

A CASE STUDY OF DIFFERENT LIMESTONES DURING QUICK LIME AND SLAKED-LIME PRODUCTION

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Abstract

We have examined 5 different limestones in order to study their behavior i) during calcination at different temperatures (900, 1050 and 1200°C for 30 min) and ii) after hydration of quick limes derived to slaked lime. Quick limes calcined at 900°C show the lower reactivity values. This could be related to the low calcination temperature or to the short calcination time of 30 min which was unable to produce enough lime. The samples calcined at temperatures of 1200°C are less reactive compared to the hydrated limes which were prepared by hydration of quick lime calcined at 1050°C, indicating by parameters such as the $(CaO+MgO)_{Lime}$, the time required to become the temperature maximum and the reactivity rate. These, probably could be due to crystal growth at relative high temperatures.

Key words: Quick lime, calcination temperature, reactivity, hydration.

1. Introduction

Limestones and their varieties represent the most frequently used rocks in industry and are included among the thirty more important raw materials. Carbonate rocks mainly consisted by carbonate minerals of calcium and magnesium (calcite, dolomite, magnesite)(e.g. Oates 1998). The industrial limestones in the world economic market possess the 11th place depending on their value (apart from the industry of cement where they possess 5th place).

In the industry, the more important chemical property of limestones is their calcination due to the following reaction:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$. This reaction is endothermic occurred at very high temperatures (>900°C); in closed systems is highly influenced by the partial pressure of the gas phase (P_{CO_2}). The theoretical dissociation temperatures of $CaCO_3$ to produce lime is around 900°C whereas those of the $MgCO_3$ ranging from 402 to 550°C (e.g. Boynton, 1980; Schwarzkopf, 1994; Moffat and Walmesley, 2004). Thus, the temperature required for calcination process of limestone is not constant and

depends on various factors; the $\text{CaCO}_3/\text{MgCO}_3$ ratio is one of them, also differences on crystallinity (grain size) and the heat rate could also play a significant role in the final quality of the resulted lime (Ar and Dögu 2001).

Another important process is the slaked lime production through the exothermic reaction $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)}$. In multivariable systems, relative high MgO content could also react with water to earlier form $\text{Mg(OH)}_2\text{(aq)}$. Both reactions increase the maximum temperature on the added water influencing the observed reactivity values. So, it is important to check the MgO behaviour in such systems. According to various authors, reactivity of lime depends on the presence of admixtures in the used limestones; in particular admixtures like MgO lower the reactivity (Potgieter et al. 2003). As a consequence, the higher the amount of MgO, the lower the lime reactivity reducing the maximum hydration temperature and increasing the hydration time. Another factor that influences the hydration process is the initial temperature of the added water (Boynton 1980). An increase in the initial temperature of the water used for hydration of the lime increases the rate of the hydration reaction due to faster dissolution of the CaO particles.

The aim of this paper is to analyze the physicochemical properties of the studied limestones testing their influence in the quality of lime. Additionally, three datasets, arise from the three different calcination temperatures (at 900, 1050 and 1200°C), of hydrated limes are studied in terms of reactivity changes.

2. Experimental Work-Analytical Methods

Five samples (K1, A2, T3, T4, T5) of limestones from different quarries from Greece were collected for this study. Limestone particles were reacted in a pre-heated oven at three different temperatures (900, 1050 and 1200°C) for 30 min in order to produce lime. The tests were done by heating a 200 g sample of a specific particle size (1.6-2 cm) at the required temperature. Subsequently, 25 gr of the produced lime were hydrated by adding distilled water to produce Ca(OH)_2 through the reaction $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(aq)}$. This reaction is highly exothermic, increasing the temperature of the added water. We measured the temperature difference in the water until a maximum value is reached; this value represents the reactivity of the produced slaked lime.

Chemical composition of each limestone was carried out using atomic absorption spectroscopy (AAS) method. We used an Perkin Elmer 3300 spectrometer at the Department of Chemical Engineering, National Technical University of Athens. The mineral chemical analysis of limestone and lime was performed using a JEOL JSM-5600 scanning electron microscope (SEM) at the Institute of Geology and Mineral exploration. The operating conditions were: 15 kV, 5 nA, data acquisition time 100 s and beam diameter 4-8. All samples were measured with energy dispersive system (EDS).

