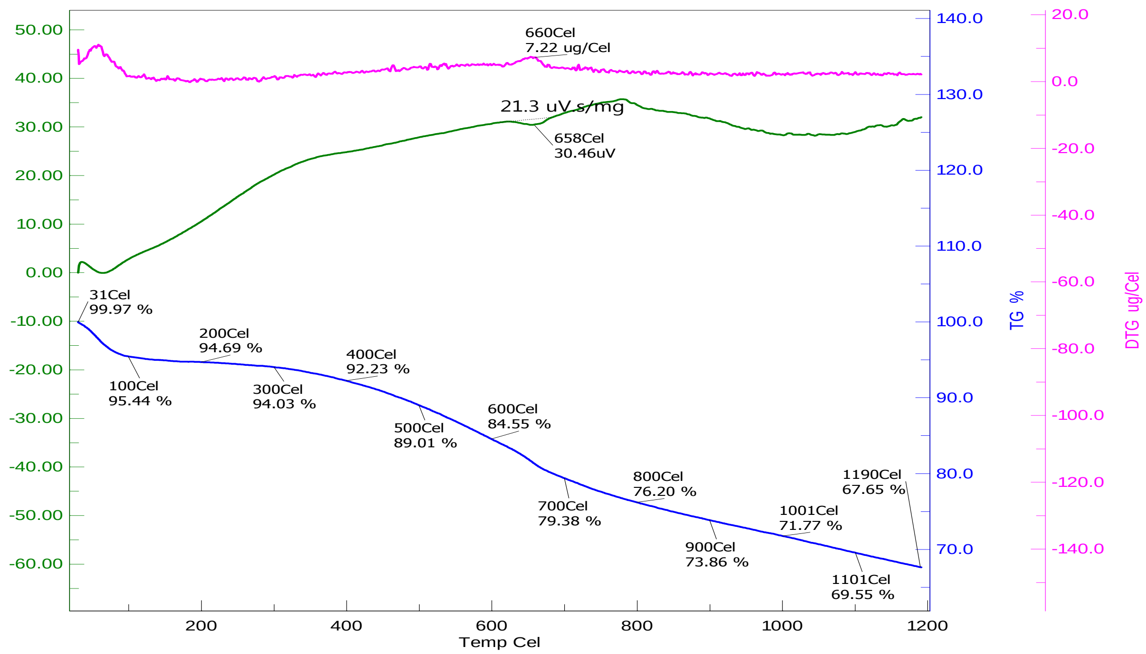


Figure 5.23: Simultaneous thermal analysis of AB composite briquette

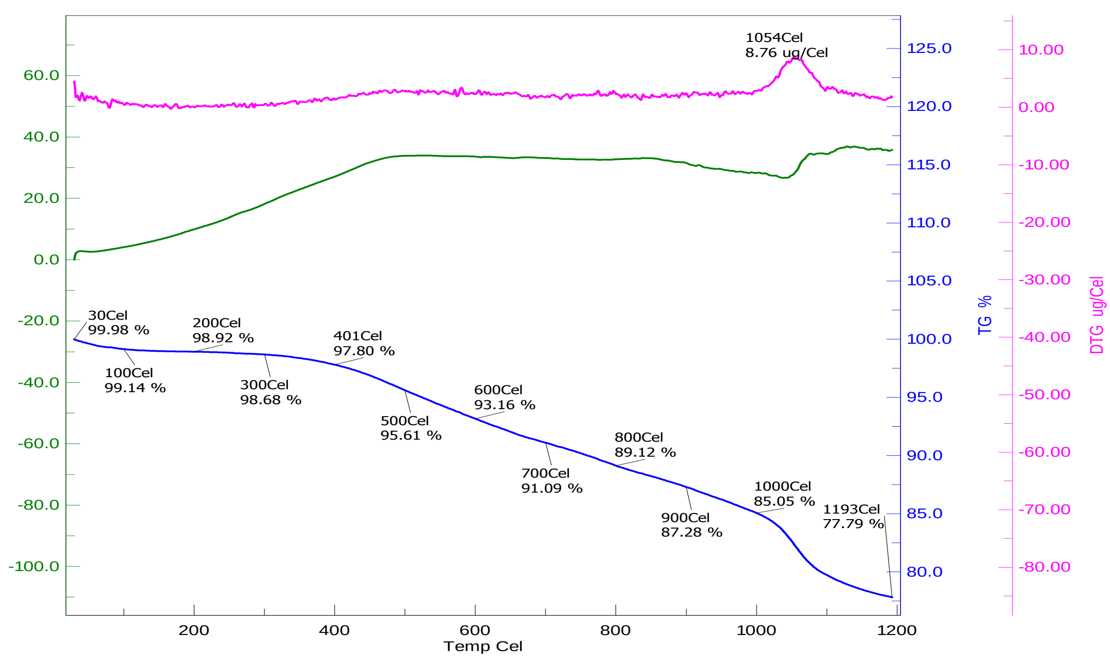


Figure 5.24: Simultaneous thermal analysis of BA composite briquette

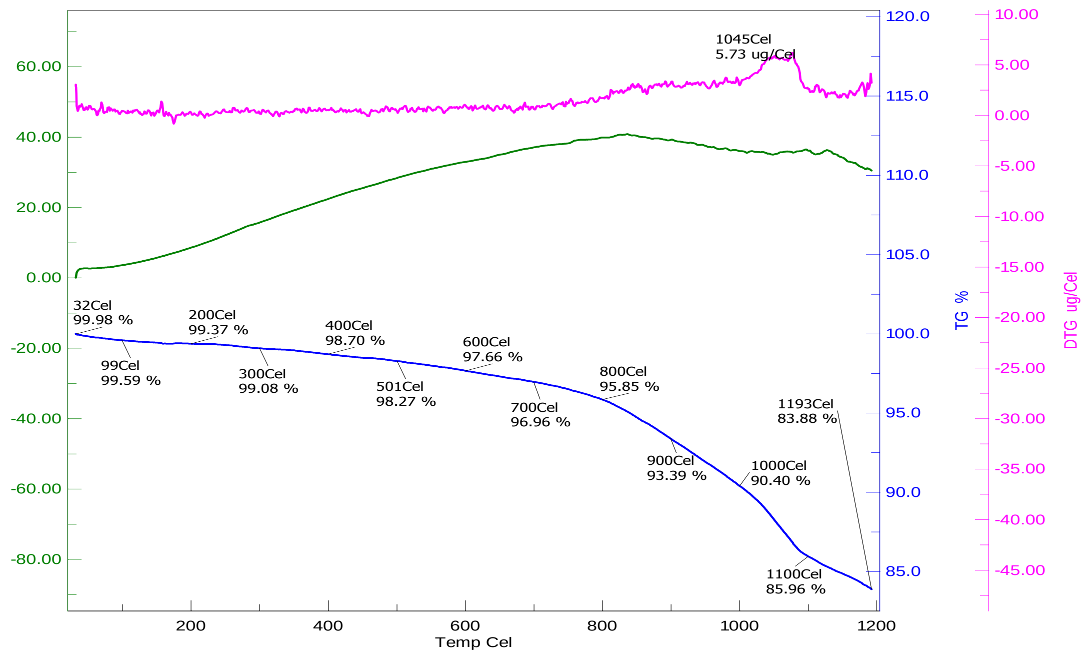


Figure 5.25: Simultaneous thermal analysis of BB composite briquette

Table 5.15: TG results for non-isothermal reduction of composite briquettes

Conditions:- Pan: Alumina Heating rate: 10 K/min ; Program temperature: 300 to 1473 K Atmosphere: Argon; Ar gas flow rate: 200 ml/min					
Time (t), s	**Temp. (T), K**	**TG value (µg)**	**Fractional wt. loss, f_{wl}**	**Fraction of reduction, f**	**Rate of reduction, k (s^{-1})**
AA Composite Briquette; *Initial weight – 10530 µg*					
0.5	305.2	10528.76	0.0001	-4.63	-9.26502
796	423.3	10253.46	0.0263	4.81	0.006044
1679.5	573.0	10178.42	0.0334	7.38	0.004397
3499.5	883.0	9707.783	0.0781	23.52	0.006724
4637	1073.1	9211.816	0.1252	40.54206	0.008743
5720.5	1253.0	8878.116	0.1569	51.98	0.009088
6440	1373.1	8657.63	0.1778	59.55	0.009247
6987.5	1463.9	8431.29	0.1993	67.31	0.009634
AB Composite Briquette; *Initial weight – 10520 µg*					
0.5	303.5	10517.68	0.0002	-10.27	-20.5528
803.5	423.0	9984.955	0.0509	7.72	0.009608
1681	573.1	9891.971	0.0597	10.86	0.006461
2556.5	723.0	9554.552	0.0918	22.26039	0.008707
3734.5	923.0	8616.086	0.1810	53.96	0.01445
5234	1173.1	7769.15	0.2615	82.57	0.015777
6438	1373.0	7318.519	0.3043	97.79	0.015191

