Reactivity of hydraulic lime binders: A proposed laboratory testing technique

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Session ERE5.3 Sustainability of traditional construction materials in modern society

Hydraulic limes are traditional construction materials that have re-emerged in 21st century as binders used in restoration works, since compatibility with the original structures is one of the fundamental principles of modern conservation. Natural hydraulic limes are produced by firing of raw materials, such as argillaceous or siliceous limestones at relatively low temperatures with reduction to powder by slaking with or without grinding. During firing silica reacts with calcium oxide (CaO), produced by the decomposition of calcite, to form calcium silicates wich induce hydraulic properties to the end products. Natural hydraulic limes contain mainly portlandite, $Ca(OH)_2$ and dicalcium silicate (mineral phase of larnite - Ca_2SiO_4).

Production of good quality hydraulic lime binders is as much a craft as a technology. In order to produce natural hydraulic lime with great performance characteristics, it is of great importance to determine those calcination conditions in which the produced binder is composed not only with a high amount of hydraulic phases, but also a great percentage of soft-burned lime, which is characterized by high specific area and chemical reactivity. The free lime content is responsible for workability and self healing in NHL mortars.

The raw material used in this study is a Neogene marly limestone from Central Crete, Greece. The main minerals present in the raw samples are calcite and quartz, whereas clays, micas, dolomite and feldspars where detected in minor amounts. The chemical analyses (Table 1) showed that the CaO/SiO_2 ratio is sufficient for formation of calcium silicate mineral phases after firing (Ref. 4).

A series of calcination experiments was undertaken in the range 850 – 950 °C for 3, 6, 9 and 12 hours respectively. The calcination products were examined by means of X-ray diffraction (XRD). In the region 30 - 42° 2θ, peaks of lime, larnite and portlandite dominate each pattern. Gehlenite, aluminate and ferrite phases and quartz are present in minor amounts (Fig. 3). The time of calcination affects the crystallinity of larnite. More crystalline products are derived after 12 hours of calcination (Ref. 3). An increase in the percentage of larnite is observed after 12 hours of calcination at any temperature. The products retain a high percentage of available lime which decreases slightly as the firing becomes more intense (Table 2).

This case study proposes the laboratory testing of the reactivity of hydraulic limes that have been classified regarding their degree of hydraulicity (Cementation Index equals to 0,3) as feebly hydraulic (Ref. 4), according to the slaking rate test. Optimization of calcination conditions is aimed in order to obtain a product with a high ratio of hydraulic components and a highly reactive content of free lime, at firing temperatures below 1000 °C.

Slaking rate tests provide a measure of the overall degree of reactivity of the material. Slaking rate curves indicate that calcination of the raw materials at 950 °C for 12 hours yield products with less reactive lime (Fig. 4). Temperature rise (T_u) as long as the time required for the reaction to be completed (t_u) are largely dependent not only on the available lime content of each sample, but also from calcination conditions (Fig. 5). The ratio of β-Ca_2SiO_4/CaO follows the calcination conditions effect upon reactivity (Fig. 6). The duration of calcination affected considerably the reactivity of the produced calcium oxide. The great variance of reactivity of the samples calcined at 950 °C for 3 and 12 hours is obvious. The specific surface area of the binders varies and affects the rate of reactivity (Fig. 7).

Based on the experimental results it is obvious that calcination conditions mostly affect the reactivity of the produced hydraulic limes and not so much the quantity of the mineral phases produced. Calcination at lower temperatures and shorter time periods, produces more reactive free lime. The most reactive binder which also retains a sufficient amount of hydraulic phase present, results at 850 °C after 12 hours of firing.