Raman micro-spectroscopy and X-ray diffraction methods were applied in order to identify the carbonate phases (calcite and dolomite) in the studied limestones. Analyses were performed using a Renishaw confocal RM1000B Raman Microprobe and a Siemens D-500 with a graphite crystal monochromator. Raman spectra were excited at room temperature using the 632.817 nm line of the He-Ne laser. The spot at the surface of the sample is about 5 μm using a 100 \times objective with laser power < 5 mW. The diffraction interval was between 2° and 50° 2 θ with a narrow 0.02° step. Raman micro-spectrometer is based at the Department of Geosciences of the National Technical University of Athens and the X-ray diffractometer at the Institute of Geology and Mineral exploration. The modal percentage of each mineral (calcite, aragonite, magnesite, dolomite, others) in 5 limestones was calculated applying a quantitative XRD method. Confirmation of the quality of the XRD results

Table 1. Major element compositions and mineral modes of the studied limestones.

Sample	K1	A2	T3	T4	T5
SiO ₂	0.89	1.21	1.10	0.85	0.99
Al ₂ O ₃	0.38	0.58	0.36	0.33	0.35
FeO	0.20	0.51	0.25	0.08	0.65
MgO	0.61	5.53	5.17	0.36	2.17
CaO	53.20	46.82	48.76	54.17	50.54
Na ₂ O	0.22	0.31	0.25	0.25	0.25
K ₂ O	0.21	0.12	0.12	0.08	0.08
H ₂ O	0.27	0.43	0.18	0.23	0.40
CO ₂	44.00	44.12	44.45	44.35	44.55
Total	99.98	99.63	100.64	100.70	99.98
Calcite	95%	75%	80%	98%	90%
Dolomite	3%	20%	15%	-	8%
Albite	<2%	3%	<2%	<2%	<2%
Quartz	-	<2%	<2%	-	-

-: Only in trace amounts.

Table 2. Chemical composition of the resulted lime at three different calcination temperatures.

at 900°C					
Sample	K1	A2	T3	T4	T5
CaCO ₃	48.1	50.86	47.17	46.76	45.07
MgCO ₃	-	0.52	-	-	-
CaO	11.2	-	7.65	14.34	14.19
MgO	0.71	5.45	5.8	0.4	2.58
CO ₂	37.75	40.18	37.02	36.7	35.37
Other	2.24	2.99	2.35	1.79	2.78
Total	100	100	99.99	99.99	99.99
at 1050°C					
Sample	K1	A2	T3	T4	T5
CaCO ₃	14.73	21.06	7.33	4.29	4.57
MgCO ₃	-	-	-	-	-
CaO	69.41	49.37	74.17	88.95	84.18
MgO	1.04	8.71	9.07	0.62	3.69
CO ₂	11.56	16.53	5.75	3.37	3.59
Other	3.26	4.33	3.67	2.77	3.98
Total	100	100	99.99	100	100.01
at 1200°C					
Sample	K1	A2	T3	T4	T5
CaCO ₃	12.01	21.59	5.4	1.5	2.46
MgCO ₃	-	-	-	-	-
CaO	74.18	48.13	77.52	93.83	87.4
MgO	1.06	8.9	9.14	0.64	3.95
CO ₂	9.42	16.95	4.24	1.17	1.93
Other	3.33	4.42	3.7	2.85	4.25
Total	100	99.99	100	99.99	99.99