BA Composite Briquette; *Initial weight – 10530 µg*					
0.5	302.8	10529.06	0.0001	-4.64	-9.28744
1678.5	573.1	0.0017	10421.97	0.0103	-0.99923
2548.5	723.0	10202.11	0.0311	6.48	0.002544
3434.5	873.0	9810.406	0.0683	19.81	0.005769
4623.5	1073.1	9384.212	0.1088	34.31	0.007423
5824.5	1273.1	8956.035	0.1495	48.89	0.008394
6424.5	1373.1	8395.478	0.2027	67.96	0.010579
6987.5	1466.2	8191.549	0.2221	74.90	0.01072
BB Composite Briquette; *Initial weight – 10530 µg*					
0.5	304.9	10539.12	0.0001	-10.32	-20.6507
1098	473.0	10473.46	0.0063	-8.12912	-0.0074
1971.5	623.1	10429.64	0.0105	-6.66368	-0.00338
2845.5	773.1	10357.95	0.0173	-4.26568	-0.0015
4024	973.0	10219.54	0.0304	0.36	9.04E-05
4619	1073.0	10102.03	0.0416	4.29	0.00093
5221	1173.0	9841.577	0.0663	13.00	0.002491
5824.5	1273.1	9528.637	0.0960	23.47	0.00403
6425.5	1373.0	9060.673	0.1404	39.12	0.006089
6987.5	1465.7	8841.444	0.1612	46.45	0.006649

Figure 5.26 shows Arrhenius plots for non-isothermal reduction. Data are so scattered that a graph cannot be drawn on an average linear line. There are two tendencies: i) initial stage and ii) later stage; hence activation energies are calculated in two stages. Results are shown in Tables 5.16 and Table 5.17.

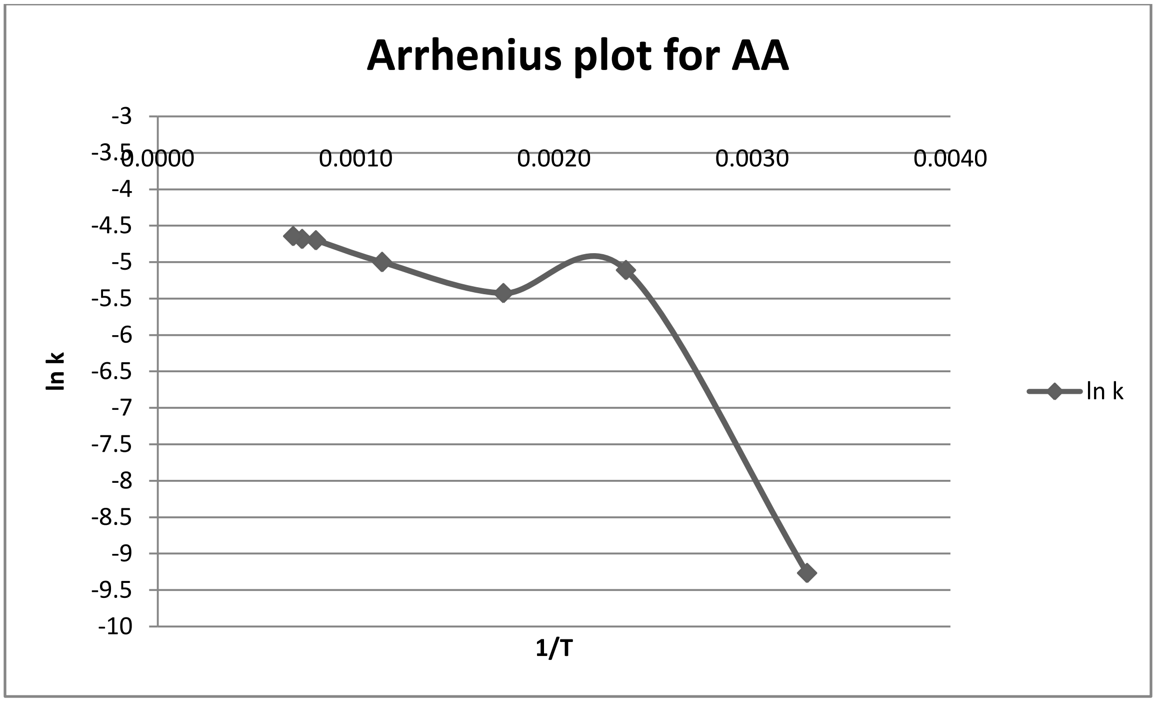


Figure 5.26: Arrhenius plot for non isothermal reduction - AA composite briquette

