



Impact of Physical Properties and Chemical Composition of Limestone on Decomposition Activation Energy

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(Received: 17 January 2013;

Accepted: 5 August 2013)

AJC-13885

The aim of this study is to evaluate the effect of chemical composition and physical properties of limestone on bulk density, apparent porosity, water absorption rate and P-wave velocity, on the activation energy required for its decomposition process. The activation energy of calcination of spherical particles was calculated from the Arrhenius equation. The samples were calcined by TG-DTA at a temperature range of 25-1000 °C and gradient of 10 °C/min. Samples with higher % CaCO₃ content and P-wave velocity and lower bulk density and porosity show relatively higher activation energy and rate of lime crystallite growth. This is due to the original grain channel pores and the formation of triple junction fractures during calcination, which facilitate transfer of hot gases and diffusivity of the evolved CO₂. It is finally concluded that the decomposition of limestone is a temperature, chemical and physical properties dependent process.

Key Words: Limestone properties, Thermal decomposition, Activation energy, TG-DTA.

INTRODUCTION

In broad sense definition, the limestone is any rock rich in CaCO₃. Limestone can be obtained from a variety of sources and various limestones differ considerably in their chemical compositions and physical structure. The chemical and physical properties of carbonate rocks are interdependent. Physical characteristics of limestone play an important role in evaluating a deposit. Certain physical characteristics in limestones may indicate a general disposition description during calcination. However, all stones with these characteristics will not decrepitate. Limestones display the following attributes or conditions, alone or in combination, are prone to decrepitation; coarse crystallinity, friability, foliation, excessive calcite veining, microfracturing, highly porous and thinly bedded. The chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silica, iron, magnesium, manganese, sodium and potassium. Magnesium and ferrous iron cations occurring in limestone may change the carbonate mineralogy of limestone as well as its physical characteristics such as colour, brightness, specific gravity, hardness, tenacity and decomposition properties^{1,2}.

The main chemical property of limestone is its thermal decomposition, known as calcination, during which lime (CaO) and carbon dioxide are produced (eqn. 1)^{1,3}. The calcination process is explained with a partly decomposed piece of carbonate

(Fig. 1). A core model is established to simulate limestone decomposition process, which consists of four sub-processes (Fig. 1) *i.e.*, heat transfer from ambient to particle surface (a), heat conduction from surface to reaction front (b), chemical kinetics at front, diffusion of the CO₂ through the porous oxide layer to surface (c-d) and then transfer into ambient.

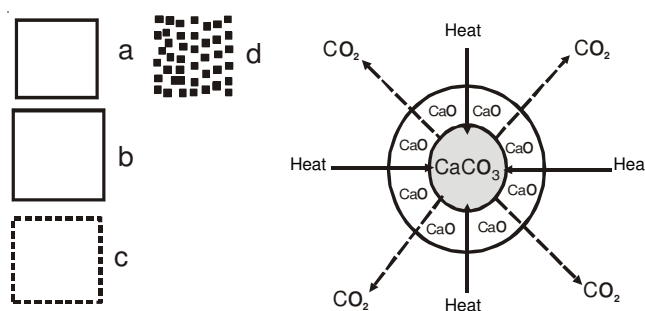


Fig. 1. Model of the decomposition of limestone

The calcination reaction is endothermic



which means that the forward reaction is favoured by higher temperatures. The reaction will proceed only if the partial pressure of CO₂ in the gas above the solid surface is less than the decomposition pressure of the CaCO₃. The latter pressure is determined by equilibrium thermodynamic considerations⁴.

The activation energy in solid-state reactions can be calculated from Arrhenius equation. In the case of calcination of spherical particles, eqn. 1 can be used for the calculation of the main parameters determining the kinetics of decomposition processes (eqn. 2): k is the rate coefficient, A is a constant, E is the activation energy, R is the universal gas constant and T is the temperature (in degrees Kelvin). R has the value of $8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}$, entering the Arrhenius equation (eqn. 2):

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

In the evaluation of the kinetics of calcination is shown to complicate by CO_2 concentration, which inhibits the reaction; particle size, which may introduce both thermal and mass transfer limitations and catalysis/inhibition by impurities. When calcination takes place (eqn. 1), the product calcium oxide weighs only 56 % of the parent carbonate. Since the relative molar volumes are $36.9 \text{ cm}^3 \text{ mol}^{-1}$ for CaCO_3 and $16.9 \text{ cm}^3 \text{ mol}^{-1}$ for CaO , if there is negligible particle shrinkage, the porosity of the product from a pure non-porous carbonate will increase to a theoretical value of 0.55. Hence a lime may have a porosity greater than 0.6. For maximum adsorption efficiency, care must be taken on the one hand to ensure that calcination is complete and on the other that the CaO grains formed do not sinter after formation.

