

## HIGH-GRADE BURNT LIME PRODUCTS: IMPACT OF CALCINATION KINETICS ON SLAKING REACTIVITY, STICKING TENDENCY AND BLOCKS FORMATION AT HT (1300 °C)

GABRIELE VOLA

Dipartimento di Fisica e Scienze della Terra, Università di Ferrara, Via Giuseppe Saragat 1, 44122, Ferrara

### INTRODUCTION

This work deals with results obtained in 3 years of doctorate research activity dedicated to the study of quicklime products for different industrial applications (Boynton, 1982; Oates, 1998). In particular, the main objective was concerned to solving a couple of “critical issues” of industrial interest and scientific relevance. The first one is related to the analysis of factors affecting the systematic decrease of the lime reactivity at HT (1150-1250 °C), which is generally associated with the use of solid fuels, *i.e.* coal and carbon coke, into vertical kilns. The second one regards the lime agglomeration, densification and occasional melting, *i.e.* the so-called “sticking tendency” occurring at the highest (potential) temperature of process, *i.e.* 1300 °C. Therefore, the heating behavior or burnability of different carbonate rocks was investigated considering typical crushed rocks fractions, *i.e.* from 15-30 mm up to 40-80 mm, used for feeding parallel flow regenerative (PFR) kilns (Cheng & Specht, 2006; Hai Do *et al.*, 2011). This study was possible thanks to the collaboration between Cimprogetti S.r.l., a company that designs and produces lime plants, based in Dalmine (Bergamo) and the Physics and Earth Sciences Department of the University of Ferrara. Indeed, carbonate rock samples were selected and supplied from different lime producers worldwide. They include high-grade limestones and dolomites (dolostones), calcitic and dolomitic marbles, marly limestones, and other impure carbonates. A multidisciplinary analytical approach allowed performing raw materials and burnt products characterization. In particular, the following analytical techniques were adopted: chemical analysis by Wavelength-Dispersive X-ray Fluorescence Spectroscopy (XRF-WDS), isotopic signature and Elemental Analysis coupled with Isotope Ratio Mass Spectrometry (EA-IRMS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Total Organic Carbon by C-S analyzer, Quantitative Phase Analysis by X-ray Powder Diffraction using the Rietveld method (XRPD-QPA), clay mineralogy, crystallographic and microstructural analysis by the Fundamental Parameter method (XRD-FP), optical microscopy and cathodoluminescence analysis (OPM-CL), Scanning Electron Microscopy with the Energy Dispersive X-ray Spectroscopy (SEM-EDS), Electron Microprobe Analysis (EMPA), Mercury Intrusion Porosimetry (MIP), gas Pycnometry (PYC), BET specific surface area by nitrogen absorption (BET SSA), thermogravimetric analysis on massive samples (TG-DTG), thermal analysis on powders (TG-DTA) and, finally, Synchrotron X-ray powder Diffraction analysis in-situ at HT (HT-XRD) at the ESRF, Grenoble, France. Burning trials were performed on crushed rocks as received and the lime reactivity was determined according to the European water slaking rate method for building limes (EN 459-2).

### BURNABILITY AND REACTIVITY OF QUICKLIME FROM THE NEOARCHEAN LIMESTONE (TRANSVAAL SUPERGROUP, SOUTH AFRICA)

This part of the study deals with the influence of chemical, mineralogical and petrographic features of the Neoproterozoic limestone from the Ouplaas Mine (Griqualand West, South Africa) on its burnability and quicklime reactivity, considering the main use as raw material for high-grade lime production in twin shaft regenerative (TSR) kilns. This limestone consists of laminated clotted peloidal micrite and fenestrate microbial boundstone with herringbone calcite and organic carbon (kerogen) within stylolites. Diagenetic modifications include hypidiotopic dolomite, micrite to microsparite recrystallization, stylolites, poikilotopic calcite, chert and saddle dolomite replacements. Burning and technical tests widely attest that the Neoproterozoic limestone is sensitive to

high temperature, showing an unusual and drastically pronounced sintering or overburning tendency. The slaking reactivity, according to EN 459-2 is high for lime burnt at 1050 °C, but rapidly decreases for lime burnt at 1150°C. The predominant micritic microbial textures, coupled with the organic carbon, are key-factors influencing the low burnability and the high sintering tendency. The presence of burial cementation, especially poikilotopic calcite, seems to promote higher burnability, either in terms of starting calcination temperature, or in terms of higher carbonate dissociation rate. In fact, the highest calcination velocity determined by thermal analysis is consistent with the highest slaking reactivity of the lower stratum of the quarry, enriched in poikilotopic calcite. Secondly, locally concentrated dolomitic marly limestones, and sporadic back shales negatively affects the quicklime reactivity, as well. This study confirms that a multidisciplinary analytical approach is essential for selecting the best raw mix for achieving the highest lime reactivity in TSR kilns (Vola *et al.*, 2018a).