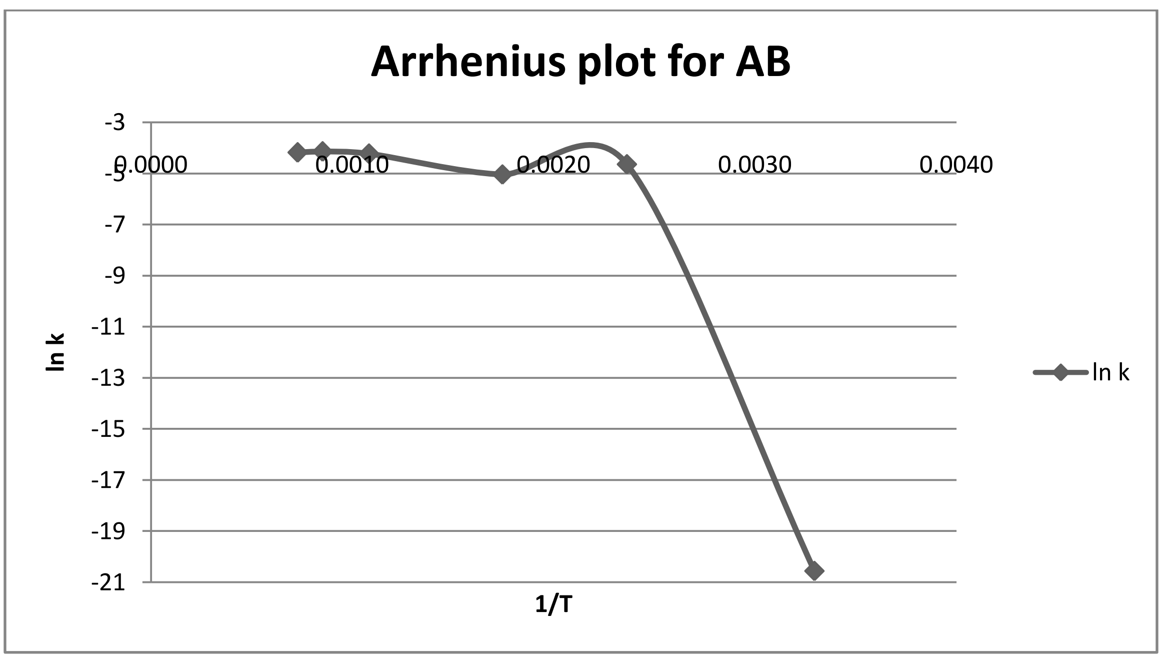


Figure 5.27: Arrhenius plot for non isothermal reduction - AB composite briquette

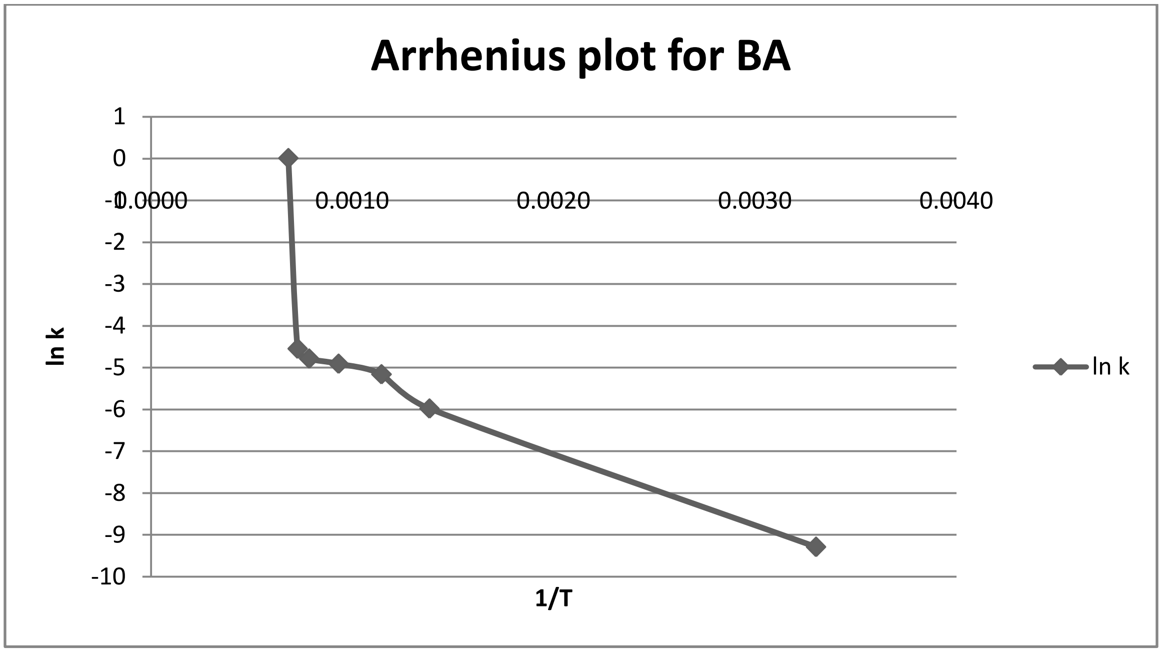


Figure 5.28: Arrhenius plot for non isothermal reduction - BA composite briquette