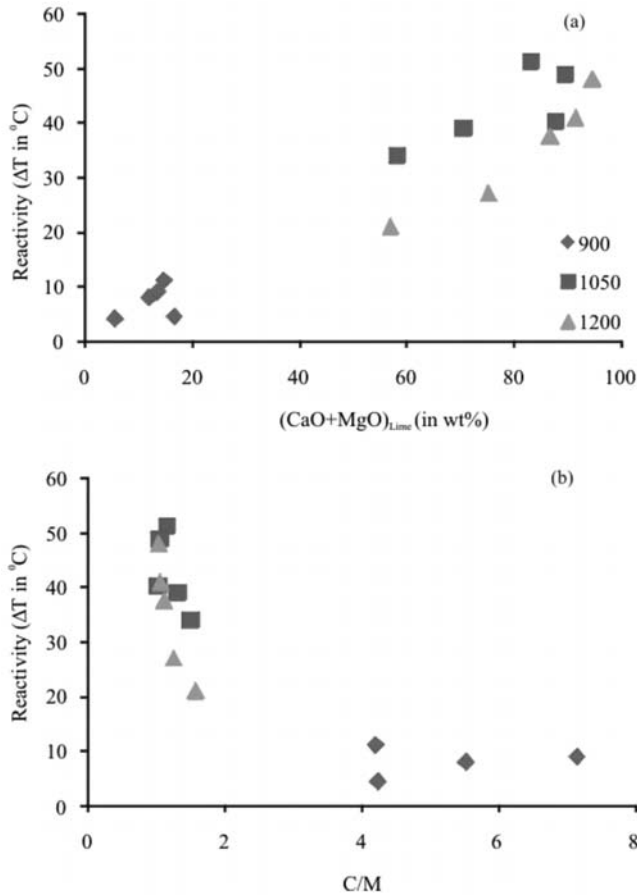


Fig. 1: Variations of Reactivity against (a) $(CaO+MgO)_{Lime}$ and (b) C/M ratio. C/M is expressed as $(CaO_{Rock} \cdot MgO_{Lime}) / (CaO_{Lime} \cdot MgO_{Rock})$.

was established using Raman micro-spectroscopy. Representative whole-rock limestone and lime compositions and mineral mode results are summarized in Table 1 and 2, respectively.

3. Results and Discussion

The reactivity represents a factor that characterizes the quality of the used lime. According to literature, the lower calcination temperature, the higher the reactivity value and the higher the quality of the resulted lime (e.g. Moropoulou et al. 2001). However, our results indicate an inversion of such process at low temperature side. In particular, the 900°C calcinated samples show the lower values of reactivity. An increase in calcination temperature (at 1050°C) indicates a switching in the reactivity behavior and become maximum for all of the studied samples. We construct bivariate plots of reactivity against $(CaO+MgO)_{Lime}$ and $CaO_{Rock}/CaO_{Lime} / MgO_{Rock}/MgO_{Lime} = (CaO_{Rock} \cdot MgO_{Lime}) / (CaO_{Lime} \cdot MgO_{Rock})$ (denoted here as C/M) in order to check, consistent or not, trends of reactivity with composition of limestone or lime. In figure 1a, we observe a systematic increase of reactivity with increasing $(CaO+MgO)_{Lime}$ for all of the calcined samples; however, for a given $(CaO+MgO)_{Lime}$ content, the reactivity is higher in the 1050°C calcined samples indicating that the optimal reactiv-