Based on the results of this multidisciplinary study the following conclusions can be traced.

*i)* The Neoproterozoic limestone from the Ouplaas Mine (Altermann & Wotherspoon, 1995) is very much sensitive to high burning temperatures showing an unusual and drastically pronounced sintering or overburning tendency. Especially, burnt lime presents a high reactivity at 1050 °C ( $t_{60} = 1.5$  min,  $T_{max} = 70$  °C), but it rapidly decreases at 1150 °C ( $t_{60} = 9$  min,  $T_{max} = 65$  °C). This fact can be better displayed plotting the reactivity against the burning temperature.

*ii)* The unusual very low thermal behavior or burnability is strongly influenced by depositional textures, diagenetic history and secondly by presence of non-limestone impurities (Sumner, 1995). Especially, the high sintering or overburning tendency and the low quicklime reactivity are related more to the micritic texture of the microbial boundstone, even if affected by diagenetic recrystallization into microsparite, rather than to the restricted presence of non-carbonate mineral contaminations.

*iii)* The sample 2P1 represents the most significant exception. It shows characteristic marine herringbone calcite associated with late diagenetic burial cementation, *i.e.* the centimeter-size poikilotopic calcite (Sumner & Grotzinger, 1996). This sample presents the highest carbonate dissociation rate or calcination velocity and the least sensitivity to the high temperature, and thus the highest quicklime reactivity either at 1050 °C ( $t_{60} = 0.8$  min.,  $T_{max} = 73$  °C) or at 1150 °C ( $t_{60} = 1.8$  min,  $T_{max} = 70.3$  °C) according to the literature (Soltan & Serry, 2011).

*iv)* The sample 4P2 is also not so much sensitive to high temperature, but its quicklime reactivity is medium either at 1050 °C ( $t_{60} = 4$  min,  $T_{max} = 62.8$  °C) or at 1150 °C ( $t_{60} = 6$  min,  $T_{max} = 63.9$  °C), because strongly affected by its impure composition, *i.e.* diagenetic replacive dolomite and clay minerals.

*v)* The presence of locally concentrated dolomitic marly limestones, back shales, an organic carbon (kerogen), negatively affects the quicklime reactivity because significantly lowers the available lime index, moreover kerogen burns during the heating process, facilitating the sintering or overburning tendency.

According to these conclusions, the typical actions recommended to the industrial plant are as follows:

*i)* to perform a deep geological survey of the mine stratigraphy, finalized to the correct determination of the real thickness of the impure strata, to identify dolomitization fronts and impurity distribution to optimize the quality of the extracted stone; *ii)* to perform an in situ log survey, finalized to evaluate the real thickness of the bottom stratum of the mine (2P1) below the current quarrying level, to evaluate the feasibility of its more consistent extraction in the early future.

The detailed knowledge of the mine stratigraphy, combined with the technical characterization of each stratum, allows calculating the real average weighted reactivity of each bench, and subsequently, the expected reactivity of different raw mixes feeding to the TSR kilns. This multidisciplinary approach must be repeated on more representative volumes of material extracted over the months and the years to validate the above results. If the higher reactivity of bench 2P will be validated by a massive campaign of tests, it could be successfully adopted to improve the raw mix feeding to the kilns, depending on the target parameter required by the industrial

plant. The judicious selection of raw material from different benches of mines could also reduce the negative influence of strata with a higher overburning tendency, and/or with a lesser compositional quality.