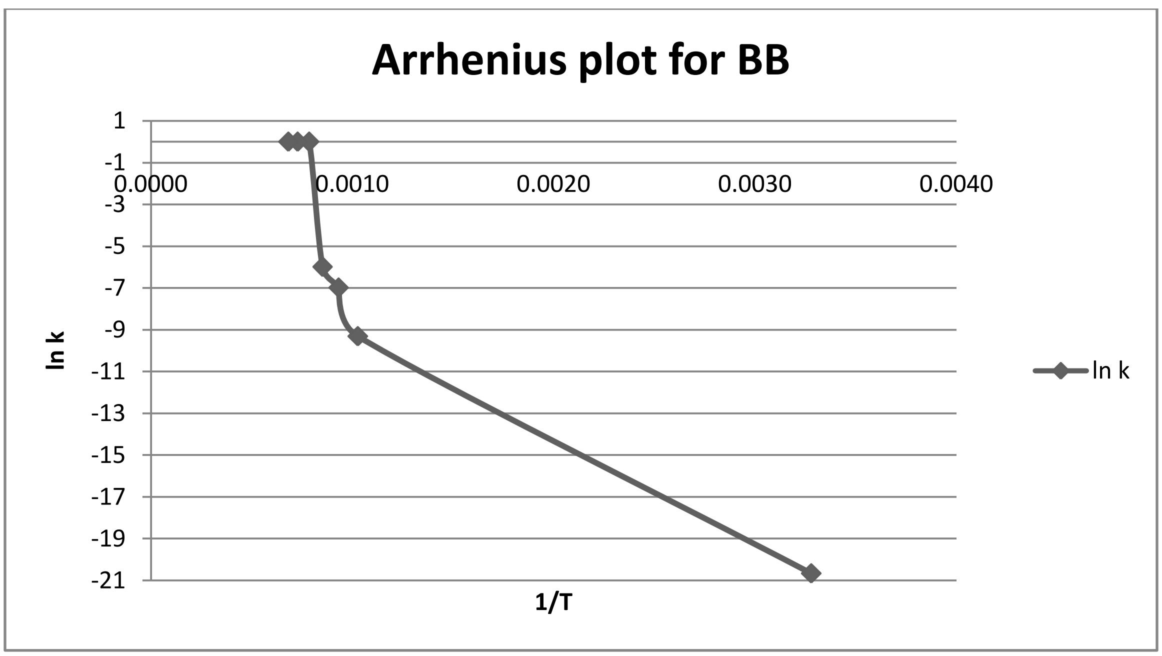


Figure 5.29: Arrhenius plot for non isothermal reduction - BB composite briquette

Table 5.16: Activation energy of non-isothermal reduction of composite briquettes

Sr. No.	Composite briquette	Activation Energy, kJ/mol	
		Initial Stage	Later Stage
1	AA	2.51	7.53
2	AB	6.85	10.11
3	BA	45.18	57.44
4	BB	56.6	103.12

Table 5.17: Comparison of activation energy by isothermal and non-isothermal studies

Sr. No.	Composite briquette	Activation Energy, kJ/mol		
		Isothermal reduction	Non-isothermal reduction	
			Initial Stage	Later Stage
1	AA	36.93	2.51	7.53
2	AB	28.16	6.85	10.11
3	BA	84.58	45.18	57.44
4	BB	24.04	56.6	103.12

Based on the fraction of reduction data, activation energy is calculated. Initial values of the fraction of reductions are negative. At low temperatures, there is the least possibility of moisture removal and release of volatiles. So in eq. 4.2, f_{wl} is less than of ($f_{coal} \times f_{vm}$). BA and BB briquette have major reduction takes place after 1273 K which is due to the dominant role of CO in the reduction process at higher temperature. Activation energies of non isothermal reduction are shown in Table 5.16. Activation energies are compared for isothermal and non isothermal studies. Activation energy values of isothermal reduction are higher than non isothermal reduction because of longer and constant heating time. BB composite briquette has achieved the highest activation energy in non isothermal reduction studies. Table 5.17 shows activation energy by isothermal and non isothermal studies. In non isothermal studies, the activation energy of initial stage has lower values than later stage.

