CHAPTER 11.3

Calcination

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Calcination involves the application of thermal energy to dissociate and remove water from hydrates, carbon dioxide from carbonates, and/or other chemically bound gases from ores or green coke. Commercial calcination operations are generally conducted at higher temperatures than drying; because the reactions are more endothermic, more heat must be supplied to sustain the reaction at relatively high temperatures.

Calcination is frequently performed in directly fired rotary kilns. However, shaft kilns, fluidized-bed reactors, flash calcining systems, and other equipment are also suitable for calcination operations. When a controlled atmosphere is required, calcination can also be performed using indirectly heated furnaces.

Applications for calcination products are wide ranging, and the impact of those applications extends beyond the products themselves. Magnesia (MgO) uses include environmental remediation applications and refractories for steel production. Calcined petroleum coke is used in aluminum and steel production. Other calcined materials fulfill many other chemical and industrial needs. *Calcine* comes from the Latin word for lime, *calx*, and lime (CaO) is a widely used calcination product.

Few mineral products have as many or as varied applications as lime. Most lime is produced specifically to meet customer specifications. The largest consumer of lime is the steel industry, where lime is used as a flux for impurity removal in steel production (basic oxygen furnaces, electric arc furnaces, and secondary refining). Other major uses of lime include environmental remediation applications, such as water treatment and flue gas desulfurization (FGD); stabilization in construction; pH control in mining and mineral processing; sugar production; and for the production of precipitated calcium carbonate (PCC), which is used for paper manufacturing, medicinal applications, and so forth. The United States has 75 commercial lime plants; some of these are lime kilns producing lime for internal (captive) use, such as in the sugar industry (USGS 2009; National Lime Association, n.d.).

Limestone is a sedimentary rock that is the third most abundant sediment in the earth's crust (behind shale and sandstone). It occurs in varying degrees of purity, and most deposits are not suited to the production of high-grade lime. Mineralogically, four calcium or magnesium carbonate minerals are important as constituents of limestone. Two calcium carbonates ($CaCO_3$) are of interest: calcite, which has a rhombohedral structure; and aragonite, which has an orthorhombic structure. The magnesium carbonates of interest are dolomite ($CaCO_3 \cdot MgCO_3$) and magnesite ($MgCO_3$); both dolomite and magnesite have a rhombohedral structure (USGS 2009; Downey 2013).

Limestone is classified according to the amount of magnesium carbonate that it contains. High-calcium limestone contains less than 3% magnesium carbonate. High-calcium limestone is used to produce chemical grade lime for applications such as for PCC and sugar production. Magnesian limestone contains 5%–35% magnesium carbonate and is used to produce magnesian quicklime. Dolomitic limestone contains 35%–46% magnesium carbonate and is used to produce dolomitic quicklime. Glass manufacture is one application for dolomitic lime. The most significant impurities in limestone include silica (quartz, chert, clay, shale, feldspar), alumina, hematite, sulfur (often in pyrite), and sulfate (gypsum and anhydrite). Magnesium carbonate ($MgCO_3$) occurs in practically all limestone deposits (Downey 2013).

Most limestone mining operations in the United States are quarries, but there are a few underground mining operations. After quarrying, the ore is crushed and sized before calcining. Crushing for rotary kiln calcination is optimized to reduce the formation of fines, which are not normally a salable product. Off-gases from calcination are treated to remove particulate matter, and air-quality monitoring is conducted.

HYDRATED LIME

Hydrated lime, an important lime product, is often used in neutralization, construction and pharmaceutical applications, water treatment, FGD, and for soil stabilization. Lime hydration is a highly exothermic reaction commonly known as *slaking*. The heat of reaction for the following reaction was calculated from the appropriate heats of formation (Kubaschewski et al. 1967). Quicklime readily hydrates to form calcium hydroxide, $Ca(OH)_2$, when it is slurried in water:

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$$CaO + H_2O = Ca(OH)_2 \qquad \textbf{(EQ 1)}$$
$$\Delta H°_{R\ at\ 298.15\ K} = -15.400\ kcal$$

Hydrated lime may be marketed as a dry solid, which is sold as both bulk material and bagged, or as milk of lime. The $Ca(OH)_2$ slurry is called *milk of lime*. Wet hydration is conducted in a single stage. Dry hydration can be performed in one, two, or three stages, but the three-stage process described here is becoming more prevalent.

A more rapid hydration tends to produce finer particles, because there is less time for agglomeration to occur. It is important to balance the initial lime particle size with reaction considerations, because a smaller particle, while producing fine hydrated lime caused by the rapid reaction, may react so quickly as to expose the particles to excessive temperatures, resulting in a delay in the hydration. Important parameters for optimal size $Ca(OH)_2$ production therefore include proper feed sizing, adequate mixing, sufficient hold times, good water-spray distribution, and adequate monitoring and controls. To produce hydrated lime with the highest surface area (>40 m^2/g), which is used in FGD, additives are employed (Collarini 2012).