#### IMPACT OF ROCK FABRIC, THERMAL BEHAVIOR, AND CARBONATE DECOMPOSITION KINETICS ON QUICKLIME INDUSTRIAL PRODUCTION AND SLAKING REACTIVITY

This part of the study deals with thermal analyses, burning trials and reactivity tests on 15 carbonate rocks, *i.e.* pure and impure carbonates, mud-supported and grain-supported limestones, crystalline marbles and dolomites, used for the production of different lime products in industrial vertical shaft kilns worldwide. Especially, thermogravimetric and differential thermogravimetric analysis (TG-DTG) on massive (80, 100, 120 g) fine-grained (< 3.35 mm) samples, allowed the extrapolation of the Arrhenius kinetic parameters, *i.e.* the (apparent) activation energy ( $E_a$ ) and the pre-exponential or frequency factor ( $A$ ) according to Fuoss-Salymer-Wilson (FSW) method. Other calcination parameters, *i.e.* the duration time, starting and ending calcination times and temperatures, and peaks of maximum calcination rate were also extrapolated in order to enhance their relationships with quicklime reactivity. Moreover thermal analyses (TG-DTA) were repeated on powders (90 mg) using a more accurate analyzer to compare results. The study is completed by a thoroughly chemical-physical and mineralogical-petrographic characterization of carbonate rocks and derived burnt products. Results pointed out that medium- up to coarse crystalline materials, *i.e.* grain-supported limestones, diagenetic dolomites, and granoblastic marbles presented the highest activation energy, burnability and slaking reactivity. Conversely, microcrystalline carbonates with the highest micrite to sparite ratio, *i.e.* mud-supported limestones, and impure carbonates, enriched in quartz, clay minerals, and other subordinated non-carbonate impurities, presented the lowest activation energy, burnability, and slaking reactivity. This study also investigated the effect of BET specific surface area and real density, depending on specific sintering tendency, on quicklime reactivity. Results from this multidisciplinary research activity put further constraints on carbonate rocks calcination kinetics and their suitability in the lime industry (Vola *et al.*, 2018b).

The preliminary result of this work was the validation of TG-DTG analyses performed on massive samples, by means of comparison between the Nabertherm TG furnace and the Netzsch TG-DTA thermo-analyzer. Experimental activity allowed reaching the following conclusions: *i*) the linear regression analysis between LOI measurements performed by the Nabertherm muffle furnace and the Netzsch thermo-analyzer pointed out acceptable data reproducibility (the regression factor is 0.90); *ii*) the optimum sample mass to test with the Nabertherm furnace is about 80-120 g; *iii*) Calcination kinetic parameters extrapolated according to Fuoss-Salymer-Wilson (FSW) method by Nabertherm furnace and Netzsch thermo-analyzer are not comparable in the absolute scale because reaction rates reflect differential samples mass, particle-size distribution, thermal conductivity, and heat flux; *iv*) The Arrhenius parameters, *i.e.*, the activation energy ( $E_a$ ) and the pre-exponential or frequency factor ( $A$ ), extrapolated by Nabertherm furnace on massive samples by the FSW method are fully consistent with data from the literature ( $E_{a\ mean} = 103.7 \pm 14.2\ \text{kJmol}^{-1}$ ;  $A_{\ mean} = 23.5 \pm 59.5\ \text{s}^{-1}$ ).

Subsequently, kinetic parameters by Nabertherm furnace were investigated in order to point out possible relationships between intrinsic or geological features of carbonate rocks, and derived technical properties of burnt lime products. For this purpose it was adopted the so-called “Micrite-to-Sparite ratio” (MSR), a mineralogical-petrographic factor suitable for distinguishing carbonate rocks burnability. Indeed, the fundamental following correlations were observed: *i*) the inverse logarithmic correlation between the MSR and  $E_a$  (the regression factor is 0.42); *ii*) the logarithmic correlation between the MSR and the calcination duration time (the regression factor is 0.45); *iii*) the inverse logarithmic correlation between the Max Heating Rate (MHR) of the slaking reactivity and the MSR (the regression factor is 0.59 for limes burnt at 1200 °C); *iv*) the inverse potential correlation between the Max Heating Rate (MHR) of the slaking reactivity and the impurity content, *i.e.* the insoluble residue (regression factors are 0.81 for limes burnt at 1200 °C, and 0.60 for limes burnt at 1150-1250 °C, respectively); *v*) the linear correlation between the slaking reactivity, *i.e.*  $t_{50}$ , and the cementitious/hydraulic indexes (regression factors are 0.72 and 0.67, for cementitious and hydraulic indexes,

respectively); *vi*) the exponential correlation between the Maximum Heating Rate (MHR) of the slaking reactivity, and the BET specific surface area (regression factor is 0.69 for high-calcium limes burnt at 1200 °C); *vii*) the inverse linear correlation between the real density and the BET specific surface area of limes burnt at 1200 °C (regression factors are 0.68 and 0.93 for high-calcium and dolomitic limes, respectively).

