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Non-isothermal decomposition of Indian limestone of marine origin

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Abstract Thermal decomposition behaviour of ten Indian limestones of marine origin have been studied by thermogravimetric (TG) and differential thermal analysis (DTA). DTA curves of limestone samples show asymmetric peak with index of shape about 0. 25. The size of calcite characteristic endothermic DTA peak remains unaffected due to the presence of impurities such as SiO_2 and Al_2O_3. The presence sodium and potassium carbonate salts in the limestone have a strong effect on their decomposition. From the thermogravimetric data the activation energy, Arrhenius factor, order of reaction and entropy for activation were calculated using three different methods. TG and DTA results indicate that both temperature of decomposition and the activation energy for decomposition of limestone is reduced and that the rate of decomposition is enhanced relative to pure calcium carbonate. The formation of portlandite and wollastonite are strongly exothermic and thus helps in maintaining the required retorting temperature.

Keywords Limestone · Thermal decomposition · TG-DTA · Activation energy · Arrhenius kinetic parameters · X-ray diffraction

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Introduction

Limestone is a sedimentary rock composed of more than 50% carbonate minerals. The estimated limestone deposits in India are about 1,69,941 million tones [1]. Limestone, the principal raw material for cement manufacture forms one of the most important mineral deposits of India and provides a solid base for the industrial prosperity of the country. Thermal decomposition of limestone has been the subject of intensive study over the years due to its importance in the flue gas desulfurization and in the hydration of cement in concrete. Many attempts have been made to elucidate the mechanism of the thermal decomposition of limestone [2–10]. Dong-Myoung Kim and Young.Woo Rhee [11] studied the sulfidation and sulfation reactions of Daesung limestone in order to investigate the reaction mechanism needed to apply new desulfurization concepts to the next generation PFBC. On the basis non-isothermal kinetic measurements, various values have been reported for the activation energy, e.g., 133–198, 101–234 kJ mol^{-1} [12], 30.97–58.91 kcal mol^{-1} [13], 45.14–50.80 kcal mol^{-1} [14] and 157.79 kJ mol^{-1} [15]. Mangaonkar et al. [16] reported the TG curves of few Indian limestone samples. Singh and Singh [17] studied the effect of 5% tartaric, succinic and citric acids on the decomposition of calcium carbonate and observed that the decomposition temperature was not decreased. Although the main constituent of limestone is calcium carbonate, certain other impurities such as magnesium, silicon, aluminium, iron, alkali salts etc. are often present and they affect the decomposition reaction considerably. In view of the importance of this phenomenon in building materials further extension in this direction was considered necessary. The sedimentary limestone deposits and associated rock types of the sample area belonging to cretaceous age of Indian stratigraphy.

The rock formations indicate transgressive marine origin. This work was undertaken in order to investigate the thermal decomposition kinetics of 10 Indian limestones of marine origin using non-isothermal thermogravimetry and differential thermal analysis.

Experimental procedures

Ten limestone samples collected from quarries located strategically around Ariyalur, Tamil Nadu, India (North latitudes 10°55′ and 11°20′ and East longitudes 78°45′ and 79°5′) was used in this study. Limestone samples were ground with agate mortar and pestle. XRD analysis were performed with a SEIFERT X–ray diffractometer with CuKα radiation ($\lambda = 1.54$ Å), Cu filter on secondary optics, 45 kV power and 20 mA current. The powder sample was mounted on a quartz support to minimize background. A small quantity of the powder sample was heated in a muffle furnace at 950 °C for 6 h and the XRD analysis was carried out to confirm the decomposition reaction at the particular temperature.

