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Effects of Limestone Characteristic Properties and Calcination Temperature on Lime Quality

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This study has examined the effects of limestone characteristics (microstructure and texture) and calcination temperature on the quality of the produced lime. Two types of limestone have been studied for physico-mechanical properties and calcined at selected temperatures (650, 700, 750, 800, 850, 900, 950, 1000, 1050 and 1200°C). Chemical, physico-mechanical and mineralogical analyses have been performed in limestone samples, determing lime quality and reactivity. Test results indicate that higher the limestone calcination temperature (950 and 1000°C), the more reactive the produced lime. Concerning the lime, the reactivity is related to its impurities and microstructure, which is, in turn, related to microstructural characteristics of the limestone (texture, grain size, porosity). The most reliable factors for the estimation of lime reactivity are the specific surface area, porosity and hydration rate (T_{60}) of the lime and the temperature during the calcination process.

Key Words: Limestone characteristics, Lime reactivity, Calcination.

INTRODUCTION

Limestone can be obtained from a huge variety of sources and various limestones differ considerably in their chemical compositions and physical structures. The chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silicon, iron, magnesium, manganese, sodium and potassium[1, 2].

Limestone and lime has been used as an essential binder for the production of mortars and plasters. Also, lime is used in a number of different areas: road paving, construction, traditional building sector, highway stabilization, soil neutralization, sugar refining, chemical industry, participated calcium carbonate (PCC), paper industry, environmental sector, flue gas desulfurization, magnesia production and refractories[1–3]. The pyramids of the Egyptians, however, are the first recorded use for limestone and employ huge nummilitic limestone blocks and lime along with alabaster (gypsum) for mortar and blaster between 4000 and 2000 BC[1–3].

By the middle of the 19th century, the process of lime production changed and launched to use traditional lime kilns with modern vertical and rotary lime kilns. By using oil, gas and carbon dust as fuel in lime kilns, the dissociation temperature was exceeded and the produced lime was overburnt[1, 4, 5].

In the literature, there are several references concerning factors that may affect the quality of lime. Generally, these factors are characteristic of limestone: calcination temperature, pressure acquired in kilns, rate of calcination and fuel quality[6–14]. Thermal decomposition of limestone has been the subject of intensive study over the years due to its importance in the flue gas desulfurization[15–19]. Studies have not been reported to the best of our knowledge, about the specific effects of the various factors (raw materials, calcination, temperature) to the reactivity of the produced lime.

In this paper, in order to study the effects of limestone characteristics and calcination temperature on lime production, the investigation of the characteristic properties of the produced lime has been performed properly.

EXPERIMENTAL

The raw materials used in the production of lime were two different limestone regions, Ceyhan (L_c) and Karaisali (L_k), Adana, Turkey. These limestones were selected in order to evaluate the characteristics of Ceyhan and Karaisali lime, which is the most commonly used binder in restoration mortars and steel making industry in Turkey.

Limestones present macroscopically different characteristics. L_c is a light-coloured dirty white variety with hardly tiny crystals, whereas L_k is a dirty white and light coloured grey limestone comprising of discriminate and tiny crystals. Microcracks have not occurred throughout the mass of both limestones.

Physico-mechanical properties (unit weight, water retention ratio, porosity, void volume and compressive strength) of the limestone were determined.

Samples of limestone (*ca.* 30 × 30 × 30 cm) were calcined at different temperatures (650, 700, 750, 800, 850, 900, 950, 1000, 1050 and 1200°C) for 135 min for the production of lime. The evaluation of the lime characteristic properties, quality and behaviour on calcination has been performed.

Analytical methods and techniques

Analyses were performed in limestone and lime samples by using the following analytical procedure:

- X-ray Flouresans Spectrometer (XRF) (Siemens SRS 300) was used to determine the chemical compositions of limestone samples.
- Transmitted light microscopy (Nikon, Optiphot-Pol) was carried out in polished thin sections of the limestone in order to identify the texture, shape, and size of the grains.
- Physico-mechanical properties (unit weight, water retention ratio, porosity, void volume, and compressive strength) and the Los Angeles Abrasive index of the limestones were determined to be contingent with the quality of stone available and stringency of requirement (ASTM-373-56 and TS 699)[20].
- X-ray diffraction (XRD) analysis of finely pulverized limestone samples for the identification of the presented crystalline compounds. The analyses were performed with a Shimadzu XRD-6000. The diffraction interval was between 2θ–20°–60° with a step of 0.02°.
- 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 and lime in azot