## INVESTIGATION AND PREDICTION OF LIME STICKING TENDENCY, BLOCKAGES AND OCCASIONAL MELTING AT 1300 °C BY THE OVERBURNING TEST METHOD

This part of the study deals with the thermal behavior characterization of 46 carbonate rock samples used for the production of quicklime in industrial (vertical) kilns. The “Overburning Test” (OT) method was developed to simulate and predict the so-called “sticking tendency” (ST) of the lime at 1300 °C (Fig. 1). This critical issue is mostly related to the lime densification, agglomeration and occasional melting at HT. It essentially consists in the formation of “annular rings”, *i.e.* encrustations, occlusions and blockages within the kiln’s section (Tran *et al.*, 1993; Oates, 1998).

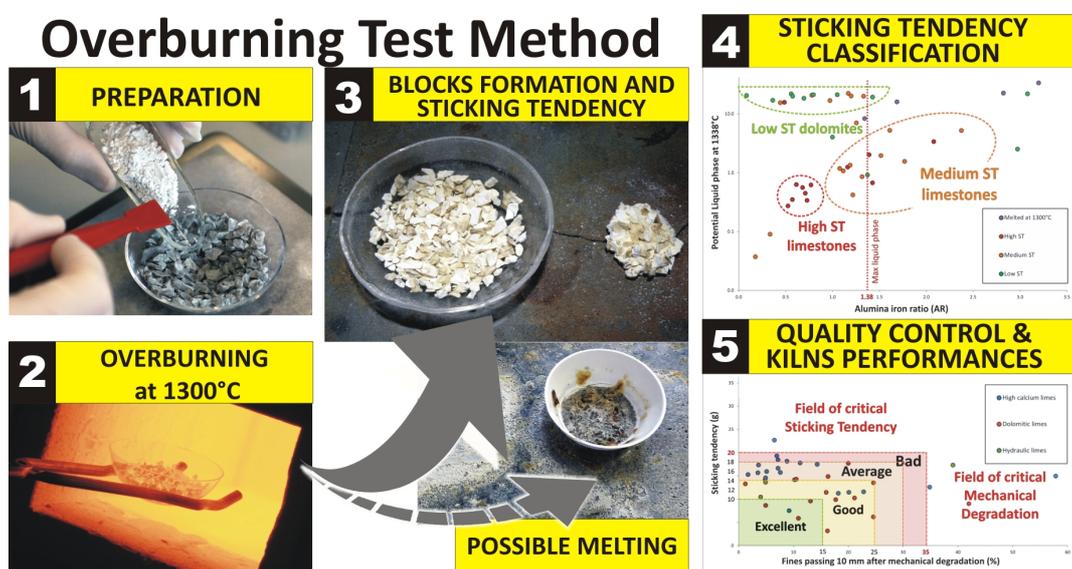


Fig. 1 - Performing steps of the OT method and applications for ST classification and kiln performances.

Different carbonate rocks, *i.e.* mud- and grain-supported limestones, reefoidal and massive limestones, stromatolites and microbialites, diagenetic dolomites, calcitic and dolomitic marbles and other impure carbonates were selected worldwide. A multidisciplinary analytical approach, including physical-chemical, mineralogical-petrographic, microstructural and thermal analyses, was performed for characterizing rocks, insoluble residua and derived burnt products. The statistical analysis of different data-sets allowed identifying four groups of rocks with wide differences in burnability and ST. The first group (A), consisting of impure carbonates enriched in fluxes, *i.e.* clays and feldspars, was completely melted. The second group (B), consisting of mainly pure high-calcium carbonates, presented high ST and sintering. The third (C) and the fourth (D) groups, deriving from slightly impure carbonates and pure dolomites, pointed out medium and low ST. Lime blocks from groups (B) and (C) can be explained by solid-state or liquid-phase sintering processes, respectively. This study allowed validating the OT method for predicting the ST and blockages in (vertical) lime kilns. Applications include the evaluation of raw materials suitability for designing new TSR kilns and the quality control in already working plants. Acceptable ranges, critical limits and practical solutions were subsequently discussed.