The atmospheric hydration reaction occurs in three phases: In the first few seconds after the lime is contacted by the water, a strong rapid reaction proceeds, then there is a brief period where the hydrated lime formed on the surface of the lime particle impedes contact between the lime particle underneath and the water; finally, the $Ca(OH)_2$ crystals separate from the particle and the remaining lime reacts with the water. The hydrator is therefore constructed with three chambers. The first chamber is a reaction compartment, where the lime and the water are vigorously agitated; the lime/hydrate then proceeds to a further mixing compartment and finally advances to a seasoning compartment. The resulting product of this process is a dry powder, which is the predominant commercial form (Collarini 2012; Cimprogetti 2017).

CALCINATION REACTIONS AND THERMODYNAMICS

Thermodynamics allow the determination of operating parameters where a calcination reaction will be spontaneous. In the van't Hoff reaction isotherm shown in Equation 2, ΔG_R is the Gibbs free energy of the reaction, and $\Delta G_R°$ is the Gibbs free energy in standard state of the reaction. From Equation 3, R is the ideal gas constant, T is the temperature of interest, Q is the activity quotient, and K is the equilibrium constant. The activity quotient is equal to the product of the activities of the reaction products divided by the product of the activities of the reaction reactants. The activity of a pure condensed substance in its standard state is equal to 1, and the activity of a gas is essentially equal to the partial pressure of the gas.

$$\Delta G_R = \Delta G_R° + RT\ln Q \qquad \textbf{(EQ 2)}$$

$$\Delta G_R° = -RT\ln K \qquad \textbf{(EQ 3)}$$

The van't Hoff reaction isotherm equation can be manipulated to the form shown in the following equation:

$$\Delta G_R = RT\ln(Q/K) \qquad \textbf{(EQ 4)}$$

The van't Hoff reaction isotherm in this form allows several determinations to be made about the reaction. If Q = K, then the system is at equilibrium, and $\Delta G_R = 0$. If $Q/K > 1$, ΔG_R will be positive, the reaction will not proceed as written, and the reverse reaction is favored. If $Q/K < 1$, ΔG_R will be negative, and the reaction will therefore be spontaneous. It is possible, theoretically, to then manipulate the operating parameters, so that the value of Q is less than K. These operating conditions would allow the desired calcination reaction to proceed. The general carbonate calcination reaction is shown in the following equation, and the van't Hoff reaction isotherm for this reaction is shown in Equation 6.

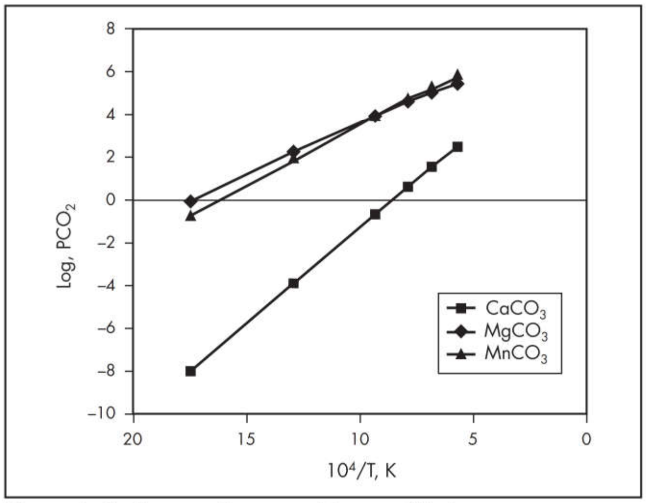


Figure 1 Carbonate decomposition equilibria

$$MeCO_{3(s)} \rightarrow MeO_{(s)} + CO_{2(g)} \qquad \textbf{(EQ 5)}$$

$$\Delta G_R = \Delta G°_R + RT\ln P_{CO2} \qquad \textbf{(EQ 6)}$$

Manipulating the van't Hoff equation yields the following equation. Further, for the carbonate reaction, it yields Equation 8. It is then useful to plot $\ln P_{CO2}$ (or $\log P_{CO2}$) as a function of 1/T.

$$d\ln K/d(1/T) = -\Delta H°_R/R \qquad \textbf{(EQ 7)}$$

$$d\ln P_{CO2}/d(1/T) = -\Delta H°_R/R \qquad \textbf{(EQ 8)}$$

A van't Hoff diagram, shown in Figure 1, can be used to determine the temperature at which the decomposition reaction is spontaneous. Temperature increases from left to right in the diagram; as a point of reference, 10 on the abscissa is equivalent to 726.85°C. The temperature necessary for the decomposition pressure to reach 1 atm varies considerably from one substance to the other. The van't Hoff diagram can also be used to select temperatures for selective decomposition.

Calcination proceeds according to the shrinking core model. As a piece of carbonate decomposes, increasing temperatures are required to calcine further into the particle, through the layer of oxide that has formed, as shown in Figure 2, because CaO, for example, has a lower thermal conductivity than $CaCO_3$. As a carbonate particle is calcined, it is enveloped in carbon dioxide (CO_2) gas film. If the ambient pressure (P_{TOTAL}) is 1 atm, then the CO_2 partial pressure around the particle will also be 1 atm. For rapid carbonate decomposition to occur, the equilibrium vapor pressure of the CO_2 must exceed the CO_2 partial pressure in the surrounding atmosphere (Downey 2013).