Thermal analysis was performed in a simultaneous TG-DTA (Netzsch STA 409) analyzer. The experimental conditions were: (a) continuous heating from room temperature to 1,000 °C at a heating rate of 10 °C/min; (b) N_2-gas dynamic atmosphere (90 cm^3 min^{-1}); (c) alumina, as reference material (d) sample: 19 mg of the sample without pressing (d) The temperature was detected with a Pt–Pt 13% Rh thermocouple fixed in a position near the sample pan. The following data was obtained by thermal analysis: (i) reaction peak temperature and main effect (endothermic or exothermic) (ii) content of bound water, which is the weight loss in the temperature range 100–200 °C and content of CO_2 released during the decomposition of carbonate phases.

Table 1 Oxide composition of limestone samples

Sample code	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	K_2O	Na_2O	Cl^-
L_{01}	46.38	0.60	12.11	0.92	2.01	0.11	0.18	0.01
L_{02}	46.05	0.70	13.32	1.18	1.75	0.06	0.20	0.01
L_{03}	52.19	0.59	4.93	0.72	0.44	0.04	0.09	0.02
L_{04}	51.46	0.65	4.41	0.64	0.84	0.05	0.14	0.03
L_{05}	50.53	0.61	2.20	4.10	1.09	0.03	0.11	0.01
L_{06}	49.22	0.60	9.38	0.58	1.11	0.20	0.21	0.01
L_{07}	49.02	0.73	6.51	0.83	1.59	0.38	0.24	0.02
L_{08}	49.87	0.62	5.62	0.89	1.57	0.28	0.19	0.03
L_{09}	54.35	0.69	nd	0.40	0.29	0.02	0.09	0.04
L_{10}	52.50	0.68	2.08	0.53	0.50	0.04	0.10	0.04

Results and discussion

Table 1 gives the chemical composition of the limestone samples, which were determined by the standard limestone analysis [18]. Typical powder X-ray diffraction pattern obtained on limestone is reported on Fig. 1. The intensity of the peaks is quite sharp with little background absorption. The principal reflections occurring at the d spacings 3.038, 1.8796, 1.9166 2.2876 and 2.4965 Å confirm that calcium carbonate in limestone (L_1–L_{10}) exhibits calcite structure [19]. The main undesirable impurities in limestone are silica, K_2O, Na_2O, Cl^- and alumina.

Differential thermal analysis

The DTA curves of limestone with $CaCO_3$ are presented in Fig. 2. The thermal curves representing the limestones are characterized by endothermic peaks at slightly varying temperatures caused by the evolution of carbon dioxide (Fig. 2). The DTA curve shows that the decomposition of limestone starts at lower temperature than pure calcium carbonate. The functional relation between the shape of the DTA peak expressed by its shape index and the order of thermal decomposition reaction was noted by Kissinger [20]. The absolute value of the ratio of the slopes of tangents to the curve at the inflection points gives slope index and it is illustrated in Fig. 3. DTA curve shows an asymmetric peak with index of shape about 0.25 and this value is comparable with the value (0.258) obtained from the equation derived by Kissinger [20]. French and Warne [21] reported that the exothermic wollastonite—forming reaction (calcite with SiO_2) which occurs in the same temperature region could be superimposed on the endothermic

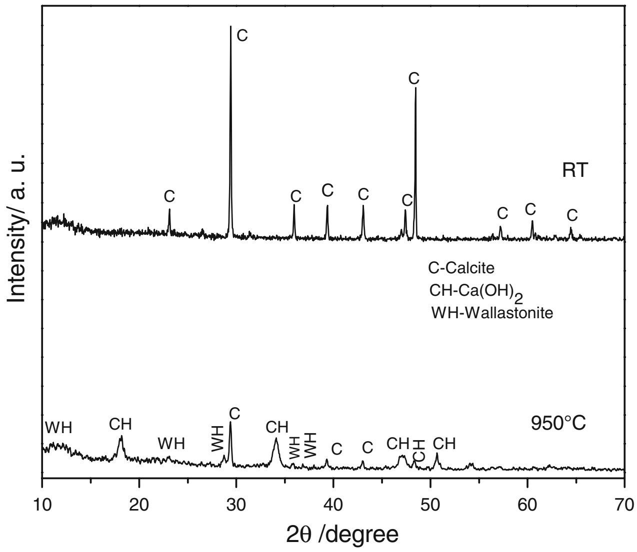

Fig. 1 Powder XRD pattern of Indian limestone at RT-room temperature and at 950 °C