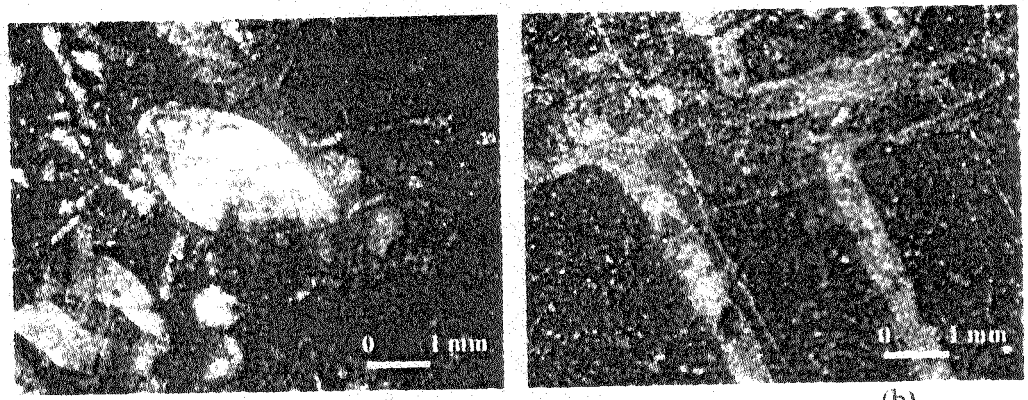
atmosphere at a temperature range of 25–1000°C and a gradient of 10°C/min.

- Mercury intrusion porosimetry (Autopore U 9220) was used to measure the microstructural characteristics of lime.
- Adsorption of nitrogen was performed on lime in order to evaluate the value of specific surface area by physical sorption isotherm data according to the method of Brunauer-Emmet Teller (BET).
- Scanning Electron Microscopy (SEM) (JEOL 840 AJXA) was carried out on limestone and calcined limes at different temperatures (600, 800, 1000 and 1200°C).
- Hydration rate $(T_{60})^{21}$ was performed in calcined lime at 1000–1050°C.

RESULTS AND DISCUSSION

Limestone samples were taken from two different limestone regions (L_c and L_k)[22]. The limestone samples for petrographic, mineralogic, physico-mechanical analysis, LA abrasion test and for calcination experiments were used.

Transmitted light microscopy (Nikon, Optiphot-Pol) was carried out in polished thin sections of the limestones in order to identify the texture, shape and size of the grains. Limestone L_k exhibited small to large size grains (470 ± 152 μ), which are distributed inhomogeneously throughout the mass. On the other hand, L_c presented fine grains (320 ± 136 μ), a compact and homogeneous texture. Microphotographs of limestones by transmitted light microscopy are illustrated in Fig. 1. Calcination will realize no problems and decrepitating will not be observed because of the fine grain size. The quality of calcinated limestone (lime) and chemical reactivity are observed to be well. The L_c limestones are taken from upper Eosen-Oligosen[23]. However, the L_k limestones are determined as of low-medium Miosen age. The determination of age is realized regarding fossils on the prepared thin sections. The fossils such as *Amphistegina* sp., *Berelin melo curdica*, Rotalidae, *Operalina* sp., *Heterastegina* sp., *Shaerogypsina* globule, *Sontes* sp., Miliolidae, *Peneroplia* sp., *Textularia* sp., algae and corals were observed in L_k.



(a) (b)

Fig. 1. Microphotographs of limestones (a) Lk, (b) Lc

The mineralogical composition of limestone was obtained by XRD analysis (Fig. 2). The main component proved to be calcite ($CaCO_3$) for both samples, although this does not preclude the possibility of the presence of small quantity (SiO_2).

Physico-mechanical properties[20] of the limestones were determined. The analysis results of limestones (L_k and L_c) are shown in Table-1. Both limestones indicate low values in porosity (lower than 1%). The value of apparent density (>2.55 g/cm^3) was found to be characteristic for a limestone. Comparing two limestones, L_k demonstrated higher values in porosity. Thus, L_c might be characterised as a more compact and harder limestone than L_k. The Los Angeles Abrasion Test is a severe accelerated test for measuring the abrasive resistance of limestone. It involves testing different specified weights and gradations of stone by a rotating mechanism in the Los Angeles machine. After 100–500 rpm, the sample is screened to determine the abrasive loss in the weight of the stone (Table-2). The calculated per cent of wear is lower (30%), the limestone is considered to be contingent with the quality of stone available and stringency of requirement.

