



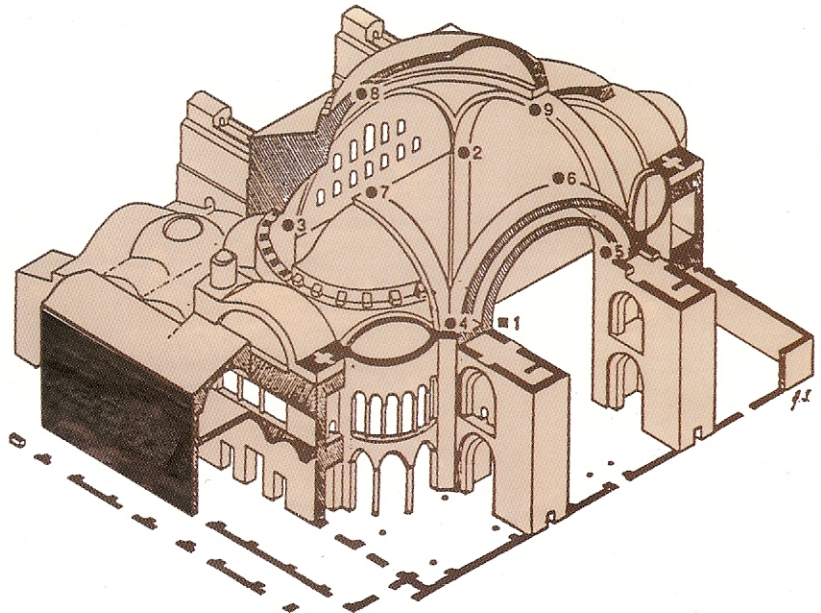
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## **COMPATIBLE MATERIALS RECOMMENDATIONS FOR THE PRESERVATION OF EUROPEAN CULTURAL HERITAGE**

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## **THE USAGE OF ULTRASONIC TECHNIQUES AT CALCINATION STUDIES**

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### **Abstract**

In the present investigation the ultrasonic techniques were used in order to determine quantitatively the quality changes of the lime during the calcination of the limestone. This method was investigated because the final product is usually very weak and the static methods are impossible to used. The P & S wave velocities were measured in different temperatures and the determined high correlation coefficients improved the reliability of the method used.

### **Introduction**

The principal chemical property of limestone is its thermal decomposition. It is due to this characteristic that the process of calcination created lime manufacturing. This process commences on the exterior surfaces and progresses inwards as the surrounding temperature increases. As the release of CO<sub>2</sub> involves a general weight loss of 40-44% the porosity of the material is increased giving a mass of CaO with a large internal surface area and hence, high chemical reactivity.

There are numerous critical variables in limestone calcination that can exert a serious effect on lime quality. In decreasing importance such variables may be (Boynton, 1980; Oates, 1998): Degree of calcite crystallinity, types and quantities of impurities, rate of calcination, calcination duration and temperature, chemical reactivity, shrinkage etc. Burning technology and kiln design are also important factors in determining the quality of the lime.

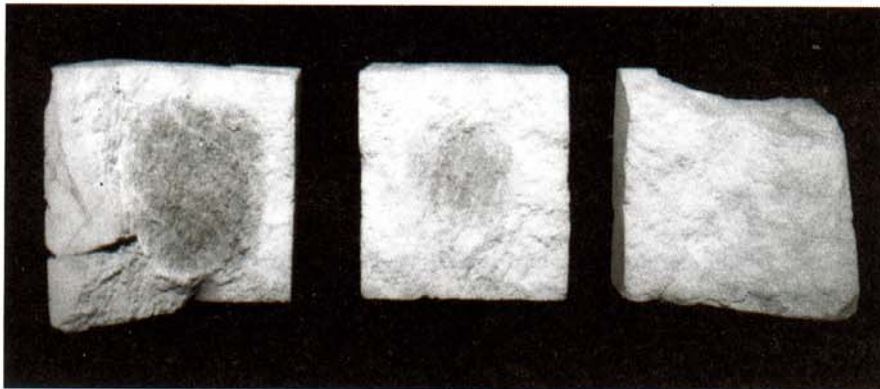
The quicklime that produced from this process has very weak mechanical characteristics, so it is very difficult to determine the quality of this product using static methods. These methods are unable to be applied on the lime

because they destroy the specimens and the results are not representative. Furthermore, the final product can easily be decomposed to powder in slightly humid environment.