This part of the study allowed validating the Overburning Test (OT) as a standard method for predicting the Sticking Tendency (ST) of the lime at 1300 °C. The average deviation standard of mass values (g) determined by the OT method is < 2 g, thus the reproducibility is consistent with the limit adopted for the

proposed ST classification (Table 1). The ST can be divided into 4 main groups, presenting large burnability differences. Three different driving processes were identified to explain the above mentioned groups. They are the solid-state sintering, the liquid-phase sintering, and the dehydration melting caused by clay minerals and other fluxes decomposition. The statistical analysis by the regression method allowed pointed out significant correlations between the ST and moduli from the cement industry, *i.e.* Lime Saturation Factor (LSF), Silica Ratio (SR), Alumina to iron Ratio (AR), potential Liquid Phase (LP) at 1338 °C, and Burning Factor (BF).

Table 1 - Lime blocks (g) from the OT and proposed ST classification.

Block weight (g)	ST (%)	ST class	ST group	Guidelines for plants performances	
				Recommended size fractions	Residual CO <sub>2</sub> Guaranty (%)
≈ 42	100	Melted	A	No fractions recommended	Material is rejected
> 20	> 47.6	very high (B1)	B	A coarse fraction to feed the kiln is warmly recommended, but mechanical degradation of the lime must be low	No guaranty
18-20	42.9 – 47.6	high (B2)		A coarse fraction to feed the kiln is recommended	5.0
16-18	38.1 – 42.9	medium-high (B3)		A coarse fraction to feed the kiln is recommended	3.5
14-16	33.3 – 38.1	medium (C1)	C	A coarse fraction to feed the kiln is recommended	2.5
12-14	28.6 – 33.3	medium-low (C2)		no specific requirements for raw materials	2.0
10-12	23.8 – 28.6	low (C3)			1.0
< 10	< 23.8	no ST (D)			D

Therefore, groups of ST were explained, as follow:

*i)* The group A includes completely melted samples, deriving from impure carbonates (IR > 5%) enriched in clay minerals, *i.e.* mostly micas, and feldspars, *i.e.* plagioclase and K-feldspar, plus other subordinated mineral phases. Clay minerals dehydration and feldspars decomposition facilitate the formation of large melts around 1300 °C. Effectively, the liquid formation may starts at temperatures >1250 °C or even at ~800-900 °C depending on the presence of halites or other fluxes (Elsen *et al.*, 2011). Melts are well-documented either in cement kiln preheaters, or in rotary lime kiln, and are often related to possible obstructions and condensation of volatiles, which are responsible for the formation of kiln rings and deposits (Tran *et al.*, 1993). Anyway, a detailed sequence of phases below 1300 °C is still not well documented in the literature (Taylor, 1997).

*ii)* The group B includes high ST samples of classes B1, B2, B3, deriving from pure (IR < 1%) or slightly impure (IR = 1-5%) limestones, with theoretical LP at 1338 °C between 0.2-1.0, and AR between 0.4-0.8. Blocks from this group are mainly constituted of lime (CaO), or lime (CaO) plus periclase (MgO), associated with subordinated cementitious mineral phases. The high ST, namely “high overburning tendency”, is related to a predominant solid-state sintering process. According to cement factors, different amounts of larnite and hatrurite can be present, depending on the SR values. An increase in SR lowers the proportion of liquid at any given temperature in the kiln, and makes the solid-state sintering more evident. Moreover, the presence of limited quantity of ferrites and aluminates is essentially governed by the AR ratio.

*iii)* The group C includes medium ST samples of C1 and C2 classes, deriving from limestones with scattered impurity content, theoretical LP at 1338 °C between 0.5-1.0, and AR between 1.0-2.0. Blocks from this group are mainly constituted of lime (CaO), or lime (CaO) plus periclase (MgO), associated with significant contents of larnite, hatrurite, aluminates, and ferrites. These blocks can be essentially explained by means of a liquid-phase sintering process, *i.e.* an incomplete clinkerization process at 1300 °C, in the presence of aluminate or ferrite mineral phases.

*iv)* The group D includes low ST samples of D1 and D2 classes, deriving from mostly pure dolomites. This group is characterized by low AR values (0.1-1.4). The low ST of dolomitic blocks is probably related to the abundance of the magnesium oxide, which acts as a sintering inhibitor within the matrix of the lime at HT.

