Factors Affecting the Quality of Quicklime (CaO)
From Mining to Manufacturing to Usage

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As a naturally occurring mineral, limestone exists nearly all over the world. The chemical composition of this mineral varies greatly from region to region as well as between different deposits in the same region. Therefore, the end product from each natural deposit is different. For a stone to be classified as limestone suitable for calcium lime processing, it should contain a minimum of 50% calcium carbonates.

In general, all limestone contains a mixture of minerals such as $CaCO_3$, $MgCO_3$, CaO, Iron, Silica, Alumina and other trace components. To review the effect of all of these constituents in the conversion of limestone to CaO is beyond the scope of this paper; however, we will concentrate on the main mineral - - $CaCO_3$.

The following are the important factors that affect the final quality of quicklime.

1. NATURAL LIMESTONE

A. Impurities

As discussed above, impurities in the limestone would affect the quality of the final quicklime. Typical limestone is composed of the following minerals:

- Calcium Carbonate
- Magnesium Carbonate
- Silica
- Alumina
- Iron
- Sulphur and other trace minerals

Of the above mineral, only calcium carbonate and magnesium carbonate are of interest. These two minerals constitute 85% to 95% of the total composition of limestone. There are two basic types of lime produced from these limestones, calcium lime and magnesium lime.

The high calcium limestone, when calcined, will have between 90% and 95% CaO and 1% to 2% MgO. The magnesium limestone when calcined will have between 60% and 65% CaO and 35% to 40% MgO. This type of limestone is called dolomitic limestone. The discussions in this paper will be limited to calcium limestone only.

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B. Crystalline Structure of Stone

Crystalline structure affects the rate of calcination, internal strength of limestone, as well as resultant CaO crystal size. The smaller crystals agglomerate during calcination, forming larger crystals, thus causing shrinkage and volume reduction. The higher the kiln temperature, the more agglomeration; the more agglomeration, the more shrinkage of volume of the final product.

C. Density of Limestone and Crystalline Structure

The density of limestone and crystal structure are somewhat related. The shape of crystals determines the void space between crystals, and thus, the density of the limestone. Larger voids will allow easy passage for CO_2 gases during calcination, but it also results in a reduction of volume during calcination.

Some limestone, due to their crystalline structure, will fall apart in the calcination process. This type of limestone is not of any value for calcining. Other limestone will act the opposite and will become so dense during calcination that they will prevent the escape of CO_2 and become non-porous. Again, this type of limestone is not suitable for calcination.

2. CALCINATION PROCESS

A. Kiln Temperature

The theoretical temperature required for calcination is about 1,000° C; however, in practice, we find this temperature to be much higher - - about 1350° C. To determine the correct temperature in the kiln is an art rather than a science, and it depends on the limestone size as well as type of kiln and type of fuel used. The kiln operator must experiment to determine the exact temperature for the particular size limestone that is being used. In general, it is best to use the lowest temperature with the shortest possible residence time to achieve full calcination. Higher calcination temperature will cause increased shrinkage and reduction in volume. Higher calcination temperature will also cause recarbonation of the surface of CaO pebbles, with the presence of CO_2 released from the stone as well as by product of combustion, which makes the lime non-porous, and thus not suitable for hydration.

B. Rate of Temperature Rise

The temperature rise must be gradual and even. It is particularly important when using large size limestone, (10 to 15 cm) (4" to 6"). When calcining this size limestone, the limestone must remain porous during the process. As the temperature rises, the outer layer of limestone is heated to disassociation temperature, where CO_2 escapes the stone, leaving capillary passages making the lime porous. As the gas escapes, the limestone shrinks in volume by as

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much as 40%. This shrinkage in volume restricts the passage of gas from the center of the limestone, preventing any additional CO_2 gas from escaping. Too long of a residence time will combine the CaO and CO_2 back to $CaCO_3$ (recarbonation) at temperatures above 1350°.

A good practical size for limestone in rotary kilns is 4-5 cm (1 ½" to 2"). This size will allow for quick heating, short residence time and minimum amount of cores, which create grit.

In conclusion, the smaller size limestone (4-5 cm) (1 ½" to 2") is most suitable for calcination in rotary kilns and will allow optimum residence time. This lower calcining temperature will also allow less fuel consumption. However, larger size limestone and low calcining temperature are needed for vertical single-shaft and multi-shaft kilns. If the temperature rise is too rapid, the outer layer of the limestone pieces are calcined very fast. As the temperature rises, the surface of pebbles will shrink, closing the pores created by the escape of CO_2. This produces increased internal pressure within the limestone. Since the gas cannot escape, the limestone will explode and disintegrate; producing unwanted "fines" reducing the quality of the resultant calcium oxide.