The reaction (eqn. 1) only begins when the temperature is above the dissociation temperature of the carbonates in the limestone. According to Boynton¹, the CaCO_3 decomposition temperature determined by several reserchers at the beginning of the 20th century is generally accepted as 898 °C at 1 atm in a 100 % CO_2 environment. However, according to some studies, this temperature is 902.5 °C⁵⁻⁷. Kilic⁸ reported that the weight loss above 600 °C, measured by DTA-TG in azot atmosphere, is attributed to the CO_2 from the decomposition of calcium carbonate that is initiated at 682-691 °C and completed at 944-961 °C.

The internal structure of a rock having open and closed pores in its texture affects its heat transfer. The specimen comprises a dense carbonate core surrounded by porous oxide layer. The changes in pore structure also play a significant role on the calcination/heat treatment mechanism and the reactivity of a calcined limestone is strongly dependent on its chemical, physical and structural properties, which in turn are highly dependent on heat treatment conditions^{9,10}. In the good calcination process, limestone should be approximately consisting of 97 % CaCO_3 and low impurities. Impurities such as iron, magnesium and aluminum oxides tend to lead to lower surface areas in both the limestones and their calcines¹¹.

Limestone calcination is a reaction requiring considerable input of energy. Calcination of calcium carbonate is a highly endothermic reaction, requiring 3.16 GJ (754753 kcal) of heat input to produce a tonne of lime (CaO)¹². To optimize the calcination process in order to save energy and ensure product quality, the decomposition behaviour of individual pieces of carbonate under given process conditions must be known.

The current demand of limestone and its product; lime, worldwide has necessitated investigation into chemical composition and physical properties on the thermal damage. In this

paper, the effect of chemical composition and physical properties of limestone on the thermal decomposition was studied, depending on decomposition temperature and activation energy of calcium carbonate. Also, energy is a very important and expensive main input for decomposition system and it must be protect for environmental policy.

EXPERIMENTAL

The limestones were taken from different large commercial deposits *i.e.*, from Karaisali region (L_k) and Yilankale region (L_y) in Adana, Turkey. During sampling, rock types having no bedding planes were selected to eliminate any anisotropic effects in the measurements of the samples. Limestones present macroscopically different characteristics. L_k is a 'dirty white' and light coloured grey limestone comprising discrete and tiny crystals. L_y is light-coloured 'dirty white' any distinguished crystals. Microcracks were not present throughout the mass of L_k limestones, but microcracks, dense vein system and schistosity were observed throughout the mass of L_y limestones.

Analytical methods and techniques: Analyses were performed on limestone samples by using the following analytical procedure. In the chemical analysis and thermal experiments (TG-DTA analysis), ground -0.5 mm size limestones were used. Cubic specimens of 5 cm mean edges (average value 5.11 ± 0.09) and core specimens (42 mm \times 85 mm cylindrical) were prepared for the physical experiments.

- XRF (Siemens SRS 300 X-ray Fluoresans Spectrometer) was used to determine the chemical compositions of limestone samples.

Physical properties (the bulk density, effective porosity, water absorption rate) of the limestones were determined using saturation and buoyancy techniques, as recomended by ISRM and TSE¹³.

- P-wave velocities were measured by the Pundit instrument (CNS Farnel Pundit Plus C-Portable Untrasonic Non-Destructive Indicator Tester), which has two transducers (a transmitter and a receiver) having a frequency of 54 kHz.

- Differential thermal and thermogravimetric analyses (simultaneous TG/DTA, Setaram 92 16 DTA-TG) were carried out to determine quantitatively and qualitatively the various compounds presented in samples. Analyses were performed in samples of limestone azot atmosphere at a temperature range of 25-1000 °C and gradient of 10 °C/min.