TABLE-1

PHYSICO-MECHANICAL PROPERTIES OF THE LIMESTONES

L	γ (g/cm^3)	Aw (%)	η (%)	W (cm^3)	σ (kg/cm^2)
L_k	2.63	1.17	3.23	2.97	808 ± 147
L_c	2.61	0.49	1.26	1.43	614 ± 107

γ: unit weight, Aw: water retention ratio, η: porosity, W: void volume,
σ: compressive strength

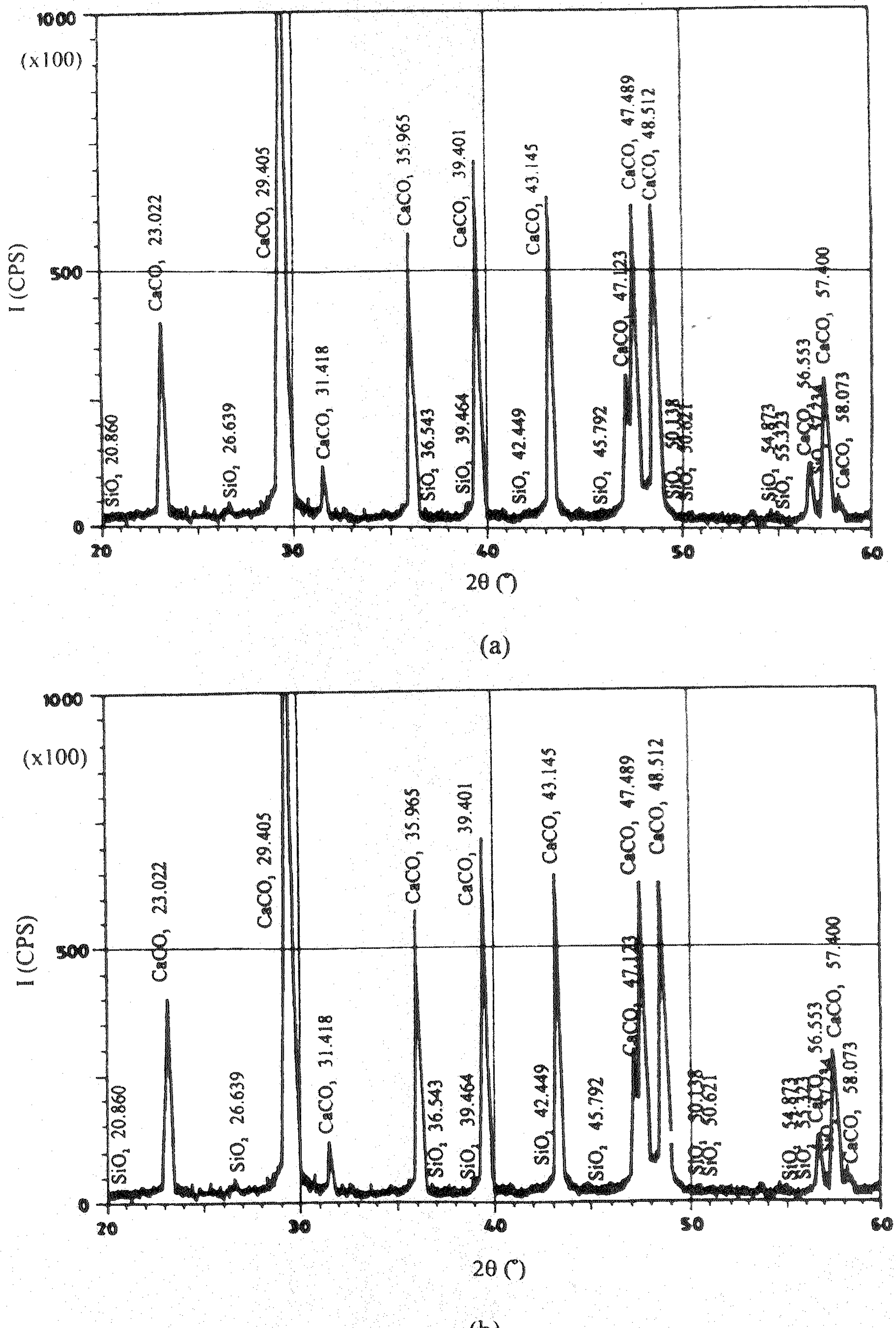
TABLE-2

LOS ANGELES ABRASION INDEX RESULTS

L_k	After the rotating drum (100 rpm), the amount of limestone remained on sieve (+1.44 mm):	4709 g	6%
	After the rotating drum (500 rpm), the amount of limestone remained on sieve (–1.44 mm):	3663 g	27%
L_c	After the rotating drum (100 rpm), the amount of limestone remained on sieve (+1.44 mm):	4702 g	6%
	After the rotating drum (500 rpm), the amount of limestone remained on sieve (–1.44 mm):	3720 g	26%

