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Effect of compaction on the kinetics of thermal decomposition of dolomite under non-isothermal condition

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Many workers [1–9] studied the kinetics of dolomite decomposition to study the effects of different parameters like, gas (CO_2, N_2 etc.) pressures, water vapor, presence of other impurities, particle size and grain size of the dolomite samples, crystallinity etc. on the decomposition kinetics of dolomite using different tools like, thermal analysis, thermo-gravimetric analyses, XRD technique etc. and different values of the activation energies for the decomposition reaction, order of reactions have been reported. It has been observed that pure dolomite decomposed in only two steps. The first stage of the thermal decomposition of dolomite resulted in the formation of Mg-calcite [$(CaMg)CO_3$] and periclase (MgO), with the liberation of CO_2. It was further observed that under CO_2, dolomite decomposed directly to $CaCO_3$, accompanied by the formation of MgO between 550 and 765°C. Calcite decomposed to CaO between 900 and 960°C and under air, simultaneous formation of $CaCO_3$, CaO and MgO accompanied dolomite decomposition between 700 and 740–750°C. At the latter temperature, the calcite began to decompose even though a significant amount of dolomite was still present and simultaneous decomposition of the two carbonates was terminated at 780°C. Also, changes in decomposition rates of the various phases correlated with changes in the rate of weight loss determined by derivative thermo-gravimetric analysis.

Again, It has been observed that in inert atmosphere the decomposition of natural dolomites take place via a single stage process. Study of the thermal behaviour and the kinetics of the decomposition process using the Arrhenious equation applied to solid state reaction revealed that dolomite decomposed via a zero order mechanism in inert atmosphere with an energy of activation of 175 kJ/mol. The kinetic parameters and mechanisms were observed to remain unaffected by a change in process variables like, flow rate, heating rate and sample size. It was further observed that besides differences in the chemical composition of samples, gaseous atmosphere and the method of calculation influenced the kinetic results obtained. Some authors proposed that the mechanism of the decomposition of dolomite in controlled atmosphere was via the formation of the two separate carbonates of magnesium and calcium. The particle size was found to affect the shape but not necessarily the position of the DTA curve for dolomite decomposition. Detailed results generated on the decomposition of dolomite confirmed that CO_2 pressure affected both the initial decomposition temperature into MgO and $CaCO_3$ and the final decomposition temperature of $CaCO_3$, but in opposite directions. This demonstrated the existence of different decomposition mechanisms.

In the present investigation kinetics of thermal decomposition under non-isothermal conditions of Indian dolomite was studied in relation to the compaction pressure from thermo-gravimetric data. The kinetic parameters, like order of the reaction, activation energy etc., were calculated and were correlated to the compaction pressure. The kinetic approach to the study of its thermal decomposition is important not only because of its economic utilization depend on the rate of these reactions, but also, kinetic studies give basic information about the inside of the mineral. Most of the studies on the kinetics of dolomite decomposition were made using isothermal models and not much work have been done on the use of dynamic, non-isothermal kinetic models to study the decomposition process, which is likely to be more practical approach.

The dolomite sample used in the present investigation was received in powder form with average particle size (d_{50}) of 12 μm. It was first chemically analyzed by conventional method and the analysis result is given in Table I. From the chemical analysis of dolomite it was

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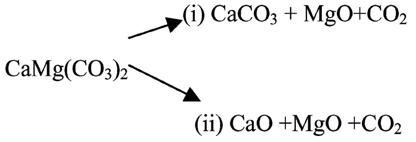
TABLE I Chemical composition of the dolomite

Constituent	Wt (%)
SiO_2	0.96
Al_2O_3	0.24
Fe_2O_3	0.34
K_2O	0.32
CaO	31.25
MgO	21.55
LOI	45.04

observed that the level of major impurity, i.e., SiO_2 and Fe_2O_3 is quite low here. The powder sample was compacted separately with pressures of 20, 30, 40 and 50 MPa respectively, with a hydraulic press in the form of circular disc (2.5 cm dia.) using starch as a binder. The thermo-gravimetric studies on the samples were made using a TG furnace. The heating rate of the furnace was maintained at 5°C/min up to a temperature of 1000°C.