The purpose of limestone calcination is to convert the calcium carbonate mineral to calcium oxide, CaO. Calcium oxide is a very important industrial commodity that is known

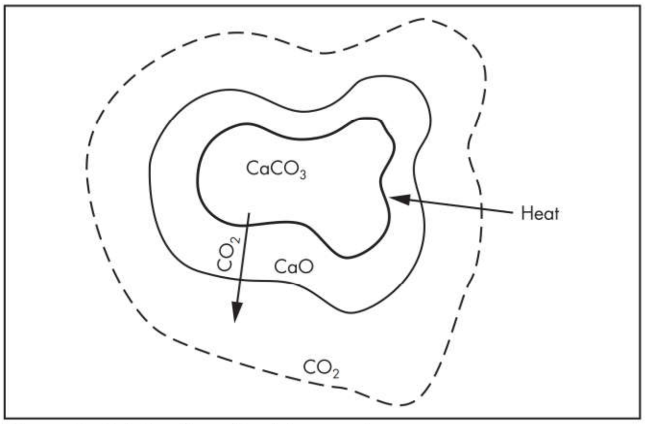


Figure 2 Calcination of calcium carbonate

Table 1 Common carbonate reactions and reaction heats

Material	Reaction	Heat of Calcination Reaction*
Calcium carbonate	$CaCO_3 \rightarrow CaO + CO_{2(g)}$	$\Delta H°_{R\ at\ 298\ K} = 42.750$ kcal
Magnesium carbonate	$MgCO_3 \rightarrow MgO + CO_{2(g)}$	$\Delta H°_{R\ at\ 298\ K} = 24.250$ kcal
Manganese carbonate	$MnCO_3 \rightarrow MnO + CO_{2(g)}$	$\Delta H°_{R\ at\ 298\ K} = 27.850$ kcal
Dolomite	$CaMg(CO_3)_2 \rightarrow CaO{\cdot}MgO + 2CO_{2(g)}$	$\Delta H°_{R\ at\ 298\ K} = 67.000$ kcal

*Data from Kubaschewski et al. 1967

as *burned lime*, *quicklime*, or just *lime*. Where the heat of reaction for each of the following reactions is calculated from the appropriate heats of formation (Kubaschewski et al. 1967), the calcium carbonate calcination reaction is

$$CaCO_3 \rightarrow CaO + CO_{2(g)} \qquad \textbf{(EQ 9)}$$
$$\Delta H°_{R\ at\ 298.15\ K} = 42.750\ \text{kcal/mole}$$

The calcination product of dolomite, $CaCO_3{\cdot}MgCO_3$, is called *dolomitic lime* or *dolime*. For dolomite, the reaction is as follows:

$$CaMg(CO_3)_2 \rightarrow CaO{\cdot}MgO + 2CO_{2(g)} \qquad \textbf{(EQ 10)}$$
$$\Delta H°_{R\ at\ 298.15\ K} = 67.000\ \text{kcal}$$

Table 1 shows the heats of reaction for some of the most common carbonate calcination reactions. The theoretical limestone dissociation temperature is 848°C. At 900°C, the CO_2 partial pressure reaches atmospheric pressure (760 mm Hg) in a pure CO_2 atmosphere. The theoretical dissociation temperature of dolomite is 725°C (Downey 2013). In all cases, the actual dissociation temperature is influenced by the impurities present. Practical calcining temperatures are considerably higher than their theoretical values because the reaction and heat transfer rates are not rapid enough for economical operation. The effects of the operating parameters on the product are very similar for the different carbonates.

For limestone calcination, high-reactivity lime is produced when the surface temperature of the material does not exceed 1,180°C as it passes through the kiln's calcination zone. The corresponding gas temperatures are typically 90–150 degrees higher than the surface temperature of the charge materials. Crystal size, pore volume, specific surface area, and reactivity are important and closely related lime properties. Other carbonates have similar temperature parameters to produce a product with high reactivity and other desired properties. Optimum conditions should be determined for each type of stone; an optimum residence time exists for each feed size distribution and temperature.

At constant residence time, increasing temperature generally reduces reactivity, causes the grains to coarsen, and reduces surface area and porosity. Temperature is more important than residence time for these qualities. Inorganic impurities (silica [SiO_2] and alumina [Al_2O_3]) have a similar effect on crystal size, pore volume, specific surface area, and reactivity.

The analyses of the feed and the product are related in a certain ratio, which depends on the amount of CO_2 removed during calcination. Loss-on-ignition (LOI) tests are performed on representative samples of the burned product as a quality control measure. Residual CO_2 content in the product is part of the LOI, which can also include relatively small amounts of moisture and organic matter in the product.

Important properties include grade, purity, and reactivity. Using lime as an example, *grade* refers to the percent CaO in the calcined product, whereas purity refers to the available CaO determined by ASTM C25-17. Reactivity is the capacity of the CaO to react with water during hydration and is tested with the ANSI EN 459-2 reactivity test (commonly referred to as the T60 test), which measures the temperature rise as a function of time when reacted with water.

The main quality control issue in limestone calcination is the balance between unreacted core versus overburned lime on the calcined particles' surfaces. The terms *soft burned*, *medium burned*, and *hard burned* relate to the lime reactivity; just as *caustic* (or *light burned*), *hard burned*, and *dead burned* refer to magnesia reactivity (Martin Marietta 2018). *Soft lime* is produced when the surface temperature of the material does not exceed 1,180°C as it passes through the kiln's calcination zone. Reactivity primarily depends on the calcination temperature, and to a lesser extent, on the calcination time and impurities (which can flux with CaO).

