Asian Journal of Chemistry Vol. 19, No. 4 (2007), 3215-3220

Effect of Slaking Water Properties to Lime Quality

ÖZEN KILIÇ
Department of Mining Engineering, Faculty of Engineering and Architecture
Cukurova University, 01330 Balcali, Adana, Turkey
Fax: (90)(322)3386126; Tel: (90)(322)3386503; E-mail: zenkilic@cu.edu.tr

The slaking of lime is important for its use in a number of industrial applications. There are normally a number of factors that can influence the rate, reactivity of the hydration of lime, which include, amongst others, production and storage conditions and the constitution of the water used in the slaking process. In this study, the influence of slaking water properties to lime quality has been investigated. It was found that soft burnt lime during slaking process dramatically increases its surface area and also reactivity. In the slaking experiments of limes were used water, distilled water and distilled water mixtures, with sugar, NaCl, ethonol and methonol.

Key Words: Lime, Slaking, NaCl, Methanol, Ethanol, Sugar.

INTRODUCTION

Limestone (mainly $CaCO_3$) is one of the most widely occurring industrial minerals world-wide. It is therefore not surprising that lime, obtained by calcining limestone, is a frequently used industrial base and features on the list of the top 50 industrial chemicals[1]. When applied as an alkali, unslaked lime, CaO, is commonly converted to slaked lime, $Ca(OH)_2$, by reacting it with water. The hydration of quiklime (CaO) is actually one stage of a reversible reaction, since dehydration, effected by subsequent heating, recreates quicklime and volatilizes the water of hydration as vapour. The conversion of limestone to lime and its slaking with water, can be represented by the following reactions[2]:

$$CaCO_3(s) + Heat \rightarrow CaO(s) + CO_2(g) \uparrow \quad (1)$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq) - Heat \uparrow \quad (2)$$

Lime is undoubtedly a highly important industrial mineral that is widely used in a number of industries. Its most common applications include water treatment, neutralization of acidic effluents, cement production and acting as a flux in the refining of steel from iron ore. Very often the desired species in a particular application is $Ca(OH)_2$, commonly referred to as hydrated lime or slaked lime. The formation of $Ca(OH)_2$ from CaO or unslaked lime, that is desired in the application, its production is closely linked to a number of physical and chemical influences[3].

During calcination of limestone to produce lime, carbon dioxide is released from the material. This caused the calcined lime to have a porous structure. The aim of the production process is to produce such a soft burnt lime with a porous microstructure that will react easily with water and possess a high reactivity. If, however, the calcining temperature is too high or residence time in the kiln is too long, the calcium oxide particles can become partially sintered together and result in a less porous structure. This material will allow less access to water that it comes into contact with and consequently it will not slake as well as the soft burnt material. The lime is then classified as hard burnt or dead burnt. Conversely, if the calcining temperature is too low or the residence time in the kiln is too short, the calcination process will be incomplete and this will also produce a low reactivity lime[2]. The specific surface area in the limestones ranges between 0.99 and 1.1 m^2/g; while for a soft burnt lime between 1.18 and 1.30 m^2/g and hydrate lime of soft burnt lime[4] between 13 and 24 m^2/g.

The lime produced during the calcinations process is a thermodynamically unstable product. It therefore reacts with any vapour present in the atmosphere to partly or completely form a thin layer of calcium hydroxide on the outside of the lime particles. It also has a tendency to reconvert back into limestone *via* reaction with carbon dioxide in the atmosphere. Both these reactions occur after production and mostly during the storage period before the lime is used and this will consequently influence the slaking behaviour of the lime[3]. These latter phenomena can cause considerable operational problems on plant level to ensure the production of lime that complies with customer demands and expectations in terms of its reactivity.

The slaking process can be studied in various ways. Frank[5] used wet slaking curves, in which he plotted temperature against time as a measure to study the slaking reaction of lime with water. Wiersma *et al.*[6] used a test method based on the changing conductivity of the milk of lime solution produced during the slaking. Potgieter *et al.*[7] have recently described the effect of production and storage conditions on the slaking behaviour of lime. It was found that calcining conditions inside the kiln used to calcine limestone to lime could yield unslaked limes with various reactivities, *i.e.* different rates of reaction with water.

Kilic and Anil[8] also found that calcining conditions could greatly influence the resultant lime and ascribed it to the effect that it had on the surface area of the lime produced during the calcination process.

Lime is undoubtedly a highly important industrial mineral and its slaking conditions that is effected reactivity and behaviour in industrial applications. The object of this investigation was to asses the effect of the slaking water properties to lime quality.