Applications of the OT method span from the evaluation of raw materials suitability for designing and commissioning new kilns, to the quality control in already working plants. Acceptable ranges, critical limits and practical solutions were discussed according to the technical expertise matured over the years on several plants worldwide. Synthetic guidelines for kiln performances are reported in Table 1. Moreover the following operative suggestions can be traced, as well: *i*) the removal of soil dust and clayey particles lumped on the surface of the raw aggregate by washing and drying rocks feeding to the kiln should allow the reduction of ST of approximately one ST class (c. 2 g); *ii*) the sample moisture affects OT results of approximately one ST class, *i.e.* higher the moisture, lower the ST; *iii*) the use of coarse-size fraction, *i.e.* 40-80 mm or 50-100 mm, for feeding to the kiln is warmly recommended for counteracting the formation of fine particles, and thus prevent sintering and ST.

#### FACTORS AFFECTING SLAKING REACTIVITY AND OVERBURNING TENDENCY OF HIGH-CALCIUM AND DOLOMITIC LIMES BURNT AT HT (1150-1300 °C)

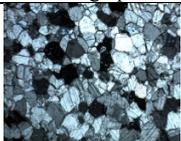
This part of the study deals with the impact of different burning temperatures on quicklime slaking reactivity. Moreover it reviews the state-of-the-art of the impact of rock fabric and calcination kinetics of different carbonate rocks for the production of quicklime in industrial kilns. The burnability and the overburning tendency of carbonate raw materials presenting different geological provenances, stratigraphic positions, fabrics and compositions were investigated. Selected samples include mud- and grain-supported limestones, reefoidal limestones, stromatolites and microbialites, diagenetic and other crystalline carbonates, *i.e.* fine- up to coarse-grained granoblastic marbles. Burning trials were performed on samples in the typical crushed rock fractions, *i.e.* 15-30, 30-60, and 40-80 mm, using electric muffle furnaces under air conditions. Different burning tests were performed at 1050, 1150, 1250 and 1300 °C for simulating the soft-, medium- and dead-burning conditions occurring in TSR kilns firing different kind of fuels. The characterization of raw materials and burnt products was performed by means of physical-chemical, mineralogical-petrographic, crystallographic, microstructural and thermal analyses. The lime reactivity was carried out according to the slaking test method (EN 459-2). The statistical analysis of different data-sets pointed out key-factors controlling the lime reactivity and overburning tendency at HT.

The results allowed evaluating the carbonate rocks burnability, overburning tendency, and lime slaking reactivity in the typical range of temperatures occurring in a TSR kiln firing solid fuels (1150-1300 °C). Crushed rock fractions were submitted to burning and slaking tests. A multidisciplinary analytical approach, including chemical-physical, mineralogical-petrographic, crystallographic and thermal analyses, was carried out on raw materials and burnt products. The first part of the study allowed identifying the rock fabric and the impurity content, *i.e.* the mineralogical-petrographic composition, as key-factors controlling the slaking rates and the overburning tendency of the lime at HT. Especially, coarse-sized granoblastic marbles, grain-supported and coralline limestones, presenting calcite cement fillings and/or replacements, are affected by higher overburning tendency than fine-grained marbles and/or mud-supported or micritic limestones. Moreover, hydraulic limes pointed out higher reactivity than pure limes at HT. This fact has to be related to the formation of different cementitious mineral phases at  $T > 1250$  °C (Elsen *et al.*, 2011), which slake at higher rates than the dead-burnt lime. Moreover, they could act as sintering inhibitors of the lime at HT (Hogewoning *et al.*, 2008a, 2008b) (Table 2).

Results from calcination kinetics performed on massive samples allowed pointing out that higher the grain/crystal-sizes of carbonate rocks, higher the (apparent) activation energy, the calcination velocity, the starting calcination time/temperature and the slaking reactivity. This is consistent with other studies on the effect of “limestone microstructure”, *i.e.* rock fabric, on the (apparent) activation energy (Soltan & Serry, 2011; Vola *et al.*, 2018a, 2018b), and pseudomorphic and topotactic calcination reactions reported by Rodriguez-Navarro *et al.* (2009). The second part of the study allowed identifying the impact of lime physical-chemical and mineralogical-crystallographic parameters on slaking reactivity. The statistical analysis pointed out the direct

correlation between BET surface area and the temperature rise, *i.e.*  $t_{60}$ , which is also consistent with the lime densification at HT. The contraction of the lime unit-cell as a function of temperature and bulk Mg content is readily explained by the higher incorporation of Mg in the CaO lattice. The higher miscibility of MgO with CaO crystal structure at 1300 °C is also consistent with a lower slaking reactivity of the lime product, considering that hydration kinetics of periclase at room pressure is extremely low. Finally, the CaO crystallite-size depends on the impurity content of burnt lime products. The Mg doping acts as inhibitor of lime crystallites coarsening; conversely, cementitious minerals promote lime crystallites coarsening, keeping relatively high reactivity in some samples. The conflicting effects of Mg incorporation in CaO, *i.e.* decreasing reactivity on one side and limiting the crystal coarsening at HT on the other side, might explain why a unique trend between crystallite-size and reactivity was not found and the BET-reactivity plots show different slopes for the different samples.