From the TG values of the samples it was observed that the major weight loss of the material takes place in the temperature range 710–910°C and this might be subdivided in two different temperature ranges 710–810°C and 810–910°C (Fig. 1).

The decomposition of dolomite can be presented by the following equations.



$$CaMg(CO_3)_2 \rightarrow \text{(i) } CaCO_3 + MgO + CO_2$$

$$CaMg(CO_3)_2 \rightarrow \text{(ii) } CaO + MgO + CO_2$$

The first temperature range can be assigned to the formation of MgO and calcite and the second range was assigned to the decomposition of calcite [9].

The rate equation of thermal decomposition of dolomite is given by,

$$-\frac{dW}{dt} = KW,$$

W being the concentration of dolomite

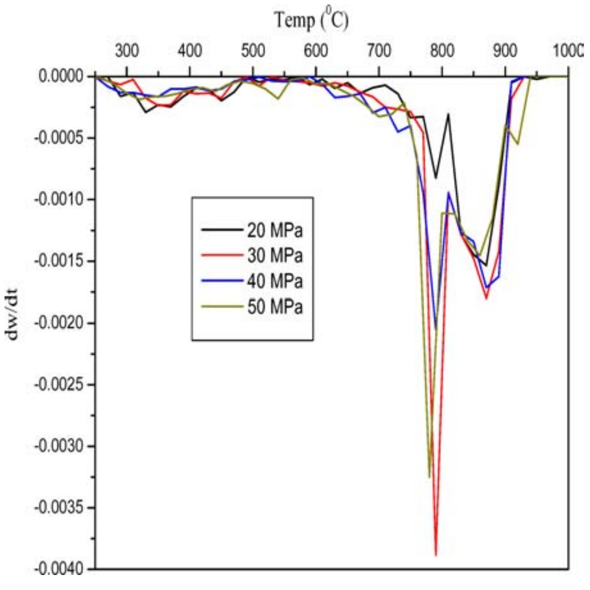


Figure 1 DTGA diagram of Dolomite powder compact under different compaction pressure.

By incorporating the Arrhenius equation:

$K = Ae^{-E/RT}$ and the heating rate, $h = dT/dt$, and rearranging, we get:

$$\left[-\frac{1}{W}\frac{dW}{dT}\right] = \frac{A}{h}e^{-E/RT}$$

The rate equation may also be expressed in terms of fractional conversion X and the reaction order n as follows:

$$X = \frac{W_0 - W}{W_0 - W_\infty}$$

(W_0 and W_α are taken as the initial weight and weight after equilibrium decomposition, i.e, when further weight change does not take place)

$$-\frac{dX}{dt} = K(1-X)^n$$

By incorporating the expressions of heating rate h and the rate constant K in the above equation, and rearranging and integrating, the following equation can be written as:

$$\int_0^X \frac{dX}{(1-X)} = \frac{A}{h}\int_0^T e^{-E/RT}\,dT$$

Different workers gave approximate solutions of the above equations [10–13]. The solution given by Agarwal and Sivasubramanium [12], which was used by the authors in studying the dehydration kinetics of calcium aluminate cement hydrate [14], was used in the present investigation.

$$\mathrm{Ln}\left[-\frac{\mathrm{Ln}(1-\mathrm{X})}{T^2}\right] = \mathrm{Ln}\left[\frac{AR}{hE}\left(\frac{1-2RT/E}{1-5(RT/E)^2}\right)\right] - \frac{E}{RT}, \quad \text{for } n = 1$$

$$\mathrm{Ln}\left[\frac{-\mathrm{Ln}\{1-(1-X)^{1-n}}{(1-n)T^2}\right] = \mathrm{Ln}\left[\frac{AR}{hE}\left(\frac{1-2RT/E}{1-5(RT/E)^2}\right)\right] - \frac{E}{RT}, \quad \text{for } n \neq 1$$

Therefore, a plot of Ln $[\frac{-\mathrm{Ln}(1-x)}{T^2}]$ vs. $1/T$ for $n = 1$ and Ln $[\frac{-\mathrm{Ln}\{1-(1-x)^{1-n}}{(1-n)T^2}]$ vs. $1/T$ for $n \neq 1$ give the value of E. The values of A can be calculated from the intercept.

