8th International Symposium on Aggregates (2016) Kutahya, Turkey

Characterization of Limestone Aggregates for Iron-Steel Industry

OzenKılıç

Cukurova University, Department of Mining Engineering, Adana, Turkey

Email: zenkilic@cu.edu.tr

Abstract: Limestone is a basic industrial raw material. It is consumed by 84% in chemical industry, 12% in refractory and road construction and 4% in civil engineering, agricultural applications and iron steel industry and substantial quantity as lime. Limestone as a source of lime should have some specific physical, chemical, mechanical and thermal properties. Furthermore, technological processes for high quality lime production are also very important. In this investigation, chemical composition, physical properties (bulk density, apparent porosity, water absorption rate), mechanical properties (Schmidt strength and Los Angeles Abrassive strength) and thermogravimetric properties (TG-DTA) of limestone samples were determined. The tests were carried out to determine the characteristic properties of limestone for high quality lime production suitable for iron-steel making industry.

Introduction

In broadest definition, limestone is any rock rich in $CaCO_3$. Limestone can be obtained from a variety of sources and various limestones differ considerably in their chemical compositions and physical structure. The chemical and physical properties of carbonate rocks are interdependent. Physical characteristics of limestone play an important role in evaluating a deposit. Certain physical characteristics in limestone may indicate a general disposition description during calcination; however, not all stones with these characteristics will decrepitate. Limestones that display the following attributes or conditions, alone or in combination, are prone to decrepitation, coarse crystallinity, friability, foliation, excessive calcite veining, micro fracturing, highly porous and thinly bedded. The chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silica, iron, magnesium, manganese, sodium, and potassium. Magnesium and ferrous iron cations occurring in limestone may change the carbonate mineralogy of limestone as well as its physical characteristics such as color, brightness, specific gravity, hardness, tenacity and decomposition properties (Boynton, 1980).

The main chemical property of limestone is its thermal decomposition, known as calcination, during which lime (CaO) and carbon dioxide are produced (Eq. 1) (Boynton, 1980, Oates, 1998). The calcination reaction is endothermic, which means that the forward reaction is favored by higher temperatures. The reaction will proceed only, if the partial pressure of CO_2 in the gas above the solid surface is less than the decomposition pressure of the $CaCO_3$.

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 182.1 Kj.mol^{-1} \quad (1)$$

In the evaluation of the kinetics of calcination is shown to complicate by CO_2 concentration, which inhibits the reaction, particle size, which may introduce both thermal and mass transfer limitations and catalysis/inhibition by impurities. When calcination takes place (Eq. 1), the product calcium oxide weighs only 56% of the parent carbonate.

The reaction (Eq. 1) only begins when the temperature is above the dissociation temperature of the carbonates in the limestone. According to Boynton (1980), the $CaCO_3$ decomposition temperature determined by several researchers at the beginning of the 20th century is generally still accepted as 898ºC at 1 atm in a 100% CO_2 environment. However, according to some studies, this temperature is 902.5°C (Borgwardt, 1985). Kılıç (2005) reported that the weight loss above 600°C, measured by DTA-TG in nitrogen atmosphere, is attributed to the CO_2 from the decomposition of calcium carbonate that is initiated at 682-691°C and completed at 944-961°C.

The internal structure of a rock having open and closed pores in its texture affects its heat transfer. The specimen comprises a dense carbonate core surrounded by porous oxide layer. The changes in pore structure also play a significant role on the calcination/heat treatment mechanism and the reactivity of a calcined limestone is strongly dependent on its chemical, physical and structural properties, which in turn are highly dependent on heat treatment conditions (Rubiera et al. 1991, Khinast et al. 1996). In the good calcination process, limestone should be approximately consisting of 97% $CaCO_3$ and low impurities. Impurities such as iron, magnesium and aluminum oxides tend to lead to lower surface areas in both the limestones and their calcines (Boynton, 1980).

Limestone is used mainly in the iron making part of steel production, where it is added to the iron ore

before entering the blast furnace. The limestone reacts with acidic impurities called slag and floats on top of the molten iron, where it is skimmed off. As a flux, the limestone helps purify the iron ore, which is the raw material used for steel.