Compared with hard-burned lime, soft-burned lime has smaller crystal grain size, larger specific surface area (>1.0 vs. <0.3 m^2/g determined via BET [Brunauer–Emmett–Teller] analysis), smaller pores, but larger total pore volume (46%–55% vs. <34%), lower apparent density (1.5–1.8 vs. >2.2), and a higher chemical reactivity (>20°C/min vs. <2°C/min) (Downey 2013).

The time available (in a particular calcining operation) to generate the heat transfer determines the maximum particle size that can be effectively calcined in the system. Additionally, the feed particle size distribution will determine the uniformity of the product quality; wider size distributions naturally lead to greater quality variations. A narrow feed size distribution is required to maintain uniform product quality.

Magnesite is calcined to produce caustic (light-burned) magnesia, hard-burned magnesia, or dead-burned magnesia. Following calcination at temperatures ranging between 700° and 900°C, the MgO is further heated to ~1,750°C to shrink the particles. This action increases the particle density and renders the MgO less reactive. Magnesia reactivity is measured as a function of time with the citric acid test. Dead-burned MgO produced by magnesite calcination has little reactivity and is often destined for use in refractory applications (i.e., basic refractory brick for magnesite, mag-chrome, chrome-mag, etc.) or in ceramic manufacturing (Downey 2013). Hard-burned magnesia is calcined at temperatures ranging from 1,000° to 1,500°C for applications requiring low reactivity, such as phosphate cement (Martin Marietta 2018). Caustic magnesia is produced by calcining magnesite at temperatures ranging from 700° to 1,000°C for applications including environmental remediation.

Other minerals are calcined as well, such as magnesium hydroxide, $Mg(OH)_2$, and magnesium sulfate, $MgSO_4$, to produce MgO. Magnesium sulfate decomposition proceeds according to the following equations (Kubaschewski et al. 1967):

$$MgSO_4 \rightarrow MgO + SO_3 \qquad \textbf{(EQ 11)}$$
$$\Delta H^\circ_{R\ \text{at}\ 298.15\ K} = -57.200\ \text{kcal}$$

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2 \qquad \textbf{(EQ 12)}$$
$$\Delta H^\circ_{R\ \text{at}\ 298.15\ K} = -33.650\ \text{kcal}$$

Petroleum coke (green coke) is calcined to remove volatile matter, moisture, and impurities. Calcining also increases the density and improves the electrical conductivity of the coke within the coke feed quality limitations. Coke calcining is performed on-site (e.g., at the anode plant) or at the petroleum refinery. Applications for the calcined petroleum coke include anodes for aluminum production, for the production of titanium, and in the steel industry for carbon and graphite electrodes and as a recarburizing agent (Aminco 2013; Edwards 2014).

Calcining of petroleum coke includes drying, devolatilization, and densification stages. Most coke calcination is performed in rotary kilns at 1,200°–1,350°C under an oxygen-deficient atmosphere. Liquid, gas, or solid fuel is utilized for process heat, which can be supplemented by the controlled combustion of a small amount of the volatiles and coke fines using secondary and tertiary combustion air. Important operating parameters include temperature and residence time. After calcination, the coke is cooled in a rotary cooler, normally by water quenching. The kiln off-gas proceeds to an afterburner, where the volatiles are combusted with injected air, and the heat is recovered for steam production (Edwards 2014).

Shaft kilns and rotary hearth kilns are also used to a lesser extent for coke calcination. Shaft kilns are predominately utilized in China. Feed for a shaft kiln can contain a higher percentage of volatile matter, because the green coke can be easily blended with calcined coke to adjust the amount of volatile matter to the approximately 11%–12% required in the feed. Green coke is fed from the top and proceeds through the kiln by gravity; the residence time of the coke is controlled by a discharge valve or gate at the bottom of the kiln, below a cooling jacket. The volatile matter that is released from the coke flows from near the top of the shaft to the surrounding flue, where it is combusted and indirectly heats the calcine. The heating rate of the calcine is very slow, ~1°C/min. Residence time in a shaft calciner is 28–36 hours, whereas a rotary calciner has a residence time of ~1 hour. The shaft calciner produces a higher yield of coke with a higher density and larger particle size (Edwards 2011).

CALCINATION EQUIPMENT

The original carbonate calcining systems were simple pot kilns. The U.S. lime industry currently favors rotary kilns, whereas shaft furnaces prevail in Europe, but some of the most recent kiln installations in the United States have been parallel shaft regenerative kilns (USGS 2009). Equipment choice is dependent on many factors: the product required by the customer (e.g., reactivity), sales volume, resource utilization efficiency (using fines as well as larger stone), capital cost, maintenance costs, and environmental impact among others. Both of these alternatives are fully automated, high-capacity systems, but the parallel flow regenerative shaft kilns are significantly more energy efficient. A rotary kiln with a preheater is approximately 55% energy efficient, where a parallel shaft regenerative kiln may be more than 80% efficient. Process control technologies have become the norm in commercial lime production. Energy costs, product uniformity, and decrepitation are important considerations in the choice of kiln. Table 2 summarizes the capacity, fuel consumption, and applicable feed size range for the main commercial lime kilns.