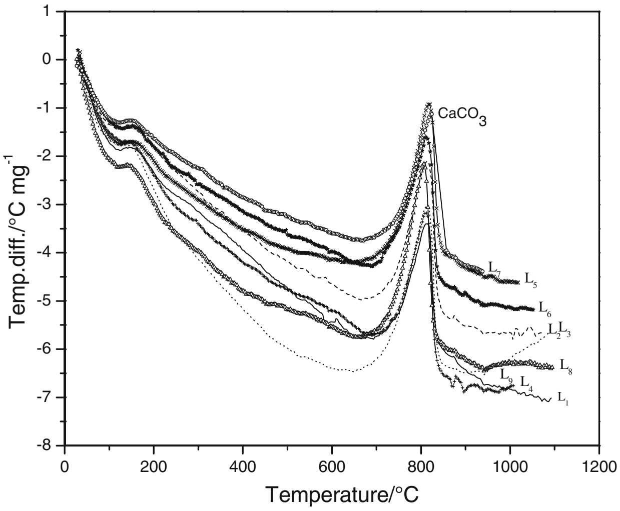

Fig. 2 DTA curves of CaCO$_3$ and different limestone samples

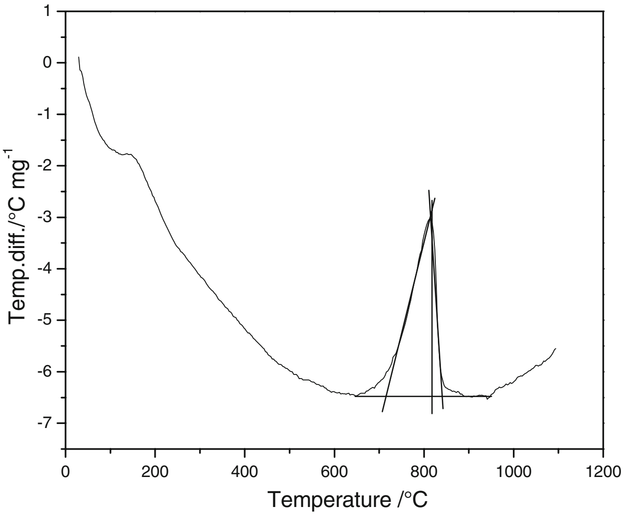

Fig. 3 Method of measuring the shape index

calcite decomposition peak, reduce its size and be completely negated itself, leaving only a much reduced, residual endothermic peak to represent the original calcite content. However, calcite peak remained unaffected in the present study (Fig. 2). XRD examinations of the sample heat treated to 950 °C exhibit the reflections at d-spacing 7.670, 3.83, 2.556 and 2.47 Å indicate the presence of wollastonite a new mineral formed [19]. The reflections occurring at d-spacing 2.6219, 4.8950, 1.9221, 1.7923 and 1.4443 Å can be attributed to portlandite (Fig. 1). The CaO liberated by the decomposition of limestone forms portlandite on reaction with atmospheric water vapour. The remaining CaO would rapidly react with atmospheric CO$_2$ forming a small amount of calcite, which was detected by the XRD analysis.

The data computed from the DTA curves of limestone have varying amount of K$_2$CO$_3$ and Na$_2$CO$_3$ are presented in Table 2 along with pure CaCO$_3$. The results obtained in the present study indicate that the effect of K$_2$CO$_3$ and Na$_2$CO$_3$ on DTA peak temperature is maximum which is similar to the observation of Malik et al. [22] and hence the DTA peak temperature is minimum. It is interesting to note that similar to peak temperature, the termination temperature is minimum with low concentration of these salts. The decomposition range tends to decrease with the low concentration of sodium and potassium salts. These observed results are in good agreement with the results reported by Malik et al. [22] for low concentration of these salts. The presence of chloride salt also enhances the decomposition of limestone but do not activate the process by lowering thermal requirements for decomposition similar to the observation of Mao Qiang Li et al. [23].