The weight loss above 600°C, measured by DTA-TG, is attributed to the CO_2 from the decomposition of calcium carbonate. Comparing the percentage values of CO_2 measured by DTA/TG, it is evident that the values are very high and similar to each other. Thus, both limestones could be characterized as high calcium ones. Furthermore, it is observed that the percentage of CO_2 for both limestones is higher than the theoretical one. DTA-TG curves for $CaCO_3$ are reproduced in Fig. 3. Limestone samples (L_k and L_c) are defined fully burned approximately at 944–961°C by DTA-TG, respectively. The endothermic peak at 195°C on DTA curve is attributed to loss of water and that is initiated at 682–691°C and completed at 944–961°C for L_k and L_c, respectively.

The chemical content of limestones is evaluated by XRF. The results are reported in Table-3. The relative content of carbonate compounds is analogous to that attained by XRD, DTA-TG and petrographic investigation. This fact might be ascribed to the presence of a small amount of dolomite in the limestone. Thus, from the chemical analyses, it can be concluded that both limestones presented identical chemical composition, with a percentage of calcite compounds greater than 98%.

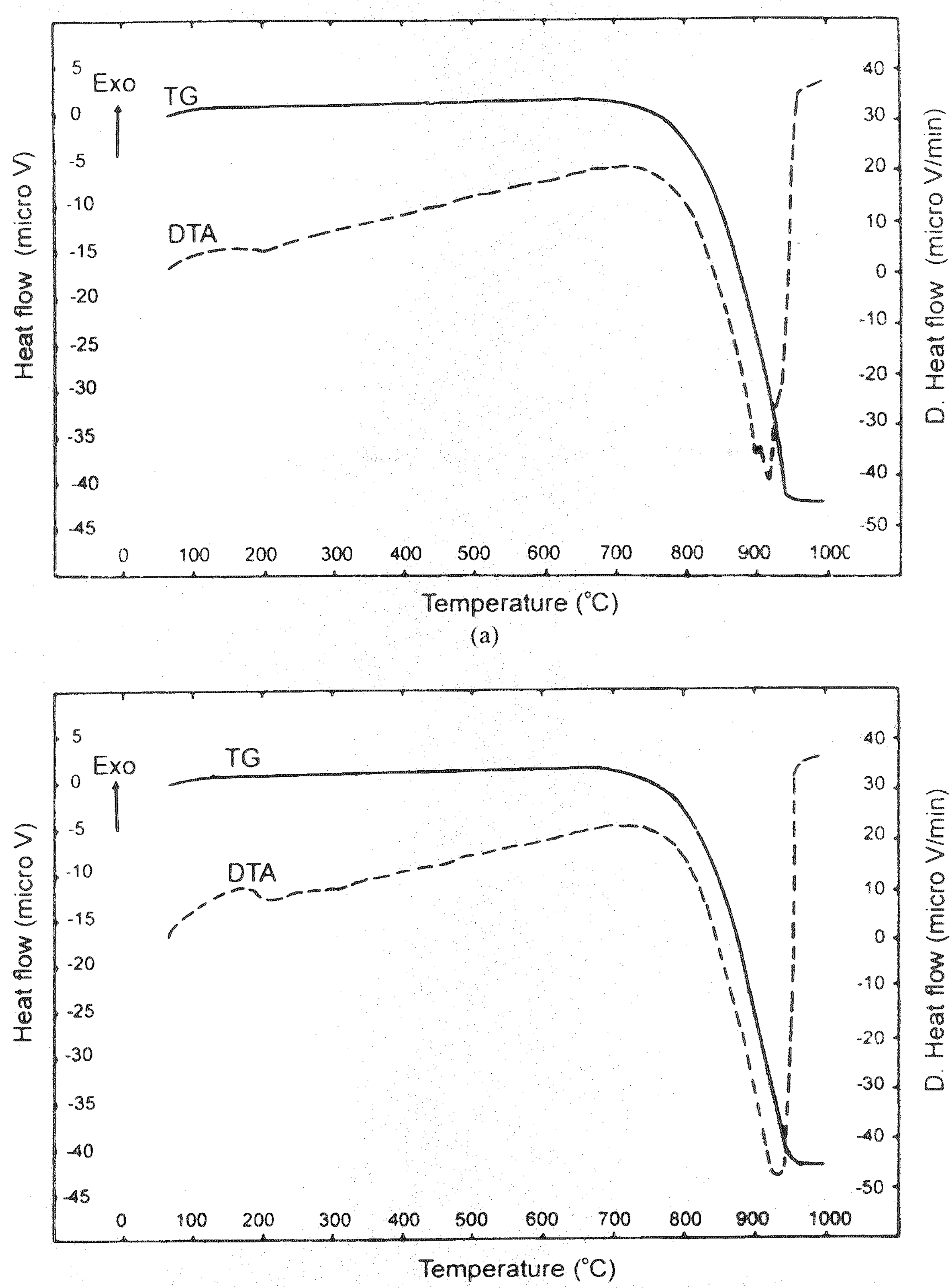


(a)

(b)

Fig. 2. Mineralogical analysis results of limestone: (a) L_k, (b) L_c

SEM shows that the most reactive lime is calcined lime at 1000°C (Figs. 4, 5). The higher temperatures were initiated by recarbonization with CO_2 on lime surface and porosity and surface area are declined.



(a)

(b)

Fig. 3. A thermogram for decomposition of calcium carbonate in an argon atmosphere: (a) L_K (b) $L_{Ç}$