Coke calcining is typically conducted in long rotary kilns, as shown in Figure 3, but shaft kilns, which are indirectly heating by combusting the volatile matter released as the coke is calcined, and rotary hearth furnaces are utilized as well.

Rotary Kilns

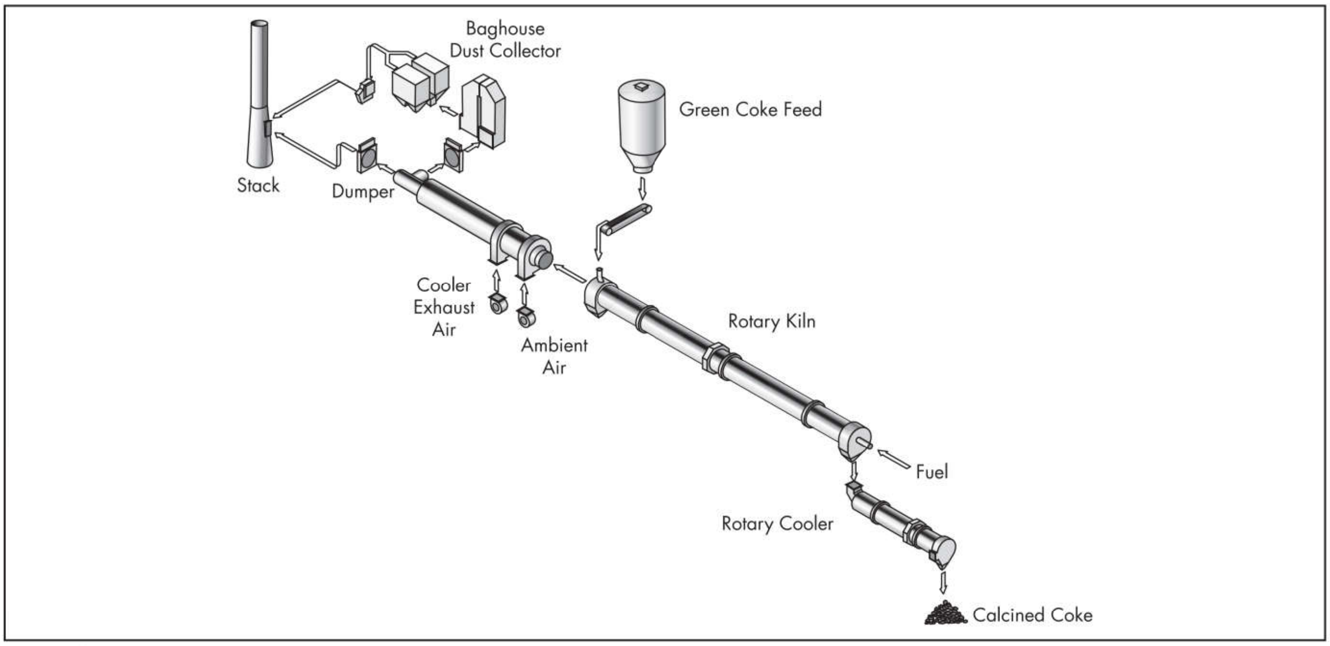
In general, rotary kilns produce uniform, high-quality products, have high availability and production capacity, require relatively low labor costs, but have relatively high fuel consumption. Rotary kilns can be operated utilizing most fossil fuels, including coal, natural gas, oil, petroleum coke, and some waste fuels. If a low sulfur lime is required, it may therefore be produced in a rotary kiln. Rotary kilns without a preheater (long rotary kiln) are used for coke calcination and can also be useful for lime that decrepitates (Rosenqvist 1974). A conventional long rotary kiln can have a capacity up to 907–1,134 t/d (metric tons per day), utilizing feed size of ~3–55 mm.

Rotary kilns are essentially heat exchangers and conveyors—heat is transferred from the combustion flame and gases to the bed as the material moves from the feed to the discharge end of the kiln. Radiation from the flame and the refractory accounts for most of the heat transfer to the charge, so it is important for the material to be continually agitated to expose fresh surface area to facilitate the heat transfer. Conduction from the refractory bricks accounts for a substantially smaller percentage of the heat transferred to the charge, and convection accounts for a minor percentage of heat transfer, as the hot gas stream contacts the charge (Downey 2013).