RESULTS AND DISCUSSION

The chemical analyses results of limestone samples are presented in Table-1. It was found that the studied limestones are very pure; with an average CaCO_3 higher than 97 %; the impurities (MgO , Fe_2O_3 , Al_2O_3 and SiO_2) are very low. Since the $\text{MgCO}_3/\text{CaCO}_3$ ratio varies with the type of limestone, the decomposition temperature does not remain constant and therefore must be determined for every type of limestone.

The physical properties of limestones are presented in Table-2. All limestone samples indicated low values in porosity and water absorption rate (lower than 1 %). The value of apparent density ($> 2.55 \text{ g/cm}^3$) was found to be characteristic for a limestone¹². Comparing the limestones, L_k demonstrated higher values in porosity.

TABLE-1
CHEMICAL COMPOSITIONS OF LIMESTONE (%)

Sample	CaO	MgO	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Loss of ignition
L _k	55.13 ± 0.14	0.44 ± 0.04	0.34 ± 0.22	0.08 ± 0.04	0.07 ± 0.03	43.95 ± 0.15
L _y	54.90 ± 0.35	0.74 ± 0.58	0.55 ± 0.31	0.10 ± 0.05	0.08 ± 0.06	43.63 ± 0.53

TABLE-2
PHYSICAL PROPERTIES OF THE LIMESTONES

Sample	Bulk density (g/cm ³)	Water absorption rate (weight) (%)	Porosity (%)	P-Wave velocities (km/s)
L _k	2.65 ± 0.08	0.72 ± 0.22	0.85 ± 0.04	5.701 ± 0.044
L _y	2.72 ± 0.12	0.39 ± 0.09	0.70 ± 0.16	5.855 ± 0.063

The physical properties depend not only on the properties of the individual minerals, but also upon the way in which the minerals are assembled and porosity, vein system and micro-cracks. The relevant information is given by P-wave velocities, which includes the pores and cracks. Information on the porous nature of rock materials is frequently omitted from physical descriptions, but is required if these descriptions are to be used as a guide to mechanical performance¹⁴. Bulk density is relevant chemical composition of the limestone. Bulk density increases with increase in % MgCO₃ content.

P wave velocity was used to determine the changes on the physical properties of the limestone samples. P-wave velocity measurements may be performed by the direct method at room conditions through ultrasonic pulse transmission technique by the Pundit instrument (Fig. 2). Velocity measurements were carried out on the cubic specimens. The test was repeated three times in three perpendicular directions and the mean values were recorded as the P-wave velocity.



Fig. 2. Method of measuring P-wave velocity

The P-wave velocity, as a natural characteristic of rocks and different materials, depends on their micro- and macro-structure, the existence of minor cracks and porosity and the characteristics of their mineralogical components, such as elastic parameters, density and micro-porosity¹⁵. Increased velocity with an increase in the dry apparent weight and *vice versa* is reported by Babuska¹⁶ and Kopf *et al.*¹⁷.

The P-wave velocity in the limestones ranges between 3.500 and 6.500 km/s^{18,19}; while, for a calcite crystal, the P-wave velocity is 6.490 km/s¹⁵. In the tests, the P-wave velocity in L_k and L_y was measured as 5.701 ± 0.044 and 5.855 ± 0.063 km/s, respectively. The P-wave velocity measurement values have showed that all specimens have minor cracks and porosity.

Calcination of calcium carbonate is a highly endothermic reaction, requiring 3.16 GJ of heat input to produce a tonne of lime (CaO). The reaction only begins when the temperature is above the dissociation temperature of the carbonates in the limestone. Once the reaction starts the temperature must be maintained above the dissociation temperature and carbon dioxide evolved in the reaction must be removed. Dissociation

of the calcium carbonate proceeds gradually from the outer surface of the particle inward and a porous layer of calcium oxide, the desired product, remains.

The differential thermal analysis technique has been used for quantitative determination of heats of decomposition of carbonate materials. It is observed that the carbonates; *i.e.*, limestone, dolomite, have lower heats of decomposition and higher energies of activation in a carbon dioxide atmosphere compared to values obtained in air.

The thermal analysis was performed in a simultaneous TG-DTA. On the limestones, L_k and L_y, continuous heating from room temperature to 1000 °C at a heating rate of 10 °C/min, TG and DTA curves (Figs. 3 and 4) were obtained, is attributed to the CO₂ from the decomposition of calcium carbonate.