C. Retention in the Kiln

Retention time depends on the size of the limestone as well as calcination temperature. The size of the limestone is the most critical element in calcination. As the limestone enters the kiln, it is exposed to the hot gasses within the kiln. The rate of heat penetration is based on ΔT (temperature of stone vs. temperature of gasses). In addition to ΔT, it takes time for heat to penetrate the limestone. The smaller the stone, the shorter the time for heat penetration. In case of pulverized limestone, this time may be reduced to less than one (1) minute.

If the retention is too short, the core of the limestone will remain calcium carbonate while the outside will convert to calcium oxide. If the retention time is too long, the surface of the pebbles will shrink and the pores created by CO_2 gas escape will close, producing an impervious surface. This type of limestone is called "hard burned" or "dead burned" lime. This lime will not slake in standard slakers. In addition, longer retention time means less production and higher costs for manufacturing.

D. CO2 Concentration in Kiln

As CO_2 is released from limestone during calcination, the concentration of CO_2 in the kiln atmosphere is increased. For proper calcination, the CO_2 must be vented on a continuous basis. If CO_2 is not vented, a combination of high CO_2 concentration and high calcination temperature will recarbonate the lime (on the surface of the pebbles) and convert CaO back to $CaCO_3$.

In addition, the CO_2 and CO will react with the limestone impurities that are part of the limestone inerts.

E. Physical Size of Limestone/Types of Kilns

Depending on the type of kiln, vertical or horizontal rotary, the size of stone charge is different.

On vertical kilns, the limestone moves downward, and the hot gases flows upward through the limestone, therefore the stones must be large enough to provide cavities for combustion gases to move upward. These kilns usually use limestone sizes between 13-20 cm (5" to 8"). In this type of kiln, the temperature rise must be slow and therefore the resultant residence time, long. Typically, vertical kilns are operated at 900 to 1000C. (Note: The temperature range listed here is an average range, and great variations exist in the industry.) Vertical kilns are fuel-efficient, but limited in capacity.

On horizontal kilns, the kiln body rotates, allowing the limestone to tumble and exposing all of the surfaces to hot gas. Typical size of limestone for this type of kiln is between 4-5 cm (1 ½" to 2"). The ideal size for calcining limestone is between 1.25-2 cm (1/2" to ¾"). Uniformity of limestone size for charging the kiln is of utmost importance for a uniform calcining process. But, from a practical point of view, tight sizing is expensive due to the multiple screening required. Small size limestone such as 0.6 cm (1/4") and smaller with a certain percentage of fine in a horizontal kiln, would tend to flop over in mass, thus reducing the exposure of particles to hot gases. This process will result in uneven exposure, thus reducing the quality of the quicklime. In vertical kilns, the presence of powdered limestone will block the voids between limestone, interfering with gas passage, and thus with the heat transfer, causing uneven calcination. In addition, small limestone particles (less than 0.3 cm (1/8")) tend to degrade and cause "fines" which will have to be removed by dust collectors.

F. Type of Fuel Used
Most calcining is done by the use of oil, coal or natural gas for fuel. Typically, vertical kilns use oil or natural gas for fuel; where as horizontal kilns use coal. However, either type of kiln can use any of these fuels. Coal is generally pulverized and blown into the combustion chamber.

Both oil and coal contain certain percentages of sulphur or sulphur compounds. These vary from 0.5% to 3%. Sulphur will combine with CaO at proper temperatures and produce calcium sulphide or calcium sulphate. This generally happens on the surface of CaO pebbles and renders them non-porous, thus not suitable for slaking. In addition, a high percentage of ash in the coal will result in buildup on the refractories in the rotary kiln, thus interfering with the flow of Limestone in the kiln. The kiln must be periodically cooled and the ash build-up removed manually, which is a very costly operation.

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Natural gas is the cleanest fuel and mostly used in vertical kilns. To calcine limestone for food-grade lime, natural gas is the fuel of choice.

G. Pre-Heating and Cooling

Limestone calcination is very energy-intensive and consumes a considerable amount of fuel. Most of the energy waste comes from dumping the kiln gases. To improve the fuel consumption efficiency, the industry has devised the following processes:

- The hot exhaust gasses are used to preheat the limestone before entering the kiln. This not only recovers substantial heat from the exhaust gases, but also will reduce residence time in the kiln, reducing the size of the kiln.