Thermogravimetric analysis

Thermogravimetric curves of limestone and CaCO$_3$ presented in Fig. 4 and DTG curves reported in Fig. 5 are found to be similar in shape. DTG peak temperature of the samples studied almost equal to 810 °C. Mass loss detected around 150 °C in the case of limestone can be attributed to the chemically bound water. The endothermic peak related to phase transformation of α to β quartz at 570 °C was also detected. The activation energy for the decomposition of limestone samples was determined by using three popular methods [24–26] and the values are reported in Table 3. The calculated values of the activation energy in the present investigation very well agree with that reported by earlier investigators [8, 12–15]. The wide dispersion of the measured data is in relation to the influence of physical processes, namely inter- and intra particle diffusion, heat transfer resistance, sintering etc. Garcia Calvo [27] studied the influence of macro kinetic parameters on the value of the activation energy over the wide range of experimental conditions and concluded that the influence of macro kinetic parameter is low within this range. Using Garns [28] expression to estimate as the reciprocal of 2.303RT$_{\mathrm{mean}}$ where T$_{\mathrm{mean}}$ is the mean of the T$_{\max}$ given in Table 2, i.e., $T_{\mathrm{mean}} = 813.13$. This gives $a = 0.0642$ mol kJ^{-1} which is almost the same as that determined from the experimental plot. This evidence endorses that the linearity of the compensation equation may be due to the form of the Arrhenius equation (log A = 0.05E–3.4794). The values of the parameters a and b are close to the previously reported values of Ersoy-Mericboyu et al. [13]. Comparison of the values of E and A of pure calcium carbonate with limestone indicate that the presence of impurities is a cause of variation of kinetic parameters obtained. The impurities could function as catalysis owing to their influence in the crystalline structure.

Table 2 Thermal analysis data of $CaCO_3$ and different limestone samples

Sample	DTA peak temperature/°C	Temperature of decomposition/°C			Mass loss/%
		Threshold	Termination	Range of decomposition	
$CaCO_3$	799.5	710	810	200	42
L_{01}	813.5	640	840	200	35.94
L_{02}	814.5	680	825	155	40.43
L_{03}	805.1	671	836	165	39.97
L_{04}	813.6	656	836	180	40.09
L_{05}	810.1	681	830	149	38.78
L_{06}	816.0	650	843	193	37.49
L_{07}	817.4	650	847	197	37.57
L_{08}	808.9	655	842	197	35.73
L_{09}	809.6	672	839	167	43.44
L_{10}	822.6	680	842	162	40.40