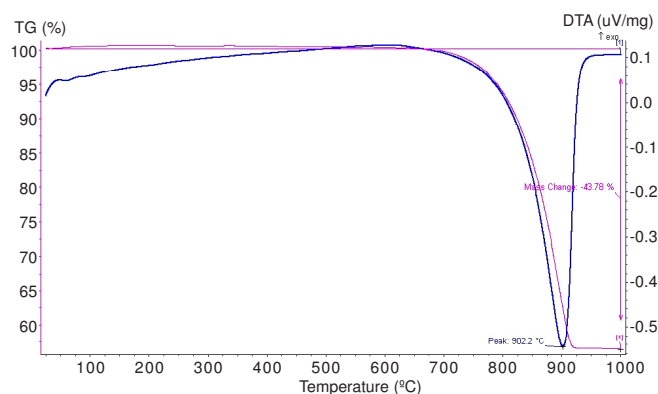


Fig. 3. A thermogram of TG-DTA curve for L_k decomposition

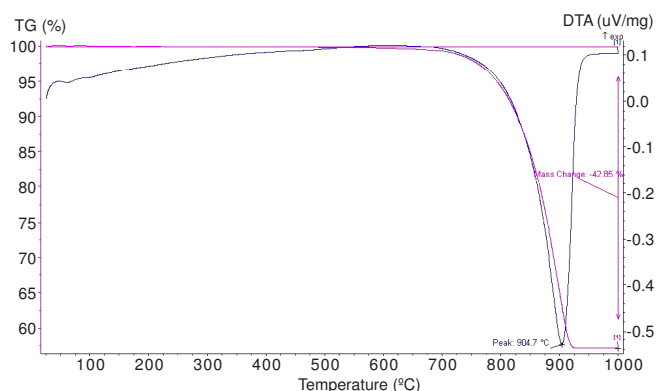


Fig. 4. A thermogram of TG-DTA curve for L_y decomposition

The figures showed that the weight loss is initiated at 625 and 675 °C and defined (eqn. 1) fully decomposed approximately at 925 and 935 °C for L_y and L_k, respectively. Comparing the percentage values of CO₂ measured by DTA/TG, it is

evident that the values are very high and similar to each other. Thus, the limestones could be characterized as high calcium ones. Furthermore, it is observed that the percentage of CO₂ for limestones is higher than the theoretical one.

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The heat treatment experiments have shown that decomposition reaction begins at above 600 °C, corresponding to the loss in carbon dioxide on limestone. The weight losses of the samples were associated CO₂ producing in limestone. The specimen comprises a dense carbonate core surrounded by porous oxide layer. During the decomposition/corresponding to the loss in carbon dioxide, micro-cracks and porosity are occurred on limestone (Fig. 1). At higher than 1000 °C, recombination started, which in turn led to an increase in sample weight. Namely, eqn. 1 initiates to return from right to left⁸.

Calcium oxide is formed during the decomposition/ corresponding to the loss in carbon dioxide (equation). This phenomena is explained with activation energy value. The value of the activation energy show that limestone has CaCO₃ ratio and compact structure or micro-crack. Activation energy values were calculated by an Arrhenius equation from DTA-TG curves (Figs. 3 and 4)/data (Tables 3 and 4 and Figs. 5 and 6).

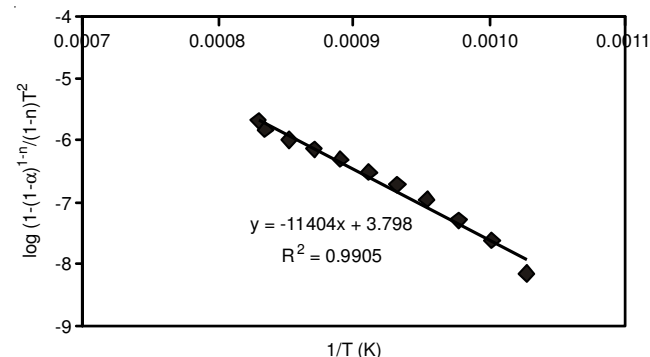


Fig. 5. Graph is used for calculation of activation energy, L_k

Temp. (°C)	TG (%)	$\alpha = \frac{w_o - w_t}{w_o - w_a}$	$\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)}$	$\log \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)}$
675	1.191	-	-	-
700	1.065	0.00341	7.21145E-09	-8.14198
725	0.712	0.01169	2.35315E-08	-7.62835
750	0.007	0.02700	5.18599E-08	-7.28517
775	-1.271	0.06021	1.10827E-07	-6.95536
800	-3.306	0.10834	1.91865E-07	-6.71700
825	-6.373	0.18350	3.14721E-07	-6.50207
850	-10.761	0.28790	4.82086E-07	-6.31688
875	-17.00	0.42539	7.03303E-07	-6.15286
900	-24.516	0.61248	1.02179E-06	-5.99064
925	-35.400	0.84429	1.48567E-06	-5.82808
935	-41.918	1.00000	2.06608E-06	-5.68485