In the literature, there are several references concerning factors that may affect the quality of lime. Generally, these factors are characteristics of the limestone, calcination temperature, pressure acquired in kilns, rate of calcination and fuel quality (Ingraham and Marier, 1963; Khinast et al., 1996). Thermal decomposition of limestone has been the subject of intensive studies over the years due to its importance in the flue gas desulfurization. Studies have not been reported to the best of our knowledge about the specific effects of the various factors (raw materials, calcination, temperature) to the reactivity of the produced lime.

In this study, in order to determine effects of limestone characteristics on the lime production for iron-steel making industry, the investigation of the characteristic properties of the produced lime has to be performed properly.

Materials and Methods

The limestones were taken from different large commercial deposits: Karaisalı region (L_k) and Yılankale region (L_y) in Adana, Turkey. During sampling, rock types having no bedding planes were selected to eliminate any anisotropic effects in the measurements of the samples. Limestones present macroscopically different characteristics. L_k is a 'dirty white' and light colored grey limestone comprising discrete and tiny crystals. L_y is light-colored 'dirty white' without any distinguished crystals. Micro cracks were not present throughout the mass of L_k limestones, but micro cracks, dense vein system and schistosity were observed throughout the mass of L_y limestones.

Analyses were performed on limestone samples by using the following analytical procedure. XRF (Siemens SRS 300 X-ray Fluorescence Spectrometer) was used to determine the chemical compositions of limestone samples.

Physical properties (the bulk density, effective porosity, water absorption rate) of the limestones were determined using saturation and buoyancy techniques, as recommended by ISRM and TSE (TS EN 1097-2 2010).

The compressive strength of the limestones was determined by Schmidt hammer. Schmidt hammer tests were carried out on the test samples having an approximate dimension of $30\times30\times20$ cm^3. The tests were performed with an N-type hammer having impact energy of 2.207 Nm. All tests were conducted with the hammer held vertically downwards and at right angles to the horizontal rock surface. In the tests, the ISRM

(1981) method was applied for each rock type. ISRM suggested that 20 rebound values from single impacts separated by at least a plunger diameter should be recorded and the upper 10 values averaged. The test was repeated at least three times on each sample and the average value was recorded as the Schmidt hammer value.

In the heat treatment process, the test samples were cut into cubes (3 cm mean edges, 3.04±0.11) were placed into temperature controlled laboratory furnace (Electromag, tmax: 1260°C ± 2°C) at the different temperature (850, 900, 950, 1000 and 1050°C). For each sample, each temperature level was operated during 150 min. All specimens were weighted before and after their ignition, and difference expressed as a percentage (wt %) is the ignition loss for every heat treatment condition.

Differential thermal and thermo-gravimetric analyses (simultaneous TG/DTA, Setaram 92 16 DTA-TG) were carried out to determine quantitatively and qualitatively the various compounds presented in samples. Analyses were performed in samples of limestone nitrogen atmosphere at a temperature range of 25-1000°C and gradient of 10°C/min.

Results and Discussion

The chemical analyses results of limestone samples are presented in Table 1. It was found that L_k and L_y are very pure with an average $CaCO_3$ higher than 97% and the impurities (MgO, Fe_2O_3, Al_2O_3 and SiO_2) are very low. Since, the $MgCO_3/CaCO_3$ ratio varies with the type of limestone; the decomposition temperature does not remain constant and therefore, must be determined for every type of limestone.

Table 1. Chemical composition of limestone (%).

Sample	CaO	MgO	SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	Loss of Ignition
L_k	55.13 ±0.14	0.44 ±0.04	0.34 ±0.22	0.08 ±0.04	0.07 ±0.03	43.95 ±0.15
L_y	54.90 ±0.35	0.74 ±0.58	0.55 ±0.31	0.10 ±0.05	0.08 ±0.06	43.63 ±0.53

The calcium oxide content of limestones (55.13% and 54.90%; L_k and L_y, respectively) falls within the range of 50% to 65% required for limestone for burnt lime production. Calcium oxide is one of the two oxides that play the most important role in the removal of oxide impurities during iron and steel-making. Calcium oxide, for example, will react with silica to produce calcium silicate that has a much lower melting point than the two oxides (Boynton, 1980).