- When limestone has been calcined and exits the kiln, it is red hot, about 1200°C. This represents a substantial source of heat. To recover part of this heat, the combustion fresh air is used to cool the quicklime. The resulting heated air is then fed into the kiln. This heated air improves the fuel consumption efficiency by the recovery of part of the wasted heat.

- Calcining of limestone is done on a continuous basis, thus avoiding heating and cooling of calciner. This continuous operation reduces fuel consumption and minimizes degradation of the kiln's refractory lining.

3. METHOD OF STORAGE OF LIME (CAO)

Once limestone is converted to calcium oxide, this chemical is very susceptible to moisture. Quicklime must be stored in airtight silos to avoid "air slaking," which would deteriorate the quality of the quicklime.

Air slaking is the process of converting the CaO to Ca $(OH)_2$ at ambient temperature by moisture present in the air. "Air slaked" lime is not very reactive and has extremely large hydroxide particles. It is recommended that quicklime be held as short a time as possible by the manufacturer to minimize "air-slaking."

Air slaking takes time; it is not a quick reaction. Even though moisture in the air will eventually air slake the lime but it will take days or weeks of exposure for this chemical reaction to take place. In the systems where lime remains in the silo for weeks and months, air slaking will have a noticeable effect on quality of hydrate. However, when lime consumption is high and several lime trucks are unloaded each day, the exposure time of lime to moist air to affect the quality of lime noticeably.

Exposure of quicklime to an atmosphere containing a high percentage of CO_2 also must be avoided. CO_2 will be absorbed by the lime and convert it to its original form of $CaCO_3$. This conversion is accelerated at elevated temperatures.

Degradation and reduction of the size of the pebbles will take place, due to the weight of material stored in tall storage silos. Properly calcined quicklime is very porous and soft. It can be crushed in hand by pressing between two fingers. This type of lime will degrade easily during storage and transportation to the site, as well as by pneumatic loading into storage silos. As particles of CaO become smaller due to handling, the particles' surface areas increase. This increased surface area, when exposed to moist air, will increase air slaking, which reduces the quality of the lime.

4. SIZE CLASSIFICATION

There are many different sizes of lime available from the quicklime manufacturers. The most common sizes are:

- Pulverized quicklime (100% passes 200 mesh)
- 0 x 1/8" (crushed lime)
- 1/8" x ¼" (rice lime)
- ¾" x ¼" (pebble lime)

Pulverized quicklime will slake very quickly and produce a very reactive hydrate. Due to its fine particle size, pulverized quicklime causes dusting as well as build-up within the slaker, which results in additional maintenance. Due to its fineness, it is also more susceptible to "air slaking" prior to its introduction into the lime slaking equipment.

If pulverized quicklime is to be used, it is best to pulverize the quicklime just before slaking so the quicklime does not have time to absorb moisture from the atmosphere.

The ideal size for quicklime, for slaking is 1/8" x ¼", (rice lime) with the next best size range being ¼" x ¾" (pebble lime). This size range minimizes air slaking and reduces slaker maintenance and housekeeping. Large size limestone (1 ½" to 2") is difficult to slake. The difficulty is due to the large size since a great deal of steam is generated at the moment the 2" piece of lime comes into contact with the hot slurry. The reaction, in the case of a reactive lime is like a mini-explosion with a sudden release of a large amount of steam. Splashing and build-up occur within the slaking chamber, resulting in extra build up and maintenance.

5. METHOD OF TRANSPORTATION

Based on the above comments, it is obvious that quicklime must be transported in airtight containers to isolate it from moisture in the atmosphere. Typically, this is

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done by tankers specially designed for this type of dry chemical. Loading is done mechanically, and unloading is done pneumatically. When pneumatically unloading, the transfer velocity must be kept to a minimum to reduce degradation in the case of pebble lime. For this reason, mechanical unloading is the preferred choice, but it requires a higher investment. Pneumatic unloading where fresh air is used for transport should be avoided in high humidity or rainy circumstances.

6. METHOD OF STORAGE AT THE SITE

Typically, lime is stored at the site either in super sacks or in silos. Industrial plants require a storage capacity equal to two weeks consumption. In some remote areas, the storage capacity may be as much as two months. If the lime is going to be stored for more than two weeks in the silo, some precautions are necessary to prevent air slaking:

1. Dry the air above the material in the silo by using a desiccant or refrigerant air dryer and recirculate this air periodically.

2. Purge the air above the lime in the silo with dry instrument air periodically.

3. Avoid pneumatic loading of the silo during rainy days.

4. Store the quicklime in silos painted white in areas where humidity is high and day/night temperatures are substantially different. This causes condensation inside the silo and build-up on the silo sidewall, where the sun hits during the afternoon.