The aim of our study was to establish a non-destructive methodology that could describe quantitatively the calcination progress. For this purpose the ultrasonic technique was used with application in different temperature, in order to verify the reliability of the proposed method.

### Materials and Methods

Forty two cubic specimens of the gray-green carbonate rocks from the Agios Panteleimonas region of Florina, Macedonia, Greece, with mean edge length about 60 mm were calcined at 950 and 1,050°C at different time conditions in order to determine its elastic parameters. Preheating lasted 150 min, while the retention time at each selected temperature was 60, 120 and 180 min respectively. Calcination was performed in a Naber-Multitherm N11/HR furnace (Fig. 1).



**Fig. 1:** Calcination of limestone at 1050°C at different retention times.

The elastic parameters may be determined by static or dynamic methods. In this paper a dynamic method was used. Thus, the cubic test specimens were subjected to compression and shear wave pulses. Wave velocity is calculated from the travel time of the pulse through the specimen. Specimens may be loaded to approximately field conditions because both P and S wave responses increase with compression. Ultrasonic velocities were measured as compression ( $V_p$ ) and shear ( $V_s$ ) according to the French specification AFNOR NF B 10505. Both compression and shear wave measurements were made using a Pundit velocimeter.

## Results and Discussion

The ultrasonic velocities  $V_p$  and  $V_s$ , as well as the dynamic modulus of elasticity ( $E_d$ ) and Poisson's ratio ( $P_d$ ) results are given in Table 1. The measurements are performed on cubic specimens with mean edge length 60 mm, which were calcined at 950 and 1,050°C. The elastic moduli  $E_d$  and  $V_d$  of the calcined specimens were calculated using the following formulas:

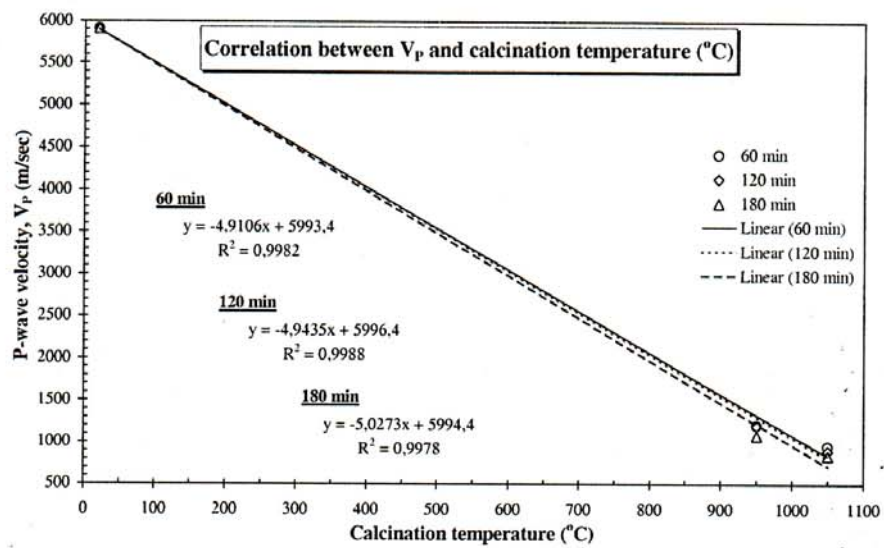
$$E_d = c \times D \times V_s^2 \times \frac{3V_p^2 - 4V_s^2}{V_p^2 - V_s^2}$$

and

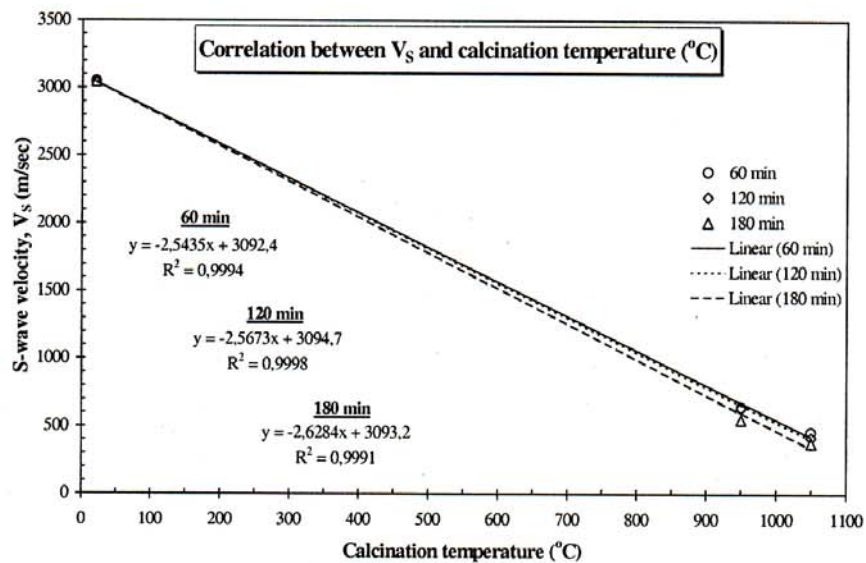
$$P_d = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)}$$