The MgO content of limestones (0.44% and 0.74%; L_k and L_y, respectively) falls within the range of 2.30% to

5.50% standard specified for limestone for direct lime production (Boynton, 1980). MgO forms the low melting point magnesium silicate with silica during iron-making.

The iron oxide content of limestones (0.08% and 0.10%; L_k and L_y, respectively) also falls within the range of 0.2% to 0.5% specified for a high grade limestone for lime making (Boynton, 1980). The content of iron oxide also helps in enriching the iron ore sample in a blast furnace.

The alumina content of limestones (0.07% and 0.08%; L_k and L_y, respectively) falls in the range of 1.0% to 2.8% for alumina content of limestone suitable for direct production of lime. Since, alumina is a highly refractory oxide; its low content in examined limestones strongly indicates the limestones as a high grade limestone. Alumina acts as a base or as an acid depending on the conditions imposed. For example, in highly siliceous slags, it may form alumina silicates, while in the presence of a strong base like lime, it may form calcium aluminate.

The silica content of limestones (0.34% and 0.55%; L_k and L_y, respectively) falls within the range of 0.80% to 2.50% standard specified for high grade limestone. Silica is not very harmful in iron-making, being the source of the important Si. However, high quantity of silica will lead to the formation of large volume of calcium silicate slag with the associated high energy requirements for fluxing. The low content of silica in L_k and L_y further shows it as being suitable for direct lime production since, acid impurities will reduce the potency of a basic slag. These results showed that the examined limestones as received is a high grade limestone that meets the specification for direct use for production of burnt lime for iron and steel-making (Boynton, 1980).

The percentage loss on ignition of limestones (43.95% and 43.63%; L_k and L_y, respectively) falls within the range of 30% to 45% specified for high grade limestone. The LOI may be due to the presence of water and some adsorbed gaseous impurities in the limestone which escape on ignition. Lime for steel making generally requires a low value LOI of 2% to 4% (or less), some plants actually require an LOI no higher than 0.5%

The results of physical properties of limestones are presented in Table 2. All limestone samples indicated low values in porosity and water absorption rate (lower than 1%). The value of apparent density (>2.55 g/cm^3) was found to be characteristic for a limestone (Ingraham and Marier 1963). Comparing the limestones, L_k demonstrated higher values in porosity. The other physical properties (e.g., porosity) determined will only be critical in the assessment of mineral oxides for refractory applications.

Table 2. Physical properties of the limestones.

Sample	Bulk density (g/cm^3)	Water absorption rate (weight) (%)	Porosity (%)
L_k	2.65±0.08	0.72±0.22	0.85±0.04
L_y	2.72±0.12	0.39±0.09	0.70±0.16

The physical properties depend not only on the properties of the individual minerals, but also upon the way in which the minerals are assembled and porosity, vein system and micro-cracks. Information on the porous nature of rock materials is frequently omitted from physical descriptions, but is required if these descriptions are to be used as a guide to mechanical performance (Smorodinov et al. 1970). Bulk density is relevant chemical composition of the limestone. Bulk density increases with increase in % $MgCO_3$ content.

The Schmidt hammer rebound hardness test is a simple and non-destructive test originally developed in 1948 for a quick measurement of UCS (Schmidt, 1951) and later was extended to estimate the hardness and strength of rock (Cargil, 1990). As a simple tool for quick UCS assessment, Schmidt hammer has been used worldwide. They have found that Schmidt hardness and the UCS are closely related.

The compressive strength of the limestones was determined by Schmidt hammer. It was found that compressive strength is 77±9.1 MPa and 63.4±10.4 MPa for L_k and L_y, respectively.

The mechanical properties depend not only on the properties of the individual minerals, but also upon the way in which the minerals are assembled. Carbonate rocks in particular occur with a wide range of porosities and hence of mechanical character. Compressive strength decreases with increase in porosity (Smorodinov et al., 1970).

The differential thermal analysis technique has been used for quantitative determination of heats of decomposition of carbonate materials. It is observed that the carbonates i.e. limestone, dolomite, have lower heats of decomposition and higher energies of activation in a carbon dioxide atmosphere compared to values obtained in air.

