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# Influence of porosity and grain size of carbonate rocks in the reactivity of lime

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Keywords: limestone, marble, lime, reactivity, slaking temperature, specific surface area

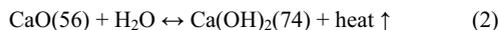
**ABSTRACT:** The influence of porosity and calcite crystal size on the reactivity of lime produced from limestones from Kefalonia (Lk) and Arta (La) areas, and marbles from Asfendou, Crete (Ma) and Naxos Island (Mn) was studied. Lime reactivity was studied in terms of specific surface area and slaking temperature. In all cases the specific surface area displays a maximum at low firing temperatures decreasing thereafter. In rocks with low porosity lime reactivity depends on calcite crystal size. Very small calcite crystal sizes comparable to that of lime crystals yield lime with low reactivity due to low porosity of the end products. The lime produced from raw materials with large crystal size has inferior reactivity due to kinetic constraints. In materials with small calcite crystal sizes comparable to that of lime crystals reactivity of lime is controlled by porosity of the starting materials.

## 1 INTRODUCTION

Carbonate rocks are among the most widespread and widely utilized mineral commodities. They constitute about 15% of the sedimentary crust (Carr et al. 1994). Limestone, the most important and abundant of all sedimentary rocks that are utilised commercially, is a general term embracing carbonate rocks and is composed primarily of calcium carbonate ( $\text{CaCO}_3$ ). The principal chemical property of limestone is its thermal decomposition, in which the co-products lime (CaO) and carbon dioxide are formed (Boynton, 1980). This reversible reaction generally known as decarbonation, is stated chemically with molecular weights for high calcium limestone as follows:



Lime is the calcined form of limestone, commonly known as quicklime, or when water is added calcium hydroxide or slaked lime ( $\text{Ca(OH)}_2$ ). The hydration of quicklime is displayed with molecular weights in the following chemical reaction:



Lime is an important industrial chemical used widely in the steel manufacturing, water treatment industries, in the desulfurization of combustion gases, cement manufacture and in the construction industry (Oates, 1998).

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 the cement paste in concrete. In the literature, there are several references concerning factors that may affect the properties of the quicklime and hydrated lime. Generally, these factors are characteristics of the rock, calcination temperature, rate of calcination, etc. (Fuentes et al. 1993).

In this study different physical characteristics of calcium carbonate rocks (two limestones and two marbles), such as porosity, crystal size and texture, are examined. These parameters affect important properties of the produced quicklime after calcination in different times and temperatures like specific surface area and thus reactivity.

## 2 REGIONAL GEOLOGY

The first limestone comes from the Kampi Area N-NW of Arta town in Greece, from a licensed limestone quarry operated by Kampi Quarries S.A. The material is an Upper Cretaceous, almost horizontal pelagic limestone, striking NNE-SSW, which belongs to the Ionian Geotectonic Unit. In the lower sections the deposit is thick-bedded and has brecciated texture. The thick limestone beds are separated by 30 cm thick intercalations of sub lithographic material with *Globotruncanidae* fossils (Monopolis, 1969).

The origin of the second limestone is the Kefalonia Island in Western Greece. Samples were collected from a quarry operated by IONIAN KALK S.A. in the SW part of the island. The material is an Eocene-Oligocene unbedded chalk, with, intercalations of chert nodules. The limestone has a limited outcrop and is usually fractured and strongly karstified in the upper horizons. They belong to the Paxos Geotectonic Unit and have maximum thickness 100m (Bergmann, 1964).

The first marble was collected from Naxos Island, Cyclades, Aegean. It is a Pre Permian coarse crystalline white marble, which belongs to the Cyclades Geotectonic Unit. A thick layering is in most cases visible in the region, often marked with thin amphibolite streaks. Other minerals found in the marbles are phlogopite, diopside and sphene. The calcite marbles are usually coarser grained than the dolomitic marbles of the same degree of metamorphism present in the area (Jansen, 1973).

The second marble comes from the Asfendou area in Chania region of Crete Island. It's a white-to-off white marble that belongs to the Plattenkalk Geotectonic Unit. This medium crystalline Upper Triassic marble is overlain by platy recrystallized marbles (Vidakis, 1987).