References
1. EN 459-2, Building lime: Part 2. Test methods, 2002.
2. Triantafyllou, G., Christidis, G. & Markopoulos, Th., (2003). *Influence of porosity and grain size of carbonate rocks in the reactivity of lime*. In: Mineral Exploration and Sustainable Delelopment, Eliopoulos et al. (eds). Millpress Rotterdam, pp. 931-934.
3. Triantafyllou, G., Markopoulos, Th. & Přikryl, R., (2010). *On the mineralogy of β-dicalcium silicate of hydraulic lime binders in various calcination conditions*. Acta Mineralogica-Petrographica Abstract series Vol. 6, p. 133. 20th General Meeting of the IMA, Budapest, Hungary.
4. Lea, F.M., The Chemistry of Cement and Concrete, Edward Arnold, London, 1976.
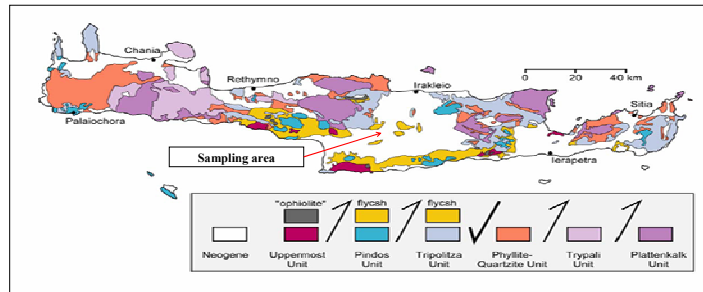
Fig. 1. Simplified geologic map of the basement units of Crete and their tectonostratigraphic relationships. The raw samples represent a middle Miocene marly limestone from the Neogene Aghia Varvara formation, which is located in Central Crete, Greece.

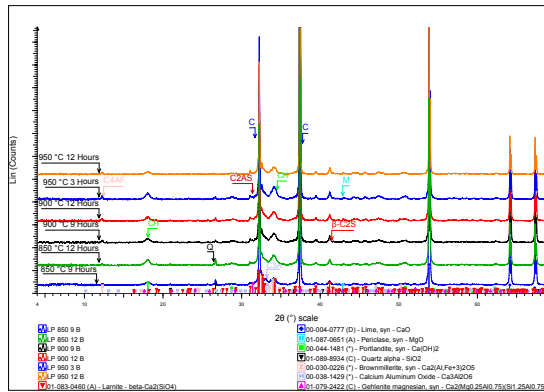Fig. 2. Apparatus for testing reactivity.

Fig. 3. Representative X-ray diffraction patterns of hydraulic lime samples produced after calcination at different temperatures and time periods. (β-C_2S: dicalcium silicate (larnite), CH: portlandite, C_4AF: brownmillerite, C: lime, Q: quartz, C_3A: tricalcium aluminate, C_2AS: gehlenite, M: periclase).
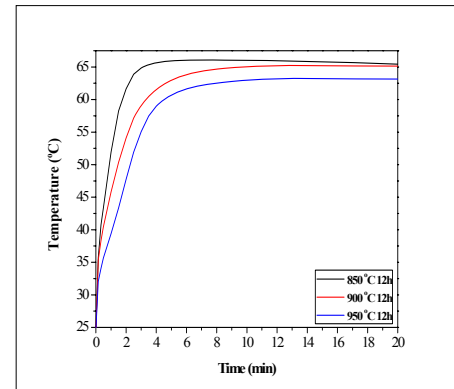

Fig. 4. Wet Slaking rate curves of the various hydraulic lime binder samples produced after 12 hours of calcination, at 850, 900 and 950 °C respectively.
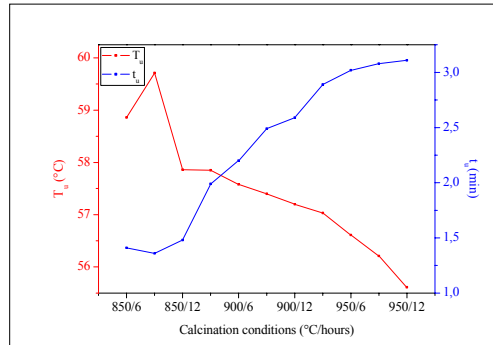