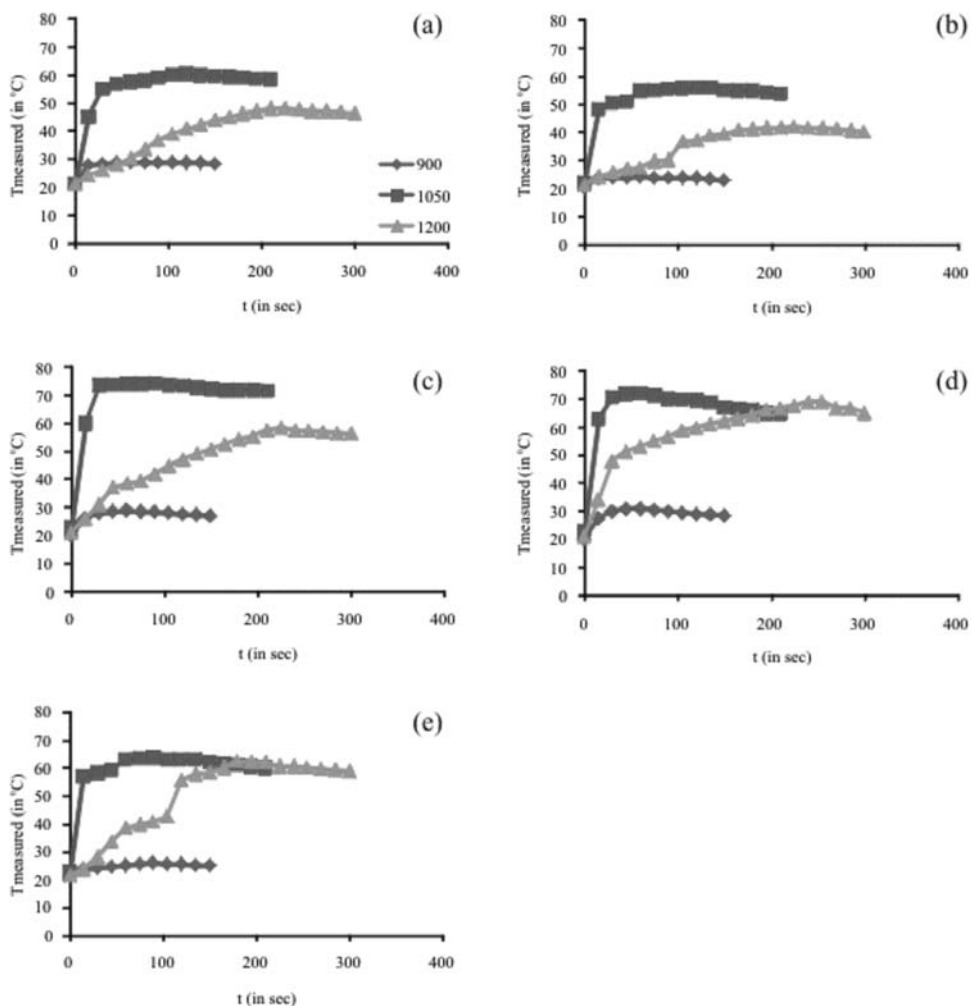


Fig. 2: (a-e) T_{measured} vs time plots showing temperature rise during hydration of quick lime at the three calcination temperatures (900, 1050 and 1200°C). Samples (a) K1, (b) A2, (c) T3, (d) T4 and (e) T5.

ity is observed at 1050°C, perhaps due to hard-burnt phenomena or densification of the quick lime structure at higher temperatures (e.g. Shin et al., 2009). A close inspection of the figure 1b, shows a systematic increase of reactivity with decreasing C/M ratio for the 1050 and 1200°C calcined samples; in oppose, the samples calcined at 900°C show a relative constant reactivity value for decreasing C/M ratios. Regarding that the CaO and MgO in limestone are constant, then the $(\text{MgO}/\text{CaO})_{\text{Lime}}$ ratio could play a potential role in reactivity behavior. Moreover, the low constant values for the samples calcined at 900°C indicates that probably the calcination temperature was rather too low or the calcination time of 30 min was too short to produce enough lime.

The Figure 2 (a-e) shows the temperature rise vs. hydration time of quick lime at temperature 900, 1050 and 1200°C for the studied samples. The limestones calcined at 1050°C shows the maximum temperature rise; at lower/higher calcination temperature the temperature rise is lower. The temper-

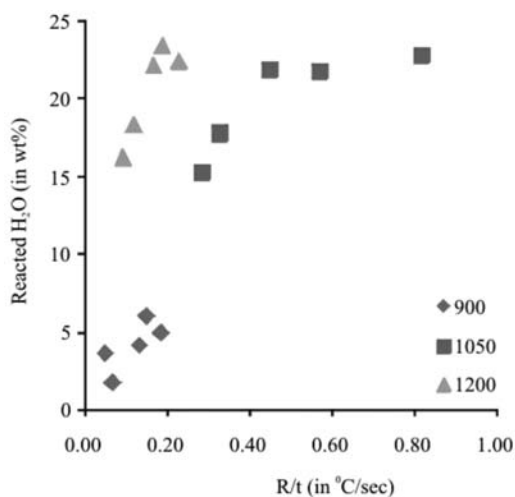


Fig. 3: Variation of reactivity rate of quick limes against the H₂O reacted with the calcined samples at various temperatures.