A rotary kiln is a cylindrical reactor that rotates about its longitudinal axis. The tube is usually sloped down roughly 1 cm per 0.24 m from the feed end to the firing end (from the horizontal). Commercial reactors are typically 2.4–5.2 m in diameter, and the length-to-diameter ratio generally ranges from 4 to >10. The charge in the kiln is normally less than 15% of the cross-sectional area. In some applications, sections with expanded diameter are included to increase burden depth

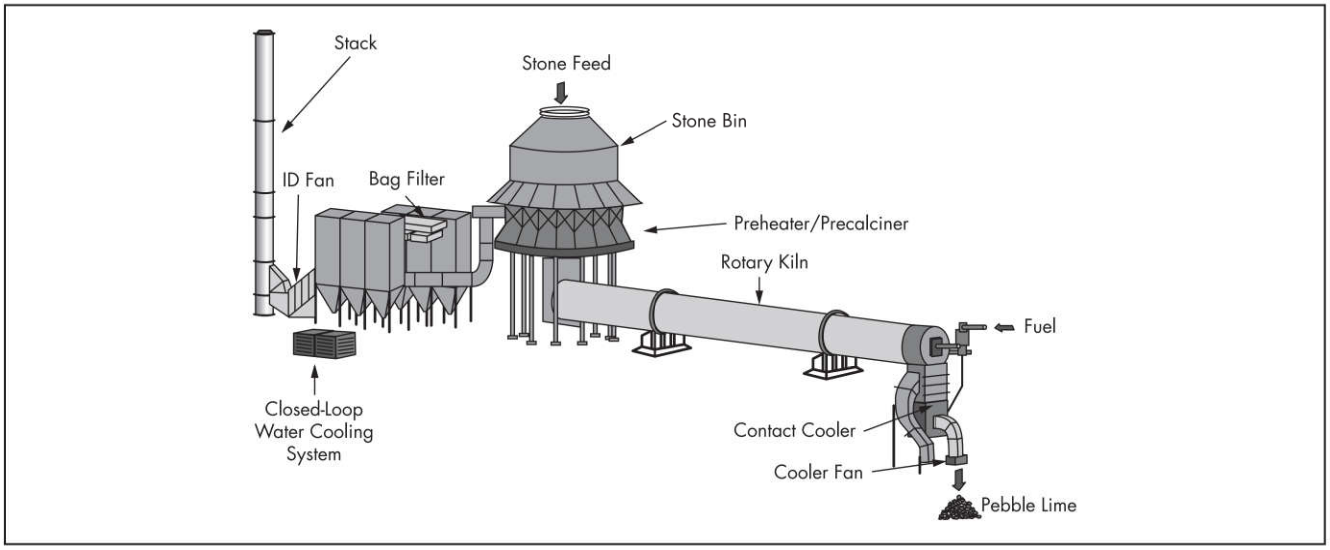
Table 2 Kiln capacity, fuel consumption, and feed size by type

Kiln Type	Capacity, t/d	Fuel Consumption, GJ/t limestone	Feed, mm
Annular shaft	200–600	3.64–3.94	15–200
Rotary kiln with preheater	300–1,200	5.1–6.3	3–55
Parallel shaft regenerative (rectangular)	100–400	3.64–3.93	30–120
Parallel shaft regenerative (circular)	300–800	3.64–3.93	30–160
Parallel shaft regenerative (fine lime)	200–400	3.31–3.56	15–40



Adapted from Metso 2017

Figure 3 Rotary coke calciner



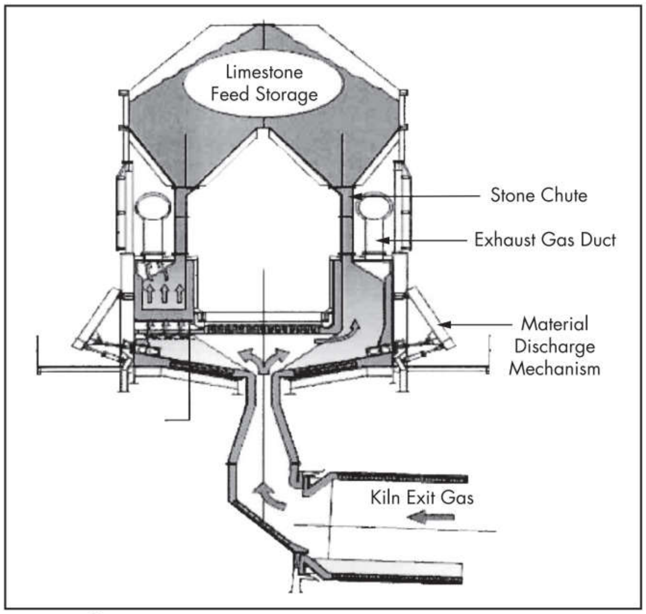
Courtesy of Metso

Figure 4 Preheater rotary lime kiln with baghouse

and residence time. Dams may also be installed to increase residence time. The steel shell is refractory lined to reduce heat loss and to protect the steel shell.

The tube ends are sealed, typically by leaf seals, to prevent gas leakage. Maintaining a slight negative pressure (0.3–2.5 mm of water) in the kiln helps control emissions. Draft is provided by induced-draft (ID) fans that are located beyond the feed end of the kiln (typically after the baghouse). Feed enters the higher end of the cylinder and works its way through the cylinder because of the feed rate; rotational speed (measured in revolutions per minute), which is controlled by a variable speed drive; and slope. These factors dictate the residence time of the burden in the tube, but only the rotational speed is controllable by the operator. Finished product discharges at the lower end of the tube to a cooler. Countercurrent gas-to-solids flow also improves heat transfer efficiency (Downey 2013). Gas analyzers are usually installed at the feed end to monitor oxygen and carbon monoxide (CO) in the off-gas.