Calcination reaction only begins when the temperature is above the dissociation temperature of the carbonates in the limestone. Once the reaction starts the temperature must be maintained above the dissociation temperature, and carbon dioxide evolved in the reaction must be removed. Dissociation of the calcium carbonate proceeds gradually from the outer surface of the particle inward and a porous layer of calcium oxide, the desired product remains.
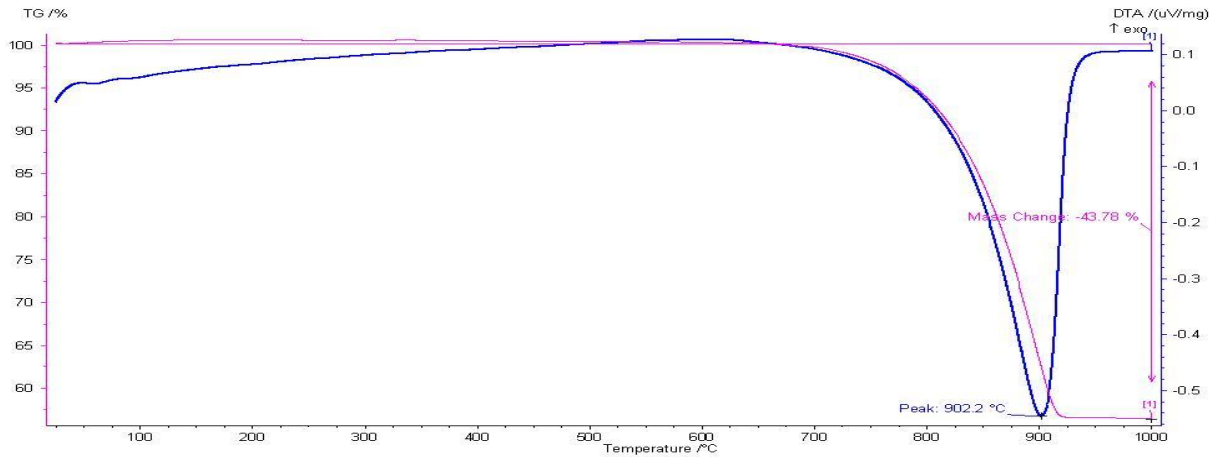
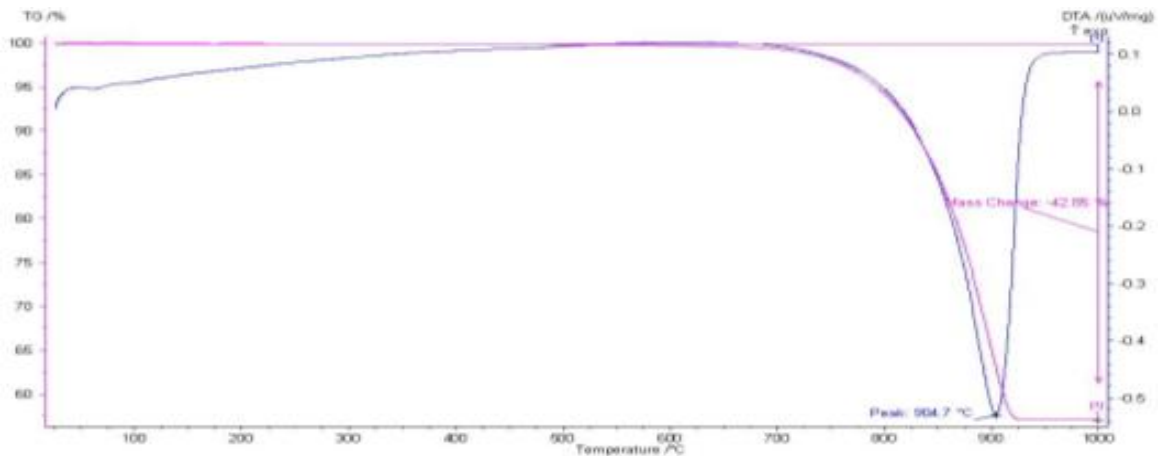Fig. 1 A thermogram of TG-DTA curve for L_k decomposition.

Fig. 2 A thermogram of TG-DTA curve for L_y decomposition.