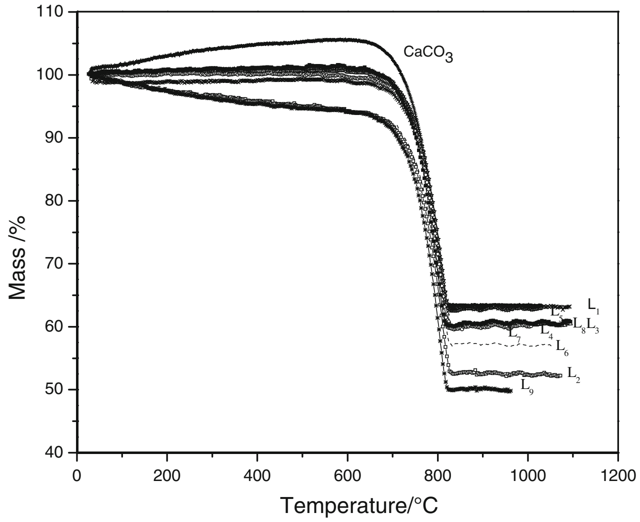

Fig. 4 Thermogravimetric curves of $CaCO_3$ and different limestone

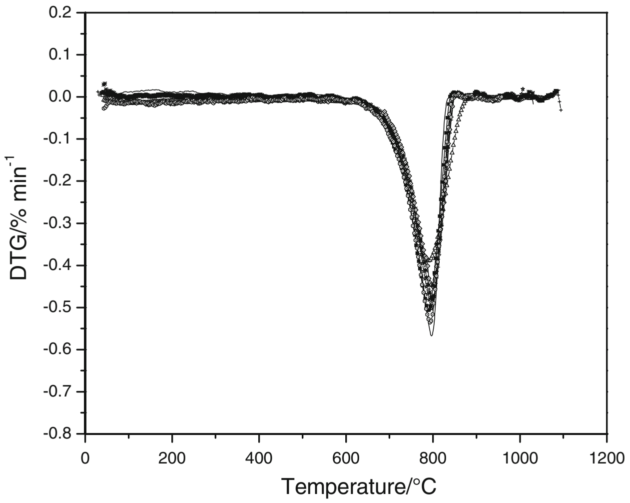

Fig. 5 DTG curves of $CaCO_3$ and different limestone samples

Table 3 Kinetic parameters for the thermal decomposition of limestone in N_2 atmosphere for the different calculation methods

Sample code	Freeman–Carroll			Coats–Redfern					Horowitz–Metzger		
	E /$kJmol^{-1}$	Log A /s^{-1}	S /$JKmol^{-1}$	E /$kJmol^{-1}$	Log A /s^{-1}	S /$JKmol^{-1}$	n	r	E /$kJmol^{-1}$	Log A /s^{-1}	S /$JKmol^{-1}$
$CaCO_3$	135.26	4.562	−72.63	152.97	5.392	−66.495	0.56	0.999	198.56	6.925	−123.561
L_{01}	166.77	5.5232	−149.696	182.412	6.3224	−134.40	0.20	0.999	221.63	8.3002	96.483
L_{02}	151.16	4.7145	−165.164	119.73	4.8378	−162.80	0.10	0.992	181.13	4.2402	−135.953
L_{03}	297.84	12.905	−8.357	281.238	11.5367	−34.55	0.80	0.999	271.80	10.8260	−48.154
L_{04}	186.00	6.4828	−131.316	229.95	8.7853	−87.31	0.59	0.997	237.96	9.0983	−81.281
L_{05}	240.71	9.252	−78.315	214.12	7.9774	−120.72	0.50	0.999	240.98	9.2657	−78.050
L_{06}	222.15	8.2943	−96.685	252.03	9.9225	−65.51	0.70	0.999	278.11	11.0912	−43.133
L_{07}	159.56	5.1286	−157.305	231.75	8.8581	−86.08	0.78	0.999	231.80	8.7739	−87.507
L_{08}	85.83	1.3022	−230.502	164.72	5.4697	−150.71	0.40	0.998	181.21	6.2233	−136.278
L_{09}	181.39	6.2754	−135.236	138.56	4.1894	−175.18	0.05	0.997	194.90	6.9603	−122.121
L_{10}	155.57	4.874	−162.237	116.59	5.0880	−177.28	0.55	0.999	228.47	8.6496	−92.158

Conclusions

The large fluctuation in the observed activation energies is due to the presence of impurities in the samples. The impurities could function as catalysis owing to their influence in the crystalline structure. DTA peak was not affected by the impurities such as SiO_2 and Fe_2O_3. K_2CO_3 and Na_2CO_3 present in the samples lowers the decomposition temperature and increases the rate of decomposition. The activation energy required for the decomposition reaction is reduced indicating that reduced fuel consumption in the lime production from limestone. The formation of portlandite and wollastonite are strongly exothermic and thus helps in maintaining the required retorting temperature and reduces costs.

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