Wang et. al [107] reported activation energy of 68.9 and 82.6 kJ/mol for iron ore-coal (low volatile and iron ore-coal (high volatile) pellets respectively. Dutta [105] found three stages of reduction reaction for iron ore-coal composite pellets at a low heating rate. Activation energy values increase with an increase in temperature. Values for stage 1 were 6.1 to 13 kJ/mol because of volatile substances diffused in iron ore particles. Values for stage 2 were obtained from 26.4 to 42.5 kJ/mol due to gas-solid reactions. Final stage 3 values were 183.1 to 268.5 kJ/mol due to carbon gasification reaction. Sah and Dutta [120] have calculated values of activation energy for iron ore-coal composite pellets are in the range of 0.86 to 8.82 kJ/mol for the initial stage of reduction and 12.37 to 38.32 kJ/mol for a later stage of reduction. The obtained activation energy values indicate that the reduction process is controlled by a gaseous diffusion mechanism. At a later stage, the activation value can be even higher value due to gas-solid reactions which is rate determining stage. A similar type of observation is found in the present study.

Jiang et. al [128] studied non-isothermal reduction studies of composite pellets. The overall activation energy of a reaction is obtained at 57.3 kJ/mol. They have observed that when temperature is lower than 1073 K, the reaction is controlled by interface chemical reaction; while the temperature is higher than 1173 K, the reaction is controlled by diffusion.

5.5 Result of Smelting Reduction

Smelting reduction of iron ore-coke/charcoal composite briquettes was carried out in a laboratory type induction furnace at Metallurgical and Materials Engineering Department, M. S. University of Baroda. The experiments were planned to investigate: i) the dissolution behaviour of composite briquettes in a molten bath and ii) the bulk dissolution of composite briquettes in a molten bath to produce steel and to measure the yield of iron. The yield of iron is calculated by equation 4.7. The calculation of iron yield is reported in Appendix 2.

Table 5.18: Chemical analysis of initial samples

Heat No.	C (pct)	Si (pct)	Mn (pct)	P (pct)	S (pct)	Cu (pct)	Fe (pct)
1	0.143	0.022	0.123	0.036	0.056	0.135	99.265
2	0.152	0.064	0.184	0.040	0.088	0.101	99.050
3	0.205	0.082	0.186	0.035	0.098	0.132	99.189
4	0.164	0.065	0.194	0.040	0.031	0.125	98.949
5	0.155	0.039	0.141	0.044	0.047	0.139	99.002
6	0.124	0.050	0.142	0.030	0.023	0.115	99.036
7	0.164	0.054	0.148	0.032	0.044	0.101	98.963
8	0.147	0.051	0.160	0.025	0.027	0.118	99.198
9	0.137	0.084	0.236	0.022	0.030	0.131	99.216
10	0.138	0.059	0.171	0.026	0.022	0.167	99.161
11	0.149	0.060	0.201	0.031	0.024	0.213	99.020
12	0.109	0.058	0.162	0.026	0.021	0.107	99.217
13	0.165	0.058	0.166	0.028	0.028	0.113	99.138
14	0.159	0.030	0.091	0.029	0.021	0.134	99.323
15	0.148	0.029	0.071	0.032	0.029	0.142	99.336
16	0.146	0.065	0.157	0.032	0.041	0.086	99.237
17	0.107	0.032	0.111	0.030	0.027	0.074	99.373

Table 5.19: Chemical analysis of final samples

Heat No.	C (pct)	Si (pct)	Mn (pct)	P (pct)	S (pct)	Cu (pct)	Fe (pct)
1	0.685	0.112	0.077	0.036	0.119	0.148	98.530
2	0.360	0.048	0.060	0.026	0.036	0.105	99.065
3	1.196	0.065	0.052	0.058	0.160	0.125	98.068
4	0.875	0.070	0.079	0.052	0.111	0.147	98.335
5	0.532	0.052	0.102	0.053	0.061	0.144	98.732
6	0.704	0.073	0.077	0.040	0.035	0.115	98.574
7	0.847	0.070	0.069	0.048	0.039	0.136	98.524
8	0.410	0.107	0.096	0.034	0.029	0.117	98.922
9	0.506	0.165	0.075	0.030	0.025	0.186	98.743
10	0.605	0.198	0.080	0.039	0.039	0.168	98.594
11	0.589	0.122	0.095	0.036	0.060	0.110	98.682
12	0.445	0.050	0.052	0.031	0.058	0.105	98.980
13	0.804	0.064	0.052	0.043	0.108	0.190	98.394
14	0.652	0.047	0.035	0.081	0.502	0.129	98.135
15	0.767	0.046	0.097	0.034	0.594	0.086	98.109
16	1.535	0.691	0.089	0.062	0.114	0.090	97.109
17	1.875	0.720	0.075	0.071	0.127	0.107	96.730