Temp. (°C)	TG (%)	$\alpha = \frac{w_o - w_t}{w_o - w_a}$	$\frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)}$	$\log \frac{1 - (1 - \alpha)^{1-n}}{T^2(1-n)}$
625	1.138	-	-	-
650	1.108	0.0038	8.22E-09	-8.0849
675	1.050	0.0051	1.15E-08	-7.93973
700	0.686	0.0104	2.21E-08	-7.65525
725	0.007	0.0261	5.29E-08	-7.27654
750	-1.182	0.0538	1.04E-07	-6.98184
775	-3.126	0.0988	1.84E-07	-6.73542
800	-6.126	0.1681	3.02E-07	-6.51959
825	-11.000	0.2776	4.87E-07	-6.31234
850	-17.000	0.4275	7.42E-07	-6.12975
875	-25.000	0.6250	1.1E-06	-5.96001
900	-34.731	0.8310	1.52E-06	-5.81878
920	-42.046	0.9998	2.11E-06	-5.67542
925	-42.053	1.0000	2.1E-06	-5.67761

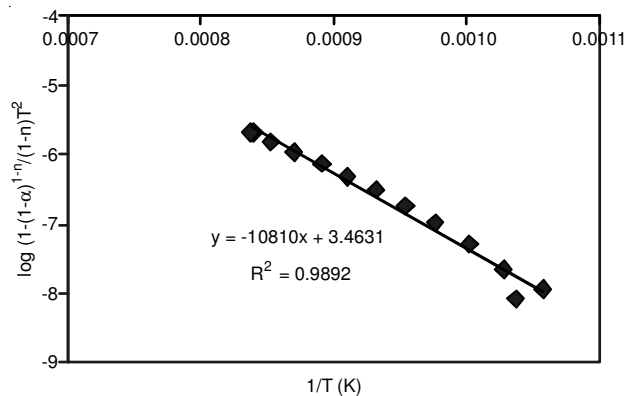


Fig. 6. Graph is used for calculation of activation energy, L_y

An Arrhenius relationship exists for the change in thermal conductivity with temperature and a plot of log κ_s versus 1/T gives a straight line (Figs. 5 and 6). According to Figs. 5 and 6, the activation energy values of the limestones were calculated 227.88 kJ/mol (54.43 kcal/mol) and 232.61 kJ/mol (55.56 kcal/mol) for L_k and L_y, respectively. The effective values of activation energy were within the range of literature values and were found.

The commonly accepted value for the activation energy of CaCO₃ dissociation is 45 kcal/mole²⁰. The activation energy of limestone dissociation varies from 30-60 kcal/mol²¹. The variation is due to the associated impurities and proportion of calcite in raw material, for example, the presence of impurities like aragonite leads to an increase in the energy barrier for decomposition, while clay minerals reduce the activation energy.

Conclusion

The study has demonstrated that thermal decomposition of limestone depending on chemical composition, physical properties like decomposition temperature and activation energy of calcium carbonate. The reaction temperature has a direct effect on the conductivity of limestone depending on its impurities, porosity and micro-cracks and hence on the rate of reaction. The reaction rate can be enhanced through improved heat transfer systems.

Samples with higher % CaCO₃ content and P-wave velocity and lower bulk density and porosity show relatively higher activation energy and rate of lime crystallite growth. This is due to the original grain channel pores and the formation of triple junction fractures during decomposition process, which facilitate transfer of hot gases and diffusivity of the evolved CO₂. It is finally concluded that decomposition process of limestone is a temperature, chemical and physical properties dependent process.

The temperature dependent terms were found using Arrhenius law and it was observed that the reaction temperature has a direct effect on the rate of reaction and limestone chemical properties. The effective values of activation energy were all within the range of literature values and were found to be 54.43 and 55.56 kcal/mol for L_k and L_y, respectively.

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