### 3 EXPERIMENTAL

The carbonate rock samples were coded as follows: Lk, La for the limestones from Kefalonia and Arta and Mn, Ma for the marbles from Naxos and Asfendou respectively. All samples were crushed, ground and classified according to their particle size. The No. 6 sieve size was picked according to the ASTM C-100 Physical Tests for Lime, for the slaking rate test and the measure of the specific surface area of the quicklime.

The crushed samples were fired at temperatures ranging between 800°C and 1000°C for 1 and 4 hours to produce quicklime. The different time and calcination temperatures were used to examine the reactivity of the produced quicklime.

#### 3.1 Analytical methods and techniques

Analyses were performed in the limestone and marble samples as well as in the produced quicklime, by using the following experimental techniques.

- Polished thin sections of all materials were examined with optical microscope (JENA LAB). Broken surfaces of the samples coated with gold were analysed with scanning electron microscope (JEOL JSM 5400). Both methods have been used to determine the texture and grain size distribution of the materials, with the Image-Pro Plus version 3.0-image analysis software.

- X-ray diffraction (XRD) analysis (Siemens D-500 XRD, CuK $\alpha$  radiation, graphite monochromator,

35 kV and 35 mA) of finely ground powders was used to study the reaction progress and to identify the reaction products.

- Calcimetry (gas volumetric method, Dietrich Frühling) was carried out in pulverized samples to determine the calcite content, by calculating the amount of carbon dioxide given off after reaction with HCl.

- Chemical analysis of the major elements present in the whole rock samples was carried out with an SRS 303 X-ray fluorescence spectrometer (XRF).

- Mercury intrusion porosimetry (Micrometrics, Autopore IV 9500 V1.05) was used to measure the microstructure characteristics of the raw samples. The total porosity, apparent density, average and median pore diameter was determined.

- BET surface area of the calcined samples was measured with a NOVA 2200 (Quantachrome) BET analyser, using N $_2$  as adsorbent gas. Before surface area determination, the samples were degassed for eight hours at 140 °C.

- Determination of the reactivity of the produced quicklime was accomplished by measuring the hydration temperature during slaking, according to ASTM C110.

## 4 RESULTS

### 4.1 Mineralogy

The mineralogical composition of the raw materials is listed in Table 1. The main component is calcite for both limestones and marbles. Traces of quartz are present in all samples except Lk and traces of dolomite were found in the La and Ma samples.

Table 1. Results of XRD analyses.

	cc	Q	dl
Lk	+++	-	-
La	+++	+	+
Mn	+++	+	-
Ma	+++	+	+

+++ = dominantly present, += traces, -= not present. cc = calcite, Q = quartz, dl = dolomite.

The materials calcined at 800°C for 1 and 4 hours and at 850°C for 1 hour contain small amounts of calcite crystals. This indicates that in these firing conditions the conversion of limestone to lime is incomplete.

### 4.2 Chemistry

The results of the chemical analyses (XRF and calcimetry) are presented in Table 2.

The theoretical composition of high calcium limestone is 56% CaO and 44% CO $_2$ . However, no limestone of this purity is commercially available. For practical purposes high-quality high calcium carbonates contain 97-99% CaCO $_3$  (Boynton, 1980).

Table 2. Chemical composition of the samples (wt %).

	XRF			
	Lk	La	Mn	Ma
SiO <sub>2</sub> %	0.05	0.98	0.30	0.40
Al <sub>2</sub> O <sub>3</sub> %	1.13	0.71	0.10	0.13
Fe <sub>2</sub> O <sub>3</sub> %	0.02	0.35	0.09	0.04
MnO%	-	0.02	0.005	-
MgO%	0.15	0.91	0.13	0.95
CaO%	54.80	54.30	55.01	54.90
Na <sub>2</sub> O%	0.02	0.03	0.04	0.04
K <sub>2</sub> O%	0.03	0.02	0.5	-
LOI	43.91	42.82	43.77	43.89
TOTAL	100.11	100.14	99.95	100.35
CALCIMETRY				
%CaCO <sub>3</sub>	99.70	98.12	98.65	98.87
%CO <sub>2</sub>	43.86	43.17	43.40	43.69

The XRF and calcimetry results show that all samples are high purity limestones and marbles. The slightly higher amounts of MgO present in the materials from Arta and Asfendou are attributed to the minor amounts of dolomite present (Table 1).