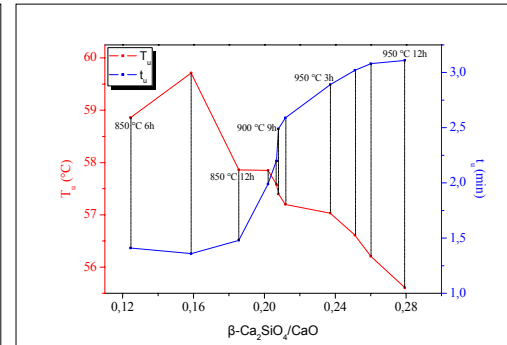Fig. 5. Values of T_u and t_u derived from the slaking rate test procedure, versus calcinations conditions.

Fig. 6. Values of T_u and t_u derived from the slaking rate test procedure, versus the β-C_2S/CaO ratio at each calcination condition.
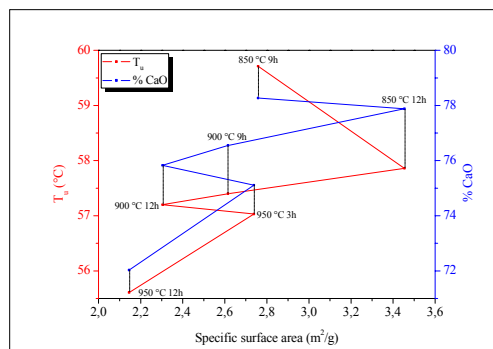

Fig. 7. T_u slaking temperature and corresponding amount of CaO present in each hydraulic lime produced in particular calcination conditions, versus the specific surface area of the binder measured by BET.

Reactivity (Procedure – Evaluation)

The reactivity of quicklime's amount (CaO) present in the produced hydraulic lime binders is measured according to the European standard (EN 459.02, 2002); a mass of 150 g of lime is introduced into 600 ml of distilled water in an adiabatic Dewar, shaken by a blade stirrer. A digital thermometer records the temperature rise of water due to the heat released during the CaO hydration (Fig. 2). The hydration reaction of quicklime is an exothermic reaction as displayed in the following chemical equation (1).

$$CaO_{(S)} + H_2O \longrightarrow Ca(OH)_{2(S)} + heat \quad (1)$$

The slaking reaction of the lime amount in the hydraulic lime sample each time tested, is assumed to be complete at the time when the maximum temp. ($T'max$) has been reached. The reactivity of the lime is reported as time (t_u) required for the reaction to be 80 % complete. The temperature T_u is defined as the temperature in °C at which the reaction is 80 % complete and is calculated using equation (2).

$$T_u = (0,8 \times T'max) + (0,2 \times T_0), \text{ in °C} \quad (2)$$

Having calculated T_u, the value t_u is determined from each wet slaking curve (Fig. 4).

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	H_2O^-	LOI	TOTAL	CI
4,58	1,29	0,64	0,06	50,51	0,66	0,08	0,08	0,15	0,07	0,32	41	99,44	0,3

Table. 1. Mean oxide composition (wt.%) and Cementation Index (CI) of the marly limestone.

	Calcination conditions					
	850 °C		900 °C		950 °C	
Mineral phases (%)	9 h	12 h	9 h	12 h	3 h	12h
β-Dicalcium silicate (Ca_2SiO_4)	12,4	14,5	15,9	16,1	17,8	20,1
Lime (CaO)	78,2	77,9	76,5	75,9	75,1	72
Physical properties	9 h	12 h	9 h	12 h	3 h	12h
Specific surface area (m²/g)	2,76	3,45	2,62	2,30	2,74	2,15
Apparent density (g/cm³)	2,63	2,09	2,32	2,56	1,65	1,85

Table. 2. Quantitative mineralogical composition (wt.%) of β-C_2S and CaO and measured values of BET surface area – apparent density in various selected calcination conditions.