To determine the exact order of the decomposition reaction, the regression coefficient and standard error values of the linear plots for different n values (as described above) were analyzed by trial and error method. The n value for which correlation coefficient value was the maximum, was taken as the order of the reaction and the values are listed in Table II.

The kinetic study was carried out for the two different zones where the weight losses were the maximum, i.e., 710–810°C and 810–910°C. These are the zones for the formation of MgO along with $CaCO_3$ and

TABLE II Kinetic parameters for dolomite decomposition

Compaction pressure (MPa)	n	R^2	E (KJ/Mol)	A (min^{-1})
A. (Temperature range 710–810°C)				
0	0.85	0.9995	103.29	4.13E05
20	0.74	0.9992	118.52	3.54E05
30	0.55	0.9987	120.41	2.21E04
40	0.50	0.9979	123.39	3.21E03
50	0.50	0.9982	124.73	1.53E02
B. (Temperature range 810–910°C)				
0	0.75	0.9991	121.17	4.32E05
20	0.83	0.9977	118.52	6.04E04
30	0.92	0.9967	115.32	5.29E04
40	1.0	0.9999	113.43	1.21E04
50	1.0	0.9996	109.73	2.23E03
C. (Temperature range 710–910°C)				
0	0.33	0.9998	133.17	1.83E06
20	0.75	0.9997	128.52	2.64E04
30	1.0	0.9997	127.35	4.27E04
40	1.0	0.9999	126.63	5.21E03
50	1.0	0.9996	126.33	8.53E01

the formation of CaO. The kinetic study for the entire range of decomposition, i.e., for the formation of complete doloma from the dolomite was also carried out. From the calculated kinetic parameters it was observed that for the first temperature zone, with the increase in compaction pressure, the order of the decomposition reaction decreased and in all the cases the orders were of fractional values. The activation energy increased steadily with the increase in compaction pressure indicating the influence of diffusion-controlled process on the decomposition reaction at this stage. For the second temperature range, with the increase in compaction pressure, the order of the reaction increased steadily, and after a critical compaction pressure, the decomposition reaction for this stage only, became first order. But the activation energy decreased significantly with the increase in compaction pressure. This could be due to the influence of interface at this stage of decomposition, which increased with the increase in compaction pressure. The decomposition reaction of the powder sample for the overall range followed fractional order kinetics and so also the sample compacted at low pressure (20 MPa) although with a higher value. With further compaction, the decomposition reaction became of 1st order and with the increase in compaction pressure further increase in the order of the reaction rate was not observed. But activation energy of the decomposition process decreased slightly with the increase in the compaction pressure.

In the case of dolomite, rhombohedral lattice is converted to the cubic lattice after decomposition. As the reaction is interface controlled, it may be assumed that in between the two stable states of reactant and product, i.e., dolomite crystal and calcined dolomite or doloma, incipiently formed doloma ($\text{CaO}^* + \text{MgO}^*$) remained in active state. As the reaction approaches an equilibrium value, the concentration of the active state is expected to rise from zero to a constant value. It is apparent that the fraction surface available for the reaction will be dependent upon the removal of oxide away from the reactant dolomite site and to the product site, i.e., lattice of the oxide crystals of the decomposed dolomite [15]. With the increase in compaction pressure the possibility of the conversion of the freshly decomposed doloma intermediate into fully stable form probably increased and the activation energy for the decomposition process is therefore slightly decreased.

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