Because of the fuel consumption issue, rotary kilns are usually equipped with preheaters and other fuel-saving devices. Major savings can be achieved by external preheaters, particularly if some of the carbonate decomposition takes place in the preheater. A rotary kiln with a preheater is shown in Figure 4. Coke is usually calcined in a rotary kiln with drying and preheating occurring in the first section of the kiln.



Courtesy of Metso

Figure 5 KVS/Metso preheater

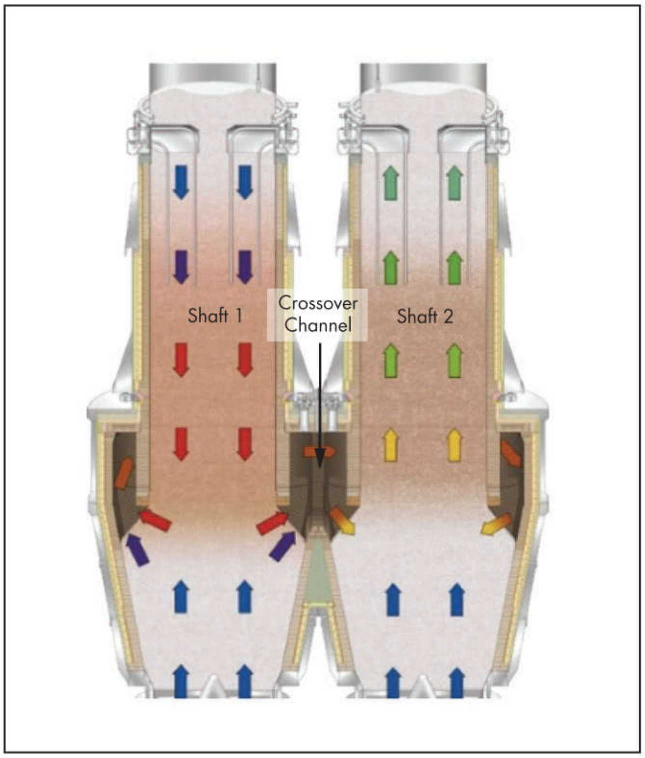
Common types of preheaters used with a rotary kiln include the FLSmidth, which is similar to the Metso but has an internal stone bin, and the Kennedy Van Saun (KVS) now distributed by Metso, shown in Figure 5, which takes advantage of the ~1,000°–1,100°C kiln off-gas to partially calcine the charge, releasing 20%–25% of the CO_2 before the stone enters the kiln. In this type of preheater, stone is fed from an integral storage bin through vertical chutes, where it is heated, moisture is evaporated, and the decomposition begins. Discharge to a transfer chute to the kiln feed end is achieved by hydraulic rams on the preheater perimeter (Metso, n.d.). Preheater off-gas averages ~230°–260°C, so filter media choice must take this into consideration if a baghouse is utilized for dust collection.

Gas suspension preheaters, consisting of multiple cyclones, are commonly used in the cement industry. Dry feed is injected into the side of the uppermost riser pipe and cyclone where it contacts the rising exhaust gas; the feed proceeds down through the other cyclones, countercurrent to the rising exhaust gas; and the preheated feed is ultimately fed into the kiln.

Shaft Kilns

Vertical Shaft Kilns

Vertical shaft kilns are frequently utilized to calcine green petroleum coke and are also used for lime calcination for captive production. The vertical shaft kilns for coke calcination are normally indirectly heated by the combustion in the flue that surrounds the shaft of the volatiles released from the coke feed (Metso 2017). The vertical shaft kilns can process between 15 and 400 t/d of lime using coke or coal as fuel. For limestone calcination, the coal or coke is blended with the feed and is conveyed to the kiln. Lime is extracted with vibrating extractors at the bottom of the kiln, and CO_2 is recovered from the top of the kiln to be used in other processes.