Table 5.20: Chemical analysis TMT steel rod

Analyte	C (pct)	Si (pct)	Mn (pct)	P (pct)	S (pct)	Cu (pct)	Fe (pct)
	0.19	0.207	0.7923	0.043	0.02	0.089	98.313

Tables 5.18 and 5.19 show chemical analyses of initial and final steel samples of smelting reduction studies. Table 5.20 shows a chemical analysis of the TMT steel rod which steel was used for stirring action. The chemical analysis of initial samples is uniform. Final samples have carbon in between of 0.4-0.8 pct. Carbon was picked up from the crucible in heats no. 3, 16 and 17 due to high smelting reduction time (65-70 min) in a furnace. So, Carbon is obtained about 1.8 pct. Table 5.21 shows an iron yield of steel samples with details weight of raw materials, cast steel and slag generated. Yield is obtained in the range of 90-95 pct. Due to the higher ash content in coke; a comparatively noticeable amount of slag is generated. Although a high amount of slag is generated in all 20 pct charges of all types of composite briquette. Slag volume was increased with an increase in the amount of composite briquette charged. Charging of bulk quantity of cold bonded composite briquette lowered down molten bath temperature. So, this briquette can act as a coolant in steel making.

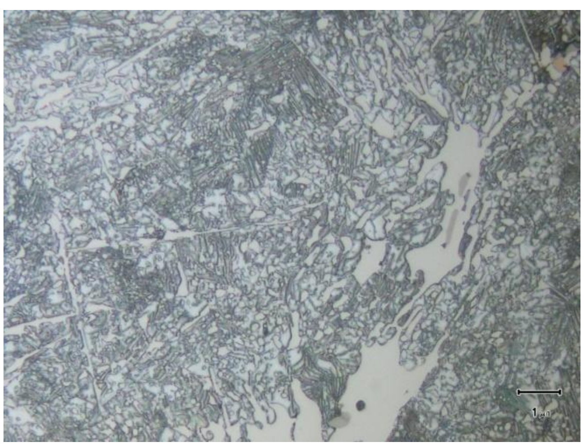
Table 5.21: Yield calculation of smelting reduction

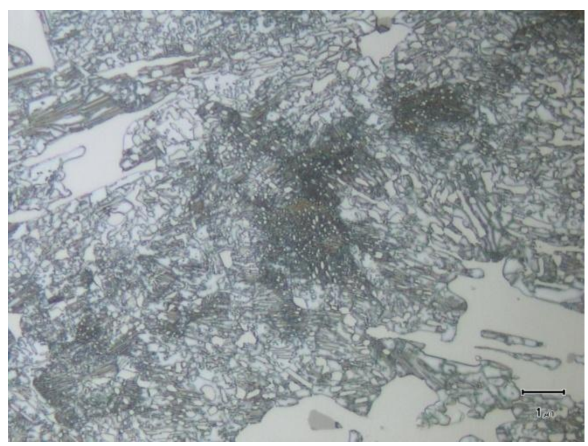
Heat No.	**Code (Briquette type and propotion)**	**Weight of scrap, W_1 (kg)**	**Weight of sample taken for analysis W_2 (kg)**	**Fe (pct) in scrap, F_1**	**Weight of composite briquette charged, W_3 (kg)**	**Weight of TMT rod dissolved during stirring briquette charged, W_4 (kg)**	**Weight of product W_5 (kg)**	**Fe (pct) in product F_6**	**Yield (pct)**	**Slag generated (kg)**
1	AA (90-10)	2.92	0.188	99.265	0.325	0.378	2.98	98.530	**91.65**	0.16
2	AA (95-05)	2.5	0.059	99.050	0.130	0.065	2.358	99.065	**92.34**	0.13
3	AA (90-10) R	2.45	0.032	99.189	0.270	0.155	2.447	98.068	**90.54**	0.155
4	AA (85-15)	2.385	0.074	98.949	0.421	0.227	2.444	98.335	**90.17**	0.295
16	AA (80-20)	1.395	0.12	99.237	0.349	0.151	1.496	97.109	**94.18**	0.286
11	BA (95-05)	2.493	0.128	99.020	0.131	0.025	2.327	98.682	**95.09**	0.14
12	BA (90-10)	2.44	0.085	99.217	0.271	0.066	2.362	98.980	**93.44**	0.27
13	BA (85-15)	2.383	0.133	99.138	0.425	0.203	2.452	98.394	**93.23**	0.337
15	BA (80-20)	1.394	0.069	99.336	0.349	0.102	1.489	98.109	**94.49**	0.261
5	BB (95-05)	2.49	0.041	99.002	0.130	0.045	2.374	98.732	**93.09**	0.15
6	BB (85-15)	2.44	0.05	99.036	0.270	0.085	2.372	98.574	**89.86**	0.28
7	BB (80-20)	2.38	0.045	98.963	0.421	0.334	2.63	98.524	**92.61**	0.36
17	BB (80-20)	1.393	0.071	99.373	0.348	0.336	1.738	96.730	**94.70**	0.272
8	AB (95-05)	2.45	0.046	99.198	0.129	0.034	2.364	98.922	**94.81**	0.14
9	AB (90-10)	2.439	0.063	99.216	0.271	0.052	2.292	98.743	**90.16**	0.191
10	AB (85-15)	2.382	0.06	99.161	0.415	0.028	2.39	98.594	**94.80**	0.248
14	AB (80-20)	1.393	0.076	99.323	0.348	0.143	1.506	98.135	**93.58**	0.245