where  $c$  = constant depending on the units used (for SI = 1000.6),  $D$  = dry apparent weight of the material ( $\text{g/cm}^3$ ) and  $V_p$ ,  $V_s$  = velocities of P and S waves (m/sec).

Sample	Calcination conditions T(°C)/Retention time (min)	L.O.I. (%)	$V_p$ (m/sec)	$V_s$ (m/sec)	$E_d$ (MPa)	$P_d$
1	Initial material	-	6014	3088	65.9	0.32
		-	5931	3054	64.0	0.32
		-	5808	3005	61.4	0.32
2	950/60	18.7	1207	640	2.2	0.30
		19.3	1163	611	2.0	0.31
		14.4	1239	666	2.5	0.30
3	950/120	24.2	1161	609	1.8	0.31
		24.6	1246	671	2.2	0.30
		18.6	1190	631	2.1	0.30
4	950/180	28.9	1089	556	1.4	0.32
		30.1	1121	580	1.5	0.32
		23.4	1028	512	1.3	0.34
5	Initial material	-	5901	3042	62.9	0.32
		-	5955	3066	64.9	0.32
		-	5835	3016	62.5	0.32
6	1050/60	37.7	962	464	0.9	0.35
		37.0	924	436	0.8	0.36
		34.9	965	466	0.9	0.35
7	1050/120	41.6	905	422	0.7	0.36
		42.0	922	434	0.7	0.36
		41.1	864	392	0.6	0.37
8	1050/180	43.8	963	464	0.8	0.35
		43.9	739	301	0.3	0.40
		43.9	822	362	0.5	0.38



**Fig. 2:** Correlation between mean velocity of P-waves (m/sec) and calcination temperature ( $^{\circ}\text{C}$ ) at different retention times.



**Fig. 3:** Correlation between mean velocity of S-waves (m/sec) and calcination temperature ( $^{\circ}\text{C}$ ) at different retention times.

The mean values of the P- and S-wave velocities were 5907 and 3045 m/sec respectively. The elastic parameters of the initial material were  $E_d = 63.6$  MPa and  $P_d = 0.32$ . Kantiranis et al. (1999) were found  $E_d=64.7$  MPa and  $P_d= 0.36$ .

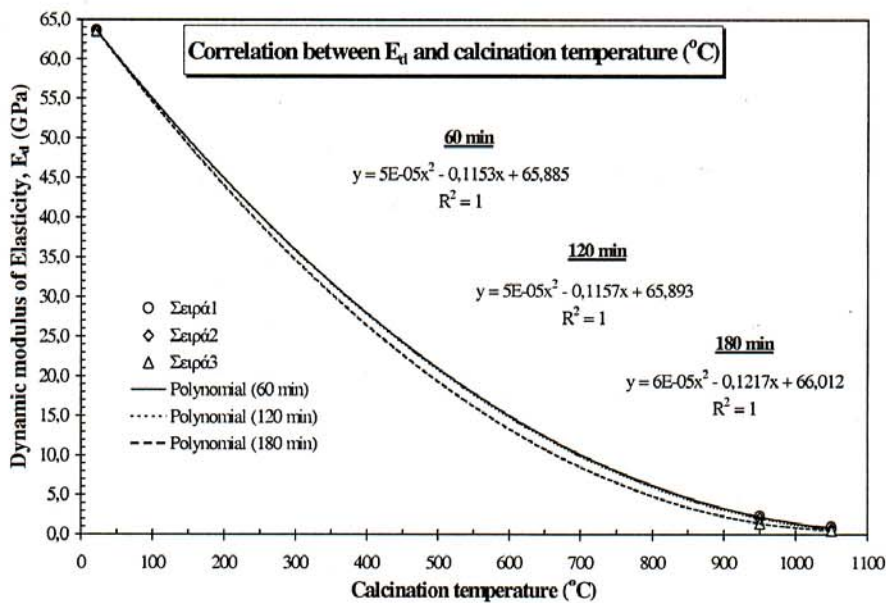
Between the P-wave velocities and calcination temperature at different retention time a very good linear correlation exists at all conditions (Fig.2). Also, a very good linear correlation observed between S-wave velocities and calcination temperature at different retention times (Fig. 3).

