

## Assessment of limestone for lime production

(The effect of burning temperature and time on properties of lime produced)

### Calcination of Limestone

Calcination is a thermal treatment process to bring about a thermal decomposition. Limestone is one of the most basic raw materials employed in the steel industry and is used both in iron making and steel making processes. Lime (CaO) is one of the oldest chemicals known to man and the process of lime production is one of the oldest chemical industries. It is used as flux in steel and iron industry, soil stabilization, neutralizing acidity of soil, food supplement for animals, waste water treatment, removing hardness from water, reducing land contamination, calcium silicate brick, purifying gases resulted from plants, power stations and refineries, sugar refining and is also used a filler in paints, plastic and rubber, paper etc.

#### Calcination process:

Calcination reactions usually take place at or above the thermal decomposition temperature. This temperature is usually defined as the temperature at which the standard Gibbs free energy is equal to zero. In case of limestone calcination, a decomposition process, the chemical reaction for decomposition of the limestone is:



Calcination of  $\text{CaCO}_3$  is a highly endothermic reaction. Dissociation of  $\text{CaCO}_3$  proceeds gradually from the outer surface of the particle inward, and a porous layer of CaO remains.

Purity, texture (grain size and shape), crystal structure and density of limestone have a big influence on the processing method. Hence it is necessary to know comprehensive information on the limestone, such as physical and chemical properties, burning characteristics and kinetic parameters of the calcination of limestone.

The following factors affect the calcination process:

1. Pressure of  $\text{CO}_2$  gas in the burning atmosphere.

2. Purity, texture (grain shape and size) of limestone. The more porous stone is more suitable for lime production. The smaller crystals agglomerate during calcination and form larger crystals which in turn cause shrinkage and volume reduction.

Calcination at higher temperature means higher agglomeration and more shrinkage. Also, the density of limestone is related to the crystal structure. The shape of crystals determines the pore space between crystals, and hence the density of the limestone. Larger pores allow easy passage for CO<sub>2</sub> gases during calcination and it results in a reduction of volume during calcination.

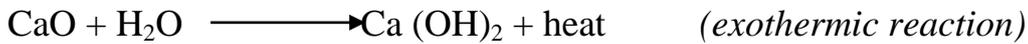
Some limestone, due to its crystalline structure, disintegrates during calcination. This type of limestone is not useful for calcining. There is another limestone whose behavior is the opposite. This type of limestone becomes very dense during calcination that it prevents the escape of CO<sub>2</sub> and becomes non-porous. This type of limestone is also not suitable for calcination.

The production of good quality lime depends upon the type of kiln (rotary or vertical), conditions of calcination and the nature of the raw material. At relatively low calcination temperatures, products formed in the kiln contain both unburnt carbonate and lime and is called '**underburnt**' lime. As the temperature increases, '**soft burnt**' or '**high reactive lime**' is produced. At still higher temperatures, '**dead burnt**' or 'low reactive lime' is produced.

Soft burnt lime is produced when the reaction front reaches the core of the charged limestone and converts all carbonate to lime. A good product is relatively soft, contains small lime crystallites and has an open porous structure. Such lime has the optimum properties of high reactivity, high surface area and low bulk density. Increasing the degree of calcination beyond this stage makes the formed lime crystallites to grow larger, agglomerate and sinter. This results in a decrease of surface area, porosity and reactivity and an increase of bulk density. This product is known as "dead burnt" or "low reactive lime".

The properties of lime considered in producing and consuming industries are:

**1. Reactivity of lime:** Obtained by measuring the temperature resulted from dissolving between 76 gm of lime in 250 liter of water at 22 C°. A thermometer can be used to measure the increase in temperature due to reaction. This reaction is exothermic, and hydrated (slaked) lime is produced:



The rate of releasing temperature depends on the surface area of lime. The higher surface area, the more temperature released and more  $\text{Ca}(\text{OH})_2$  produced.

Reactivity of lime is classified according to the resulting amount of heat:

1. **High reactivity lime:** The temperature rises  $40\text{ C}^\circ$  in less than 3 minutes. The reading of thermometer becomes ( $62\text{ C}^\circ$ ). The particle size of lime used in this test is 3.36 mm.
2. **Medium reactivity lime:** The temperature rises  $40\text{ C}$  in 3-6 minutes, and the reaction ends in 10-20 minutes.
3. **Low reactivity lime:** The temperature rises  $40\text{ C}^\circ$  in more than 6 minutes, and the reaction ends in more than 20 minutes.

The ranges of time (3 minutes and 3-6 minutes) used above is just for lime classification purposes.

**2. Surface area:** The more surface area of lime, the more heat released from reaction with water.

**3. Apparent porosity:** The higher porous lime, the higher reactivity.

**4. Bulk density:** The less density of lime, the higher reactivity. To measure this property, paraffin should be used instead of water because lime reacts immediately with water.

Relation between porosity and bulk density is reverse.

**5. Loss on ignition (L.O.I.) of lime:** defined as the weight of lime lost when heated in  $1100\text{ C}^\circ$  for 1 hour. The lost weight is due to  $\text{CO}_2$  released, which resulted from unburnt calcite grains of the stone calcined, or from  $\text{CO}_2$  and  $\text{H}_2\text{O}$  absorbed from atmosphere during storage or transportation of lime by trucks, trains etc.

This property can be measured by the consumer.

For example; a sample of 100 gm of lime (M1) burnt in ( $1050\text{ C}^\circ$ ) for 1.5 hour. The weight of lime after calcination is (M2). The loss on ignition of the sample is calculated as follows:

$$\text{Loss on ignition (L.O.I.) \%} = \frac{\text{M1} - \text{M2}}{\text{M1}} * 100$$

L.O.I. values in high quality lime are close to zero or not exceed 3%; otherwise the consumer has the right to reject the lime and return it to the factory.