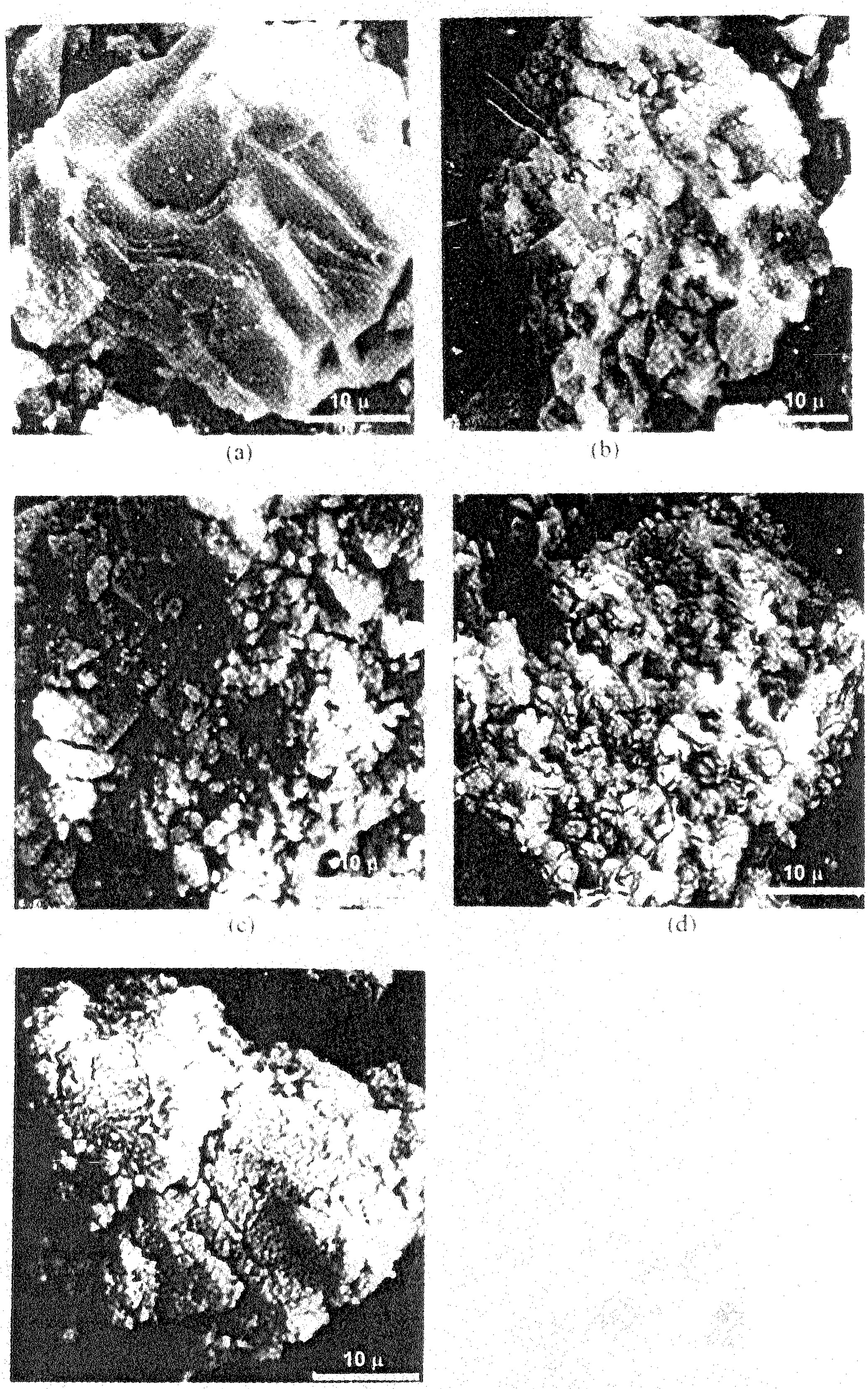