5.6 Microstructure of steel product

Figure 5.30 shows the microstructure of a normalized steel samples. Heat 5 has a medium carbon steel which has been observed in most steel microstructure. The microstructure shows ferrite and pearlite. Carbides are also present in a structure. Heats 16 and 17 have high carbon content. So, the microstructure shows cementite and lamellar pearlite. In whitish region of the microstructure, primary cementite in coarse size and secondary cementite in fine size is observed while grayish to black portion is observed as pearlite. At higher magnification, lamellar colonies are revealed.

Heat 5, 200X





Heat 16, 1000X **Heat 17, 1000X**

Figure 5.30: Microstructure of steel structure

5.7 Hardness of steel structure

Normalized steel samples were tested on the Rockwell hardness B scale. The average of three tests is reported in Table 5.22. Hardness is increased with increase in carbon pct in steel. The highest hardness is observed in Heat 17 sample and the lowest in Heat 12.

Table 5.22: Hardness of steel

Heat No.	Hardness (HRB)		Heat No.	Hardness (HRB)
1	92		10	91
2	81		11	95
3	97		12	79
4	98		13	97
5	86		14	85
6	96		15	86
7	97		16	91
8	82		17	103
9	89			

Conclusion:

1. Isothermal reduction studies carried out at different temperatures - 1223, 1273, 1323 K and time – 150, 300, 450, 600, 1200 s.
2. It was observed that the degree of reduction increases with an increase in temperature.
3. In reduction studies, the presence of volatile matter and ash content affect critically on degree of reduction and activation energy.
4. An upgraded ore by charcoal type of composite briquettes (BA and BB) have shown better reduction behavior. Out of which composite briquette BA (iron ore roasted by charcoal + coke) have a better degree of reduction at 1323 K, activation energies of isothermal and non-isothermal reduction in general.
5. Based on activation energy values of the initial and later stages of non isothermal reduction studies, two stage reduction processes is observed in the present study.
6. Highest activation energy is obtained in BA composite briquette for isothermal reduction and BB composite briquette for non isothermal reduction.
7. Presence of high ash content in Coke is adversely affects reduction process.

8. Low amount of activation energies indicates reduction is controlled by gasification reactions.
9. From XRD, iron is observed as major phase and silica as second major phase.
10. SEM images revealed metalized iron in reduced briquette.
11. In smelting reduction studies, iron yield is achieved 90-95 pct which is quite significant at laboratory level.
12. In smelting reduction, highest recovery (93 to 95 pct) is achieved by BA (iron ore roasted by charcoal + coke) composite briquette among all types.
13. Although all four types of 20 pct charged composite briquettes have ~94 pct iron yield which signifies less impact of impurities at higher temperature in smelting reduction.
14. 25 mm diameter cold bonded composite briquette are dissolved and reduced with 45 sec in molten bath which is significant for direct use of ore as composite briquette in ironmaking / steel making.
15. Bulk quantity of composite briquette lowered down molten bath temperature which can be used as coolant and another source of iron and oxygen for steelmaking.
16. Composite briquette can be act as feed material in ironmaking / steelmaking.
17. Slag volume is higher in a higher proportion of composite briquette in steelmaking which is due to higher ash and gangue content in briquette.
18. 1.5 to 1.87 pct carbon in steel has cementite and pearlite phase while medium carbon steel has ferrite and pearlite in microstructure.
19. Hardness of normalized cast structure is measured in between 85 to 95 except few values.