ature rise of the 1200°C calcined limestone was lower than that of the 1050°C and also the time required for hydration was expanded at later stage. These results confirm that quick limes calcined at temperature of 1050°C have the highest reactivity for hydration and also that the quick lime calcined at 1200°C is less reactive probably due to larger grain size (grain growth during temperature increase) and lower porosity (denser structure). Shin et al., (2009) suggested the temperature of 1100°C as the optimum calcination temperature for the highest reactivity values with the largest specific area. At this temperature seems to formed a lot of pores due to dissociation of carbonates, whereas quick limes calcined at lower temperatures (900 and 1000°C) tend to have less pores and minimum specific surface area due to incomplete lime production and remnants of the original limestone (as we observe in a previous paragraph); at calcination temperatures >1200°C the structure become more dense and compact and the grains become larger leading to minimization of the existing pores so the hydration process itself cannot entirely proceed into the interior mass of the quick lime also requiring more time to accomplished.

The MgO content plays an important role in reactivity rate of the lime due to earlier decompose of MgCO₃ to MgO producing hard burnt samples. As we previously state, the higher the amount of MgO, the lower the lime reactivity reducing the maximum hydration temperature and increasing the hydration time. Besides, in case of non-hard burnt samples, MgO content when it's low in concentration (lower than 2-3 wt%) could accelerate the hydration rate of the unslaked lime. (Potgieter et al., 2003). Three of the studied limestones share a common feature with high MgO content ranging from 2.17-5.53 wt% (samples A2, T3 and T5). These samples also possess the higher MgO content during calcination, thus the quick limes formed by this process also have high MgO content. In practice, the MgO vs. reactivity rate are inversed correlated with the samples calcined at 1200°C share a common, low reactivity rate, with those calcined at 900°C.

To visualize better the hydration process we compare the H₂O that reacted with the free lime against the reactivity rate. Reactivity values are divided by the time required for the T_{max} giving the reactivity rate. Figure 3 shows that at constant reactivity rate values the water needed to complete hydration is lower; for example, the quick lime calcined at temperature of 1050°C need much less

water for hydration relative to the respective samples at 1200°C. Also, the slope of the curve for the samples calcined at 1200°C is steeper compared to the one for lower calcination temperature. Concluding, the higher the reactivity rate the better quality of slaked lime.

4. Conclusions

The results on the behaviour of quick- and slaked- lime are summarized in the following:

- The samples calcined at temperatures of 1050°C have the higher reactivity values.
- The MgO content is not a significant factor on the control of the reactivity; instead the hard-burned effect and the structure of the original limestone and the resulted quick lime are more important. However, the $(\text{CaO}/\text{MgO})_{\text{Lime}}$ ratio plays a potential role, increasing the reactivity of the quick lime.
- For a constant reactivity rate the water required for hydration is lesser for the samples calcined at 1050°C compared to those calcined at 1200°C.

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6. References

- Ar, I. and Dögu, G., 2001. Calcination kinetics of high purity limestones. *Chemical Engineering Journal*, 83, 131-137.
- Boynton, R.S., 1980. *Chemistry and Technology of Lime and Limestone* (2nd ed.), New York, Wiley, 5 – 33, 132 -164, 592pp.
- Moffat, W. and Walmsley, M.R.W., 2004. Improving Energy Efficiency of a Lime Kiln. *Proceedings of Joint SCENZ/FEANZ/SMNZI Conference*, Hamilton, 17-24.
- Moropoulou, A., Bakolas, A. and Aggelakopoulou, E., 2001. The effects of limestone characteristics and calcination temperature to the reactivity of the quicklime. *Cement and Concrete Research*, 31, 633-639.
- Oates, J. A. H., 1998. *Lime and Limestone. Chemistry and Technology, Production and Uses*. Wiley – VCH, Weinheim, 9 – 62, 117 - 250.
- Potgieter, J.H., Potgieter, S.S. and DeWaal, D., 2003. An empirical study of factors influencing lime slaking Part II: lime constituents and water composition. *Water SA* 29 (2), 157–160.
- Schwarzkopf, F., 1994. *Lime Burning Technology – a manual for lime plant operators* (3rd ed.). Svedala Industries Kennedy, Van Saun.
- Shin, H.G., Kim, H., Kim, Y.N. and Lee, H.S., 2009. Effect of reactivity of quick lime on the properties of hydrated lime sorbent for SO₂ removal. *Journal of Materials Science and Technology*, 25 (3), 329-332.