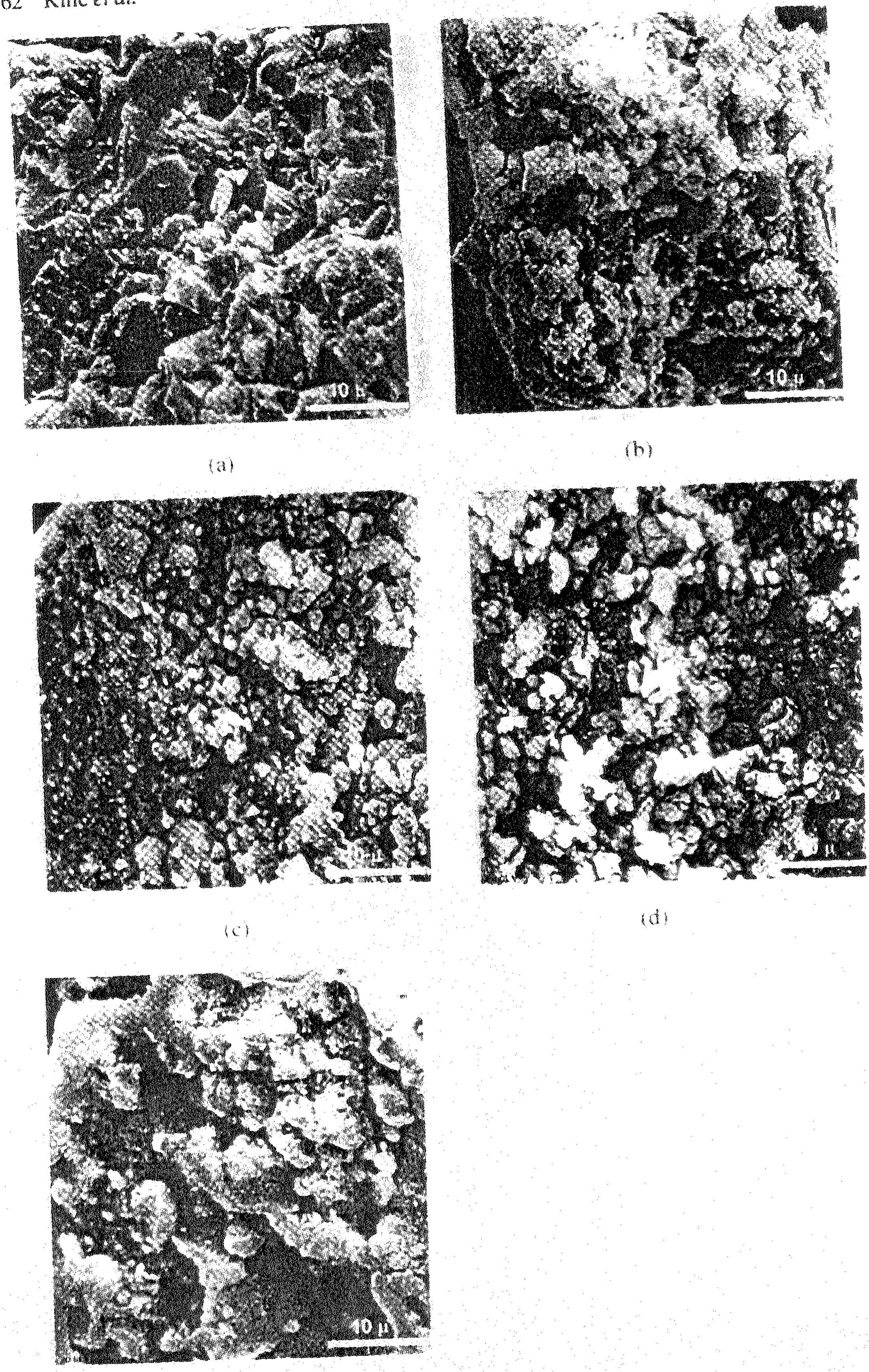