Table 2 - Combination of rock fabric and impurity content allowed identifying 4 main groups of rocks with specific slaking reactivity and overburning tendency at HT.

Rock fabric	Representative Micrographs	Impurity content	Reactivity at 1050 °C	Reactivity at 1250 °C	OT at HT	Samples
coarse-grained <i>i.e.</i> coarse-sized granoblastic marbles, grain-supported and other massive limestones		very low (0.5%)	very high (explosive) <i>i.e.</i> $t_{60} < 1$ min	very low <i>i.e.</i> $t_{60} > 10$ min	very high OT (deep slope of slaking curves)	PSP, CAR
fine-grained <i>i.e.</i> fine-grained marbles and mud-supported limestones		very low (< 0.5%)	very high (explosive) <i>i.e.</i> $t_{60} < 1$ min	medium-high <i>i.e.</i> $t_{60}$ 2-4 min	low OT (gentle slope of slaking curves)	SIM, PRO
coarse-grained <i>i.e.</i> coarse-sized granoblastic marbles, grain-supported and other massive limestones		medium-high <i>i.e.</i> quartz and clays between 2-5%	medium-high <i>i.e.</i> $t_{60}$ 1-3 min	very low <i>i.e.</i> $t_{60} > 20$ min	very high OT (deep slope of slaking curves)	IDW
fine-grained <i>i.e.</i> fine-grained marbles and mud-supported limestones		medium-high <i>i.e.</i> quartz and clays between 2-5%	medium-high <i>i.e.</i> $t_{60}$ 1-3 min	medium-low <i>i.e.</i> $t_{60}$ 4-8 min	low OT (gentle slope of slaking curves)	VER, CR1, WOP, SMA

## SYMBOLS LEGEND

BET SSA: Specific Surface Area by nitrogen absorption (BET/N<sub>2</sub> method); BF: Burning Factor (cement modulus);  $E_a$ : (apparent) Activation Energy from the Arrhenius Equation; EA-IRMS: Elemental Analysis coupled with Isotopic Ratio Mass Spectrometry; EMPA: Electron Microprobe Analysis; ESRD: European Synchrotron Radiation Facility (Grenoble, France); FSW: Fuoss-Salymer-Wilson method for kinetics of reaction; HR: Heating Rate (either slaking reactivity or thermal analysis); HT: High Temperature (burning and overburning tests); HT-XRD: in-situ High Temperature X-ray powder Diffraction analysis; ICP-MS: Inductively Coupled Plasma Mass Spectrometry; IR: Insoluble Residue by acid attack; LP: (potential) Liquid Phase (cement modulus); LOI: Loss On Ignition; LSF: Lime Saturation Factor (cement modulus); MIP: Mercury Intrusion Porosimetry; MHR: Maximum Heating Rate (slaking reactivity); MSR: Micrite-to-Sparite Ratio (digital images analysis); OPM-CL: Optical Polarized Microscopy and catholuminescence analysis; OT: Overburning Test method at 1300 °C; PFR: Parallel Flow Regenerative kiln; SEM-EDS: Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy; ST: Sticking Tendency (according to the Overburning Test method);  $T_{max}$ : Maximum Temperature (slaking test or thermal analysis);  $t_{60}$ : time to reach 60 °C (equivalent to  $\Delta T$  40 °C) according to slaking reactivity test;  $t_{50}$ : time to reach 50 °C (equivalent to  $\Delta T$  30 °C) according to slaking reactivity test; TG-DTG: Thermogravimetric and Differential Thermogravimetric analysis; TG-DTA: Thermogravimetric and Differential Thermal analysis; TSR: Twin Shaft Regenerative kiln; XRD-QPA: X-ray powder Diffraction Quantitative Phase Analysis by the Rietveld Method; XRF-WDS: Wavelength-Dispersive X-ray Fluorescence Spectroscopy.

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