EXPERIMENTAL

The raw materials used were taken from two different limestones areas: Ceyhan region (L_c) and Karaisali region (L_k) in Adana, Turkey. Limestones present macroscopically different characteristics. L_c is light-coloured dirty white with hardly any distinguished crystals; whereas, L_k is a dirty white and light coloured grey limestone comprising discrete and tiny crystals. Microcracks were not present throughout the mass of both limestones.

Analytical methods and techniques

Analyses were performed on limestone and lime samples by using the following analytical procedure. XRF (Siemens SRS 300 X-ray Flouresans Spectrometer) was used to determine the chemical compositions of limestone samples. Transmitted light microscopy (Olympus BH-2) was carried out on polished thin sections of the limestone in order to identify the minerological composition, texture, shape and size of the grains. In the calcination process, each test samples were crushed and sieved (-0.5 mm, amount of 10 g) were placed into a temperature controlled laboratory furnace (Electromag, tmax: 1260 ± 2°C) at 1000°C for 1 h. All specimens were weighed before and after their heating and the difference expressed as a percentage (wt %) as the heating loss for each calcination condition. Adsorption of azot was performed on limestone and lime in order to evaluate the value of specific surface area by physical sorption isotherm. The calcined specimens were cooled in a desiccator and lime properties at ambient temperature were determined.

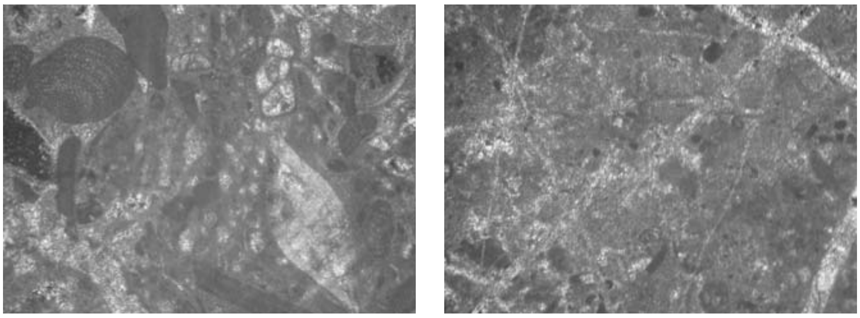
RESULTS AND DISCUSSION

The means of the chemical analyses results of the two different limestone (L_c and L_k) samples are presented in Table-1. It was found that they are pure with an average CaO higher than 98 % while the impurities (Fe_2O_3, Al_2O_3 and SiO_2) are very low. These values were used to normalize the degrees of slaking obtained for each sample during the investigation. The geological origin of the limestone and its chemical composition, especially the presence of impurities, could significantly influence the rate and degree of hydration during the slaking process. By this reason, the limestone samples were selected very pure (> 98 % $CaCO_3$), were also included in the investigation.

TABLE-1
CHEMICAL COMPOSITION (%) OF LIMESTONES

Sample	SiO_2	Al_2O_3	Fe_2O_3	$CaCO_3$	$MgCO_3$
L_k	0.32	0.19	0.06	98.71	0.72
L_c	0.49	0.06	0.07	98.86	0.52

Transmitted light microscopy (Olympus BH-2) was carried out on polished thin sections of the limestones in order to identify the texture, shape and size of the grains. Limestone L_k exhibited small to large size grains (470 ± 152 µ), which are distributed inhomogeneously throughout the mass. On the other hand, Limestone L_c presented fine grains (320 ± 136 µ) and a homogeneous texture (Fig. 1). The mineralogical composition was determine by Alizerin Red-S method. It was found that they were very pure and calcite was the main component in both samples, with a little quartz. Calcination will introduce no problem and decrepitating will not be observed, because of the fact that the limestones have a fine grain size. The quality of calcinated limestone (lime) and chemical reactivity is observed to be appropriate.



(a) (b)

Fig. 1. Microphotographs of limestones (a) L_k, (b) L_c

10 g of each limestone samples (L_c and L_k) of 0.5 mm size calcined at 1000°C for 1 h, cooled in a desiccator and 3 g of each sample was then added the water ratio of weight of % 70 of quicklimes. The previous study[9] described the water ratios, at 50 and 60 % weight of quicklime are inadequate and 70 % weight of quicklimes is adequate for slaking process. The lime properties calcined at 1000°C are presented in Table-2.