### 4.3 Grain size and texture

La is a very compact, extremely fine-grained micritic material with occasional sparitic cement and abundant foraminifers fossils. The mean grain size is 1.5  $\mu\text{m}$ . These clay- size calcite grains are the main constituents of the rock. The size of the sparite crystals exceeds 1mm in places. Trace amounts of quartz crystals have been detected. Lk is a fine-grained, biomicritic, chalky material with a mean grain size of 4.1  $\mu\text{m}$ . It is a remarkably pure rock with more than 99 per cent calcium carbonate. Some 75-90 % of the carbonate is in the form of organic particles most of which are smaller than 4  $\mu\text{m}$ .

Ma consists mainly of calcite. It is semi-coarse grained with a mean calcite grain size of 335  $\mu\text{m}$ . The calcite crystals are orientated and they display polygonal habit in places. They are frequently intergrown, and the larger crystals display multiple twinning. Trace amounts of euhedral dolomite crystals have been detected.

Finally, the marble from Naxos is coarse-grained, with small amounts of fine-grained calcitic material. The mean calcite crystal size is 656  $\mu\text{m}$ . The calcite crystals display typical polygonal habit and frequently multiple twinning.

### 4.4 Microstructural characteristics

Mercury intrusion porosimetry and density results are shown in Table 3. Data are expressed as  $P\%$  (percentage total porosity),  $d$  (apparent density),  $D_A$  (average pore diameter) and  $D_M$  (median pore diameter).

The marbles have a low porosity and high values of median and average pore diameter. There is a significant difference in the porosity of the two limestones. La has a low porosity and  $D_A$ ,  $D_M$  values, comparable to those of marbles. By difference Lk

has a high porosity and higher values of  $D_A$  and  $D_M$ . Thus, La is a more compact and harder limestone than Lk.

Table 3. Porosimetric data of samples

	$P\%$	$d$ (g/cm <sup>3</sup> )	$D_A$ ( $\mu\text{m}$ )	$D_M$ ( $\mu\text{m}$ )
Lk	18.5	2.5968	1.7458	0.5795
La	3.2	2.5874	0.2545	0.0292
Mn	3.8	2.7585	15.5094	0.9486
Ma	4.1	2.6642	6.1776	0.3683

### 4.5 Reactivity

The evolution of the specific surface area and the maximum hydration temperature after slaking, of the quicklime produced from calcination, at different firing conditions, are shown in Table 4. The relationship between specific surface area and firing temperature, which determine the reactivity of quicklime, is presented in Figures 1,2.

Table 4. Evolution of quicklime's specific surface area and maximum hydration temperatures for the different calcination conditions.

Temp	Specific Surface Area (m <sup>2</sup> /gr)									
	800 °C		850 °C		900 °C		950 °C		1000 °C	
Time	1h	4h	1h	4h	1h	4h	1h	4h	1h	4h
Lk	9.6	9.4	8.7	8.1	8.4	7.6	7.3	5.2	4.5	2.1
La	7.3	6.9	4.8	4.1	4.4	3.2	4.2	3.0	2.6	2.1
Mn	12.5	12.3	8.8	5.7	5.1	3.1	4.4	2.6	4.0	2.5
Ma	10.9	10.3	9.6	8.5	9.3	7.6	9.2	7.0	6.3	4.0
Temp	Max. Slaking Temperature (°C)									
	800 °C		850 °C		900 °C		950 °C		1000 °C	
Time	1h	4h	1h	4h	1h	4h	1h	4h	1h	4h
Lk	38	70	39	71	65	78	67	79	69	73
La	39	59	41	60	52	66	63	68	66	66
Mn	35	66	38	69	46	70	71	73	75	68
Ma	44	68	46	69	62	70	67	77	73	72

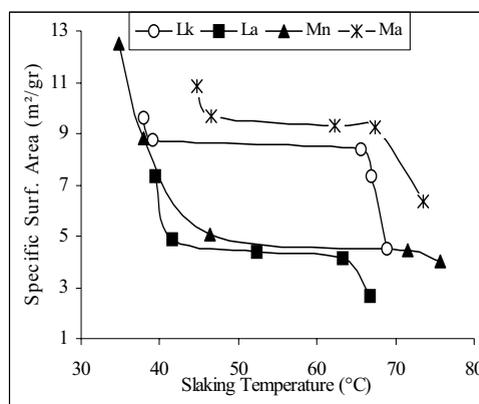


Figure 1. Relationship between slaking temperature and specific surface area of the produced quicklime. Calcination temperatures 800-1000°C, time 1 hour.