Fig. 4. L_k SEM images: (a) Limestone, (b) Calcined lime, 600°C, (c) Calcined lime, 800°C, (d) Calcined lime, 1000°C (e) Calcined lime, 1200°C



(a) (b)

(c) (d)

Fig. 5. L_c SEM images: (a) Limestone, (b) Calcined lime, 600°C, (c) Calcined lime, 800°C, (d) Calcined lime, 1000°C, (e) Calcined lime, 1200°C

TABLE-3
CHEMICAL COMPOSITIONS OF LIMESTONE

L	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	$CaCO_3$ (%)	$MgCO_3$ (%)
L_k	0.34	0.06	0.043	98.66	0.672
L_c	0.55	0.06	0.020	98.94	0.770

Calcination of the Limestone

The evaluation of the dissociation completion was performed by measuring the mass loss of the samples before and after calcination. The mass loss corresponds to the released amount of CO_2 during the calcination process. The results are considered satisfactory and in accordance with the data obtained by DTA-TG analysis (Fig. 3).

The measured percentage of mass loss is around 44% (eq. 1). Therefore, the dissociation of limestone and the production of lime are successfully accomplished.

$$CaCO_3 + Heat \rightarrow CaO + CO_2\uparrow \qquad (1)$$

Experimental calcination studies were performed by using cubic samples (*ca.* 30 × 30 × 30 mm) at different temperatures (650, 700, 750, 800, 850, 900, 950, 1000 and 1050°C) and calcination time is approximately 135 min in the small scale laboratuar furnace (Nabertherm) with thermal control. Limestone samples (L_k and L_c) are defined fully burned *ca.* at 1000°C (Table-4). The results have been supported by DTA-TG values.

TABLE-4
CALCINATION EXPERIMENTS AT DIFFERENT TEMPERATURES

Temperature (°C)	Calcination time (min)	Limestone	Weight (g)		$CO_2\uparrow$		CaO		$CaCO_3$ (g)	Size change (mm)
			BC	AC	g	%	g	%		
650		white	82.1	81.5	0.6	0.7	0.8	0.9	80.7	
		L_k grey	76.7	75.9	0.8	1.0	1.0	1.3	74.9	
		L_c beige	81.7	81.2	0.5	0.6	0.6	0.8	80.6	
700		white	79.8	78.2	1.6	2.0	2.0	2.6	76.2	
		L_k grey	82.9	80.7	2.2	2.7	2.8	3.4	77.9	
		L_c beige	78.6	72.1	1.5	1.9	1.9	2.4	75.2	
750		white	78	75	3	3.8	3.8	4.9	71.2	
		L_k grey	80.4	76.2	4.2	5.2	5.3	6.6	70.9	
		L_c beige	77.9	74.4	3.5	4.5	4.5	5.7	69.9	
800		white	80.6	73.6	7	8.7	8.9	11.1	64.7	
		L_k grey	83.5	74.7	8.8	10.5	11.2	13.4	63.5	
		L_c beige	88.0	81.6	6.4	7.3	8.1	9.3	73.5	
850	135	white	88.2	70.7	17.5	19.8	22.3	25.3	48.4	
		L_k grey	84.8	67.0	17.8	21.0	22.7	26.7	44.3	
		L_c beige	82.2	67.3	14.9	18.1	19.0	23.1	48.3	