The thermal analysis was performed in a simultaneous TG–DTA. On the limestones, L_k and L_y, continuous heating from room temperature to 1000°C at a heating rate of 10°C/min, TG and DTA curves (Fig. 1, 2) were obtained, are attributed to the CO_2 from the decomposition of calcium carbonate.

The figures showed that the weight loss is initiated at 625 and 675°C and defined (Eq. 1) fully decomposed approximately at 925 and 935°C for L_y and L_k, respectively. Comparing the percentage values of CO_2 measured by DTA/TG, it is evident that the values are very high and similar to each other. Thus, the limestones could be characterized as high calcium ones. Furthermore, it is observed that the percentage of CO_2 for limestones is higher than the theoretical one.

The heat treatment experiments of 3 cm mean edge cubic specimens of L_k and L_y at the laboratory furnace have shown that decomposition reaction begins at above 600°C, corresponding to the loss in carbon dioxide on limestone and was completed at about 1000°C (Fig. 3). The weight losses of the samples were associated with CO_2 produced in limestone. The specimen comprises a dense carbonate core surrounded by porous oxide layer.
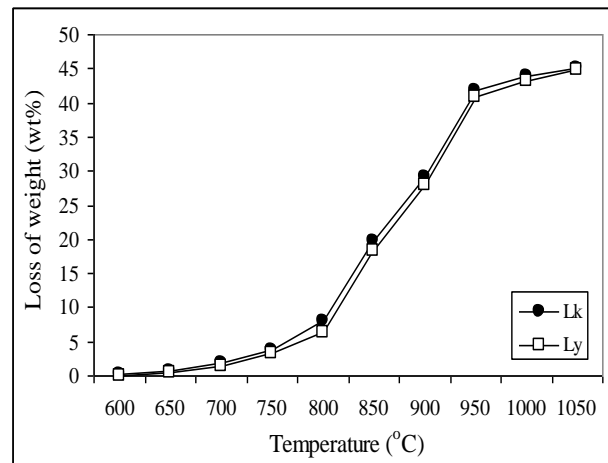

Fig. 3 Loss of ignition of 3 cm cubic specimens of L_k and L_y at different temperatures.

During the decomposition/corresponding to the loss in carbon dioxide, micro-cracks and porosity occurred on limestone. At higher than 1000°C, recomposition started, which in turn led to an increase in sample weight. Namely, Eq. 1 initiates to return from right to left (Kılıç, 2005).

Results of calcination test of cubic samples, which were carried out under identical experimental conditions and by using limestones of different regions showed that weight loss of limestones differed from each other depending on their $CaCO_3$ content, size of crystals and compact structure. Since, $MgCO_3$ content of limestones was in negligible amount with respect to their $CaCO_3$ content, weight loss of samples considered were wholly the result of decomposition of their $CaCO_3$ content (Table 1). Besides, a little change of the mean edges related to shrinkage phenomena were measured on the cubic samples (Table 3).

The samples underwent 1000°C had desired features, that is, they were soft burned, highly reactive, had low shrinkage and density and high porosity. Available CaO content of the lime (CaO) was performed in TS 32 (1999) (BS 6463). The results of the lime (L_k and L_c) analyses are shown in Table 4.

Table 3. Change of the dimension of the 3 cm cubic samples at different calcination temperatures (Decrease).

Sample	Calcination temperature (°C)	Cubic samples with mean edge (mm)
L_k	850	-
L_y		-
L_k	900	-0.1
L_y		-0.1
L_k	950	-1
L_y		-1
L_k	1000	-1
L_y		-1
L_k	1050	-1
L_y		-1

Table 4. Lime properties at different temperatures.

Sample	Calcination temperature (°C)	Available CaO (%)	Loss of ignition (%)
L_k	900	81.26	17.52
L_y		80.05	15.30
L_k	1000	93.52	2.09
L_y		94.46	1.93
L_k	1050	91.80	1.79
L_y		91.61	1.58

High quality limestone with consistent chemical properties is often not available or is scarce. Varying contents of carbonates and impurities can result in the production of over burnt or under burnt product with inconsistent values for residual CO_2 and loss on ignition. Un reacted core, along with absorbed water and carbon dioxide, will result in LOI when the lime is heated. Lime for steel making generally requires a low value LOI of 2 to 4% (or less), some plants actually require an LOI no higher than 0.5 % (Boynton, 1980).