Reasons of high values in L.O.I. of lime are: releasing  $\text{CO}_2$  resulting from unburnt calcite grains of the stone calcined, or  $\text{CO}_2$  and  $\text{H}_2\text{O}$  absorbed from atmosphere during storage or

transportation of lime by trucks, trains etc. Lime must be properly packed and stored, kept out of sunshine and humidity.

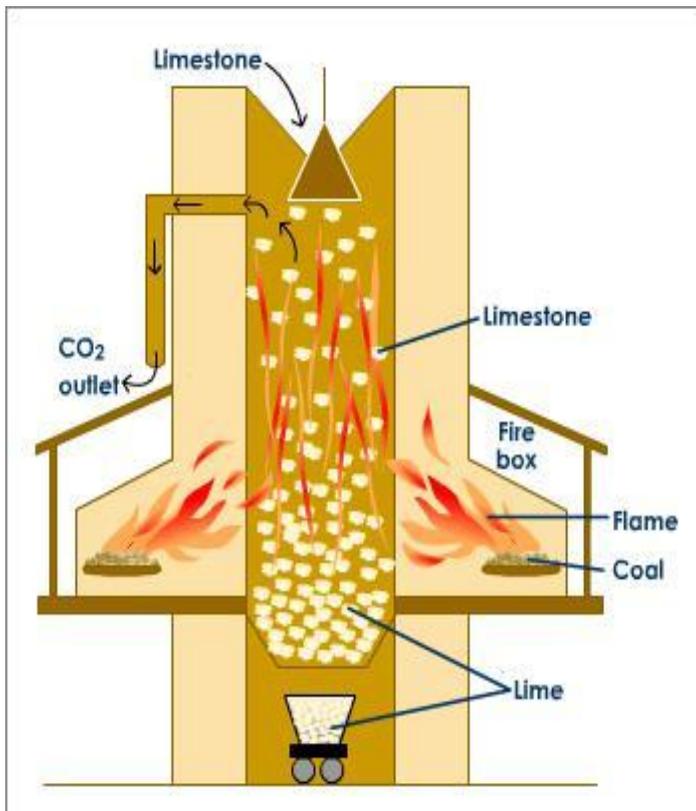
**6. Weight loss (W.L.) of limestone:** During calcination, pure limestone loses 44% of its weight due to CO<sub>2</sub> released. So, weight loss of properly burnt stone should be close to 44%.



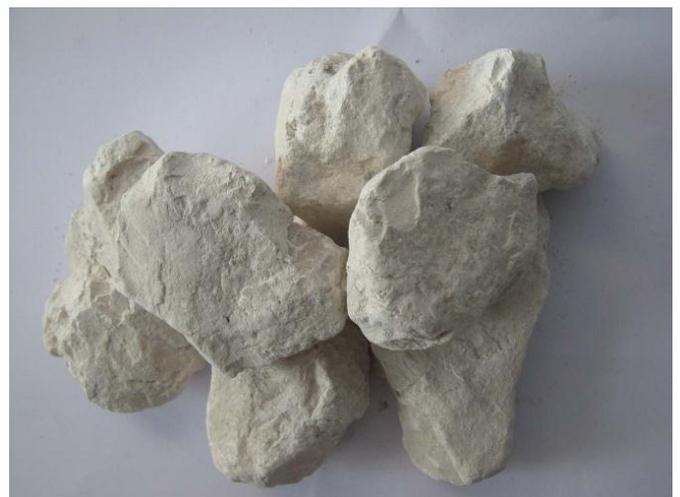
This property cannot be measured by the consumer but only by the producer because he knows the original weight of limestone calcined to produce the lime.

**7. Mechanical properties:** the lime should be strong, dense as it may be used for some chemical industries, e.g. steelmaking. The fine particles of lime go to air during refining of iron and steel and thus lead to close the work and gas escape passages.

*The good quality lime has high reactivity, high surface area, high porosity, low density, with LO.I. < 3% and weigh loss of the stone ~ 44%.*



**Lime Making**



**Quicklime (CaO)**



**Lime rotary kiln**



**Lime vertical shaft kiln**

**Answer:**

The aim of this lab is to study the effect of increasing temperature and time of calcination on the properties of lime produced from chalk. high reactivity (temperature rise is  $44\text{ C}^\circ$  after 2 minutes), high surface area, high porosity (58.3%), low bulk density ( $1.4\text{ gm/cm}^3$ ), least value of L.O.I. (0.43 %) and high value of weight loss (43.51%).

The *optimum conditions of burning (temperature and time)* chosen to produce good quality lime are ( $1050\text{ C}^\circ$  for 1.5 hour) because it give lime with the following properties:

(High reactivity, high porosity, low density, low L.O.I., high weight loss).

Organic (fossiliferous) limestone is easier to burn than recrystallized limestone because it is more porous and has less density than recrystallized limestone.

Temperature is more affecting on lime properties than the time because burning for a long time requires monitoring the burning kiln continuously, and needs more workers and waiting for long time until calcination of the stone completes. Increasing the temperature and burning for short time is better than burning in low temperature and waiting for a long time.

The duration of reaction used to measure reactivity of lime in this problem is (2 minutes). At the higher temperatures (1100, 1150 and  $1250\text{ C}^\circ$ ) the lime became of less reactivity, low porosity, high bulk density, L.O.I. increased and the weight loss decreased.