Temperature (°C)	Calcination time (min)	Limestone	Weight (g)		CO_2↑		CaO		$CaCO_3$ (g)	Size change (mm)
			BC	AC	g	%	g	%		
900		L_k white	89.6	62.5	27.1	30.2	34.5	38.5	28.0	0.1
		grey	83.3	56.0	27.3	32.8	34.7	41.7	21.3	0.1
		L_c beige	83.1	60.2	22.9	27.6	29.1	35.1	31.1	0.1
950		L_k white	85.8	49.1	36.7	42.8	46.7	54.4	2.4	–1
		grey	86.9	49.8	37.1	42.7	47.2	54.3	2.6	–1
		L_c beige	76.7	45.0	31.7	41.3	40.3	52.6	4.7	–1
1000		white	83.9	47.0	36.9	44.0	47.0	56.0	0.0	–1
		L_k grey	99.1	56.4	42.7	43.1	54.3	54.8	2.1	–1
		L_c beige	84.7	47.5	37.2	43.9	47.3	55.9	0.2	–1
1050		L_k white	83.9	50.4	33.5	39.9	42.6	50.8	7.8	–1
		grey	87.8	53.7	34.1	38.8	43.4	49.4	10.3	–1
		L_c beige	90.1	55.71	34.4	38.2	43.8	48.6	12.0	–1

At 1000°C (burning temperature) or in a shorter burning duration, a burning test yields the desirable soft burned highly reactive limes of low shrinkage and density and high porosity. The analysis results of lime (L_k and L_c) are shown in Table-5.

TABLE-5
ANALYSIS RESULTS OF LIME

L (°C)	R_m (μm)	A_s (m^2/g)
L_k 600	0.0957	1.66
L_k 800	0.0266	4.42
L_k 1000	0.0596	9.46
L_k 1200	0.5635	0.70
L_c 600	0.9850	0.58
L_c 800	0.0258	4.10
L_c 1000	0.0535	8.30
L_c 1200	0.6678	1.20

R_m: Pore radius average, A_s: specific surface area.

Table-5 presents the microstructural characteristics of produced lime evaluated by mercury intrusion porosimetry and nitrogen adsorption. It can be observed that for both samples, total cumulative volume, total porosity and specific surface area decrease as the calcination temperature rises, whereas the values of apparent density and pore radius average increase. The values of specific surface area measured by nitrogen adsorption are slightly increased in relation to the porosimetric ones. The upper increase can be attributed to the nitrogen adsorption capability to measure smaller pores. The value of specific surface area becomes maximum for the calcination temperature of 1000°C and obtained available lime CaO: 90.47, 90.90%; total CaO: 95.28, 96.91% and T_{60}: 3.25 min, 2.41 min, L_c and L_k, respectively.

Comparing the two samples, L_k (1000°C) presents higher values in total cumulative volume, total porosity and specific surface area than L_c (1000°C). Hence, the limestone and lime microstructure and texture can be related. Limestone L_k exhibits a rather porous structure and after calcination, the produced lime seems to maintain this structure, presenting high values in porosity, total cumulative volume and specific surface area. On the other side, limestone L_c, which is a hard and compact limestone with low porosity, produces lime with denser structure, lower porosity, lower specific surface area and higher pore radius average after calcination than L_k. In addition, observing the values of apparent density and total cumulative volume for the samples, it is evident that limestone L_k presents higher volume contraction than L_c during calcination.

SEM, Figs. 4 and 5, present the pore size distribution overlay for L_k and L_c, respectively, produced at 1000 and 1200°C. It is observed that with increase of calcination temperature, the pore radii are shifted to larger pores with elimination of smaller pores due to the coalescence phenomenon occurring during calcinations (eq. 1).

Conclusions

This study investigated the effect of limestone characteristics and calcination temperature on lime quality and reactivity. Lime produced by calcination of limestone L_k was more reactive than the one produced by L_c. L_k exhibits small to large size of crystals, not only an inhomogeneous distribution throughout the mass, but also a less compact structure than L_c. L_k can be characterized as high-calcium limestone with low content of impurities. Further investigation should be accomplished regarding the effect of limestone texture on lime reactivity.

In this study, the unit weight of the limestone is larger than 2.55 g/cm^3, the compressive strength is larger than 600 kg/cm^2 and Los Angeles Abrasive strength is less than 30% wear is found. These findings show the fact that these limestones have compact texture and this type of stones are preferred in the production of lime. Lime will have a good quality.

From the results obtained, it is obvious that the lower the calcination temperature, the higher the specific surface area and the more reactive the lime. The greatest surface area was obtained for limestone calcined at 1000°C which was the temperature performed in lime kilns. High calcination temperatures acquired in limekilns are the major reason for the production of low quality lime.

The specific surface area can be a reliable factor for the estimation of lime reactivity. The greater the specific surface area the more reactive the lime. The rate of temperature increase may be an additional parameter for the evaluation of lime reactivity which is augmented by increasing the lime reactivity.

In addition, according to both available lime value and low T_{60} reaction speed experiments' results, the produced lime will have a good quality and high reaction.

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