TABLE-2
LIME PROPERTIES AT CALCINED 1000°C

Sample	Specific surface area (m^2/g)	Available CaO (%)	Loss on ignition (%)
L_k	2.75	93.58	1.9
L_c	2.11	94.21	2.1

In the slaking experiments, water, distilled water and mixtures were used as the slaking water. The mixtures were prepared to add sugar, NaCl, ethanol and methanol of 5 and 10 % amount of the distilled water weight. Such waters normally contain high concentrations of impurities, most notably chlorides, sulphates and carbonates. Impurities in water are known to affect the rate of hydration of unslaked lime. Furthermore, MgO is a common constituent of many limestones and can, after calcining, also affect the hydration rate of the lime if it is present as MgO. In order to discriminate between the effects when anions and cations are present that can accelerate the specific surface area of lime simultaneously with others that retard the slaking of the lime, distilled water were used in the experiments. The chemical composition of the water is presented in Table-3.

TABLE-3
CHEMICAL COMPOSITION OF WATER (mg/L)

Ca	19.2	Fe	0.02
Mg	11.9	F	0.05
Na	18.5	Cl	18.20
K	7.6	–	–

The specific surface area was used to determine the quality, reactivity of the limestones, quicklimes and hydrated limes. The results obtained in specific surface area analyses of the samples are shown in Table-4.

TABLE-4
SPECIFIC SURFACE AREA RESULTS OF THE SAMPLES USED IN THIS INVESTIGATION (m^2/g)

Sample	Limestone	CaO	Slaked limes									
			Water	Distilled water	Sugar		NaCl		Ethanol		Methanol	
					5%	10%	5%	10%	5%	10%	5%	10%
L_k	1.90	2.75	14.27	14.48	21.67	8.73	12.72	8.56	15.50	9.99	15.17	9.61
L_c	1.65	2.11	13.10	13.15	25.63	7.66	12.92	7.21	14.21	8.72	14.82	8.65

It is clear that specific surface area decreases with an increasing concentration of sodium chloride in the slaking water. The presence of ethanol, methanol and sugar in the slaking water was increased the specific surface area of the lime. The results obtained in each case are shown in Table-4. However, specific surface area of the lime was increased in less amounts of adding material in the mixtures.

Conclusion

The geological origin of the limestone and its chemical composition, especially the presence of impurities and physical properties, could significantly influence the rate and degree of hydration during the slaking process. By this reason, the limestone samples must be selected very pure (> 98 % $CaCO_3$), compact and fine grain size. Calcination will introduce no problem and decrepitating will not be observed.

In the slaking tests, chloride, sodium, calcium and magnesium ions, forms a more soluble compound with $Ca(OH)_2$, were found to decrease the specific surface area. Specific surfaces vary less with changes in water according to distilled water. Low specific surface area was obtained with reactive soft-burned quicklimes by hydrating sodium chloride-distilled water mixtures.

High specific surface area was obtained low concentration in the mixtures, such as sugar, ethanol, methanol. In the sugar-distilled water concentration of < 5 % amount of the distilled water weight in the mixture can be obtained high specific surface area, such as 45 m^2/g.

REFERENCES

1. National Lime Association, Lime Handling, Application and Storage, Bulletin 213 Arlington, USA, edn. 7, pp. 53-66 (1990).
2. R.S. Boynton, Chemistry and Technology of Lime and Limestone, John Wiley and Sons, Inc., New York, edn. 2 (1980).
3. J.H. Oates, Lime and Limestone Chemistry and Technology: Production and Uses, Wiley-VCH Publishers, Weinheim, p. 169 (1998).
4. J. Murray, Summary of Fundamental Research on Lime (Research Report), National Lime Association (1956).
5. G. Frank, *Zement Kalk and Gips*, **4**, 172 (1974).
6. D.J. Wiersma, P. Hubert and J.N. Bolle, The Technical Reactivity and Other Relevant Properties of Milk of Lime as Applied to Water Treatment, in: Proceedings of the International Lime Association Conference, Berlin, Germany (1998).
7. J.H. Potgieter, S.S. Potgieter, S.J. Moja and A. Mulaba-Bafubiandi, *Miner. Eng.*, **15**, 201 (2002).
8. Ö. Kiliç and M. Anil, *Asian J. Chem.*, **18**, 655 (2006).
9. Ö. Kiliç and M. Anil, *Madencilik*, **45**, 15 (2006) (in Turkish); www.maden.org.tr/resimler/ekler/0f168ce8900fa56_ek.pdf

(*Received*: 13 December 2006; *Accepted*: 30 January 2007) AJC-5381