Between the dynamic modulus of elasticity and the calcination temperature a very good polynomial correlation exists (Fig. 4). Kantiranis (1998) and Kantiranis et al. (1999) applying the method of least squares it is concluded that these two variables correlate linearly by the formula:  $Y=16.4442-0.0151X$ , where  $Y$ =dynamic modulus of elasticity (MPa) and  $X$ = calcination temperature ( $^{\circ}C$ ).

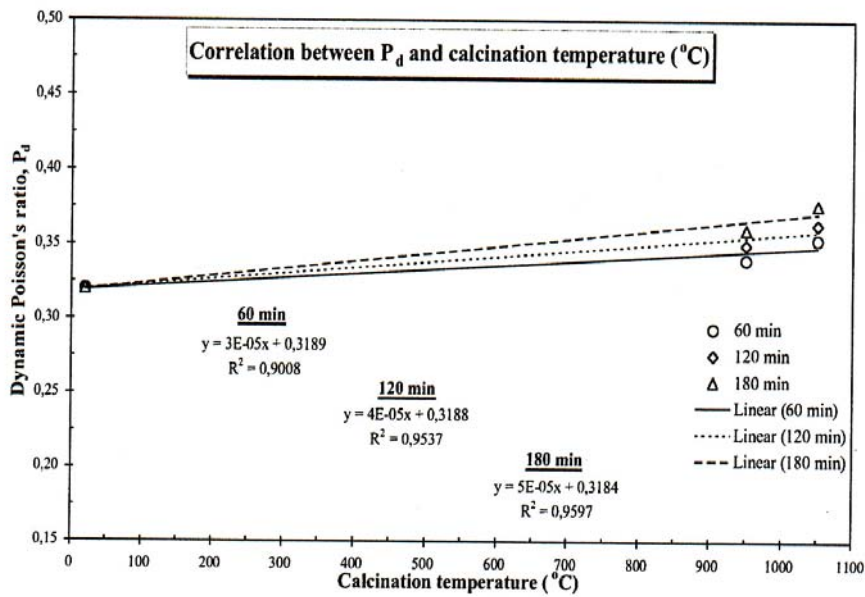
Between the dynamic Poisson's ratio and the calcination temperature a very good linear correlation is noted (Fig. 5). Kantiranis (1998) and Kantiranis et al. (1999) applying the least squares method a very good linear correlation is taken as the following formula shows:

$$Y=-0.51685+0.000846X,$$

where  $Y$ =dynamic Poisson's ratio and  $X$ =calcination temperature ( $^{\circ}C$ ).



**Fig. 4:** Correlation between mean dynamic modulus of elasticity,  $E_d$  (MPa) and calcination temperature ( $^{\circ}C$ ) at different retention times.



**Fig. 5:** Correlation between Poisson's ratio and calcination temperature ( $^{\circ}\text{C}$ ) at different retention times.

Ultrasonic velocity is not only an indication of the above two moduli but additionally is a very good index for rock quality and weathering determination (Irfan & Dearman, 1978; Auger, 1988; Topal, 1995; Christaras et al., 1994) as well as for the determination of rock anisotropy (Christaras, 1994). Decrease of the dynamic modulus of elasticity is followed by increase in the rock porosity (Hamrol 1961; Kantiranis et al., 2000).

### Conclusions

According to our investigation the ultrasonic technique gives reliable information on the quantitative changes of limestone into lime, during a calcination process, in different temperatures. The use of this non-destructive technique is very useful, tacking into account that the final material is very soft and humidity changes it easily into powder so as to be practically impossible to use static methods for tests.

For the determination of the above result, the P & S wave velocities were measured through the mass of calcinated specimens in different temperatures and test results were correlated with temperature. Young modulus and Poisson ratio were also examined.

### Acknowledgments

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