High quality limestone suitable for high-quality lime

defining a common in the iron and steel industries in Turkey and on the world;

- CaO minimum of 53%

- MgO 3% of the maximum,

- Compressive Strength Minimum 50 MPa values were determined (Table 5).

Table 5. Proper limestone properties for some iron steel plants.

Chemical Analysis	Turkey iron steel making industries (Yüceet al. 2002)			World (Kogelet al., 2006)
	Erdemir	Kardemir	İsdemir	Blast Furnace
CaO	53	53	53.5	53.36
MgO	1	0.7		3.1
SiO_2	2*	1.5**	1.5**	0.7
Fe_2O_3				0.2
Al_2O_3				0.3

*SiO_2+ Fe_2O_3+Al_2O_3, ** SiO_2+ Al_2O_3

Conclusion

This study investigated that the effect of limestone characteristics to lime quality for iron steel making industry. The limestones L_y and L_k, were subjected to chemical, physical and thermal analyses to determine their suitability for direct lime production. Chemical analysis showed that the L_y and L_k contains sufficiently high percentages of the main fluxing oxides i.e. calcium and magnesium oxides.

In this study, found that the unit weight of the limestone is larger than 2.55 g/cm^3, low porosity (<%1) and the compressive strength is larger than 50 MPa. These findings show the fact that limestones (L_y and L_k) have compact texture, low porosity, high CaO and low impurity and good thermal conductivity. These types of stones are preferred in the production of lime. Lime will have a good quality and high reaction.

The temperature dependent, it was observed that the reaction temperature has a direct effect on the rate of reaction and limestone chemical properties.

The reaction temperature also has a direct effect on the conductivity of limestone depending on their impurities, porosity and micro-cracks, and hence on the rate of reaction. The reaction rate can be enhanced through improved heat transfer systems.

References

Borgwardt, R. H. (1985). Calcination kinetics and surface area of dispersed limestone particles. *AIChE J.*, **31,** 103–111.

Boynton, R. S. (1980). Chemistry and technology of lime and limestone. 2nd Edition. John Wiley and Sons Inc., New York, 592 pages.

Cargill, J. S., Shakoor, A. (1990). Evaluation of empirical methods for measuring the uniaxial strength of rock. *Int. J. Rock Mech. Min. Sci.*, **27,** 495–503.

Ingraham, T. R., Marier, P. (1963). Kinetic studies on the thermal decomposition of calcium carbonate. *Can J. Chem. Eng.,* 170-173.

ISRM, (1981). Rock characterization testing and monitoring ISRM suggested methods, suggested methods for determining hardness and abrasiveness of rocks, Part 3, 101-3.

Khinast, J. G., Krammer, G., Brunner, C., Staudinger, G. (1996). Decomposition of limestone: The influence of CO_2, and particle size on the reaction rate. *Chem. Eng. Sci.*, **14** (5), 623-634.

Kılıç, Ö. (2005). Comparison of calcination parameters of classic (Eberhart) and parallel flow regenerative kiln (Maerz) and applications on Çukurova region limestones, PhD Thesis, Department of Mining Engineering, Institute of Natural and Applied Sciences, University of Çukurova, Adana, 171 pages.

Kogel, J. E., Trivedi, N. C., Barker, J. M. (eds.), (2006). 7th Edition Industrial Minerals and Rocks: Commodities, Markets, and Users.

Oates, J. A. H, (1989). Lime and limestone chemistry and technology production and uses. Wiley-VCH Verlag GmbH, Germany, 169 pages.

Rubiera, F., Faurtes, B. A., Pis, J. J., Artos, V., Marban, G. (1991). Changes in textural properties of limestone and dolomite during calcination. *Thermochim Acta*, **179**, 125-134.

Schmidt, E. (1951). A non-destructive concrete tester. *Concrete*, **59** (8), 34–5.

Smorodinov, M. I., Motovilov, E. A., Volkov, V. A. (1970). Determinations of correlation relationships between strength and some physical characteristics of rocks. *Proceedings of the Second Congress of the International Society of Rock Mechanics, Belgrade*, **2** (3-6), 35-37.

TS 32 (1999). Building Lime Chapter 2: Test Metots, TSE, Ankara.