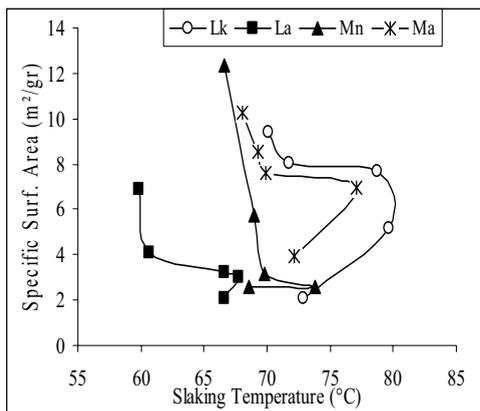


Figure 2. Relationship between slaking temperature and specific surface area of the produced quicklime. Calcination temperatures 800-1000 °C, time 4 hours.

## 5 DISCUSSION – CONCLUSIONS

Specific surface area of the quicklime is an important factor, which affects lime reactivity (Figure 1, 2). The quicklime produced by calcination of Lk has a higher reactivity compared to the quicklime produced by La, while the quicklime formed by calcination of Ma is more reactive compared to the lime produced by Mn. La and Lk have considerably different porosity but comparable grain size. La has a smaller average calcite crystal size, a more homogeneous size distribution and a smaller porosity i.e. a more compact structure compared to Lk. In this case porosity is the main factor controlling lime reactivity: the higher the porosity the higher the reactivity of the lime. Ma and Mn have comparable porosity but considerably different average crystal size. The quicklime derived from Ma is more reactive than that from Mn. Therefore in the case of marbles the smaller the calcite crystal size, the higher the reactivity of the produced lime.

Lk and Ma have considerably different grain size and porosity. Yet they yield lime with comparable characteristics both at short and long firing cycles. Also La and Mn have considerably different grain sizes but yield lime with comparable characteristics at short firing cycles. Calcite crystal size of La is comparable to that of produced lime (*ca* 1  $\mu$ m), suggesting lower lime porosity after sintering, and thus a lower reactivity. Lk also has a small calcite crystal size. However it has a high porosity yielding a very reactive lime. Finally Ma and Mn have comparable maximum slaking temperatures, but at different firing temperatures due to different reaction kinetics, caused by different crystal size of calcite.

The curves in Figures 1 and 2 consist of three parts. The first part at 800-850°C (900°C for Mn) is

dominated by a rapid decrease of specific surface area at nearly constant slaking temperatures and corresponds to the completion of reaction of lime formation. The high values of specific surface area at low temperatures, when the reaction is incomplete, are likely due to existence of amorphous material, which acts as a precursor of lime (Christidis et al. 2001). The second part is characterized by constant specific surface area and significant increase of the slaking temperature. This is better illustrated at short firing cycles and may correspond to lime crystal growth via sintering (Christidis et al. 2001). In the third part both the slaking temperature and specific surface area (i.e. reactivity) of quicklime decreases rapidly, due to dead burning of lime by prolonged sintering. Dead-burning usually begins at temperatures close to and above 1000°C, and affects adversely the quality and the hydration properties of lime (Scott et al. 1983). The different properties of lime derived from Mn at different firing times underline the influence of calcite crystal size on firing.

As a conclusion porosity, calcite grain size and pore size distribution are interrelated and affect reactivity of quicklime. Materials with very small calcite crystal size and low porosity yield lime with low reactivity. There is considerable variation in porosity, grain size and other properties of carbonate rocks which affect reactivity of quicklime. Further work is needed to evaluate the effect of crystal shape, texture and quantity of raw materials on lime reactivity.

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