Courtesy of Maerz

Figure 6 Gas flow in a PFR lime kiln

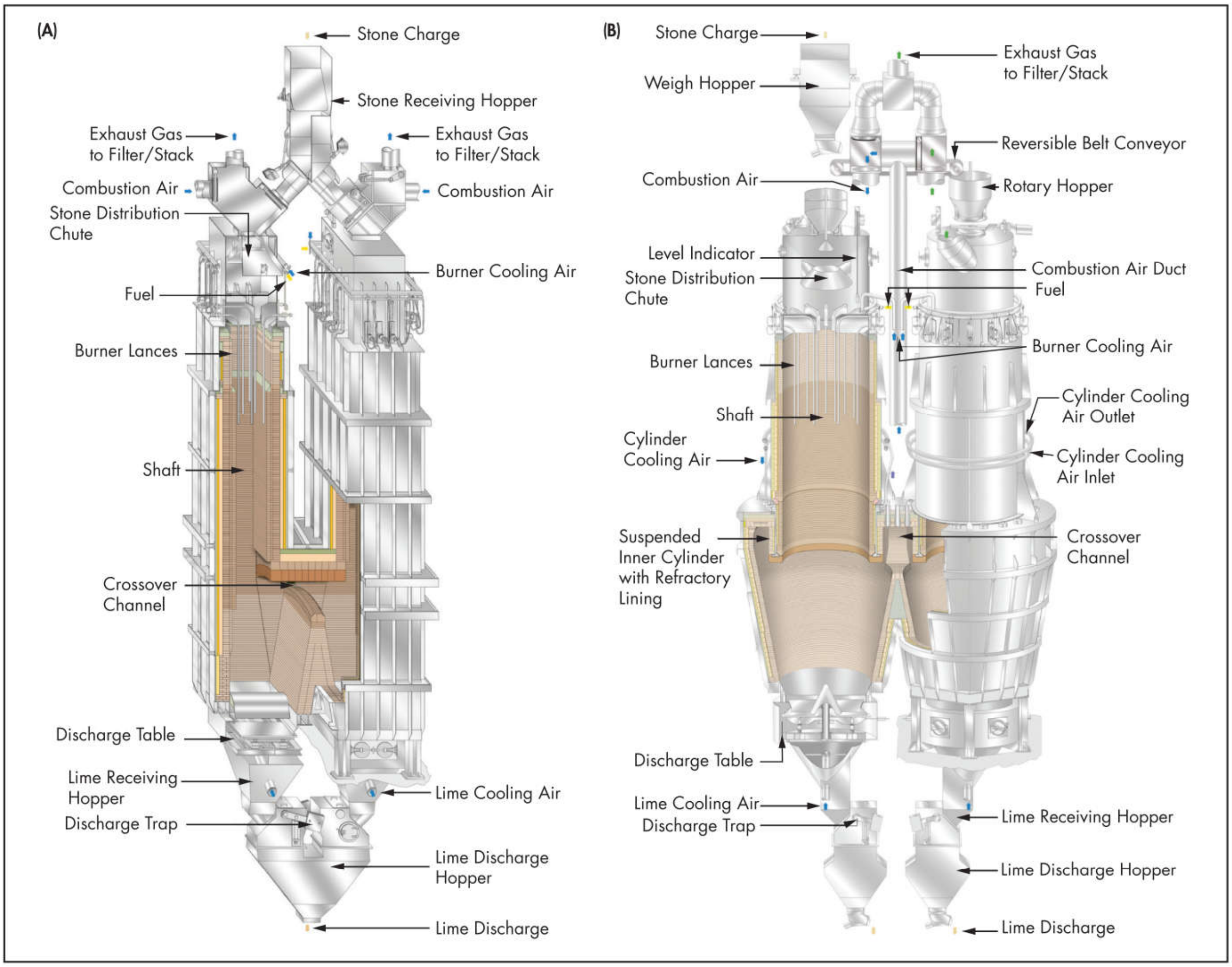
Annular Shaft Kilns

Annular shaft kilns have some commercial utilization for both limestone and dolomite. With capacities of 200–600 t/d of 15–200-mm stone, fuel consumption averages ~870–940 kcal/kg for limestone and 820–900 kcal/kg for calcination of dolomite. In gigajoules per metric ton, that is 3.64–3.94 GJ/t of limestone and 3.43–3.76 GJ/t of dolomite. These external combustion kilns have two combustion levels with four to five combustion chambers per level and normally utilize gas, fuel oil, or solid fuels (ThyssenKrupp 2016).

Parallel-Flow Regenerative Shaft Kilns

PFR shaft kilns have two vertical shafts connected by a crossover channel. The parallel flow of limestone and hot gases preheat the combustion air in one shaft (the burning shaft), and concurrently, a mixture of combustion gases and air from the lime cooler preheats the limestone in the second shaft (the nonburning shaft), as shown in Figure 6. At intervals of ~10–15 minutes, each shaft cycles through the burning and nonburning mode (Maerz, n.d.).

The parallel flow principle is ideal for producing high-reactivity quicklime at the highest thermal efficiency of all modern lime kilns. PFR kilns can be fired with gaseous, liquid, and pulverized coke, or pulverized coal with a low swell index (<1%). Accurate control of key operating parameters, such as temperature and pressure within the kiln, fuel flow rate, combustion and cooling airflow rates, stone level, and discharge rate of product are crucial to achieve the high thermal efficiency in the PFR kilns (Maerz, n.d.).



Courtesy of Maerz

Figure 7 (A) Rectangular PFR and (B) circular PFR kilns

Cimprogetti and Maerz are among the major manufacturers of PFR (or twin-shaft regenerative) kilns. Three types of PFR kilns are typically used:

1. The Maerz rectangular PFR kiln, shown in Figure 7A, is capable of producing 100–400 t/d of high-reactivity lime, handles 30–120-mm stone, with 810–870 kcal/kg or 3.64–3.93 GJ/t heat input.
2. The circular PFR kiln, shown in Figure 7B, is capable of producing 300–800 t/d of high-reactivity lime, handles 30–160-mm stone, with 810–870 kcal/kg or 3.64–3.93 GJ/t heat input.
3. The Maerz Finelime PFR kiln is capable of producing 200–400 t/d of high-reactivity lime, handles 15–40-mm stone, with 790–850 kcal/kg or 3.31–3.56 GJ/t heat input (Maerz, n.d.).

In North America, there are two additional types of lime kilns that are in very limited use, mostly in specialty applications: a rotary hearth kiln (calcimatic kiln) and a fluidized-bed kiln. They are applicable for lime that decrepitates but have limited fuel options.

Flash Calciners

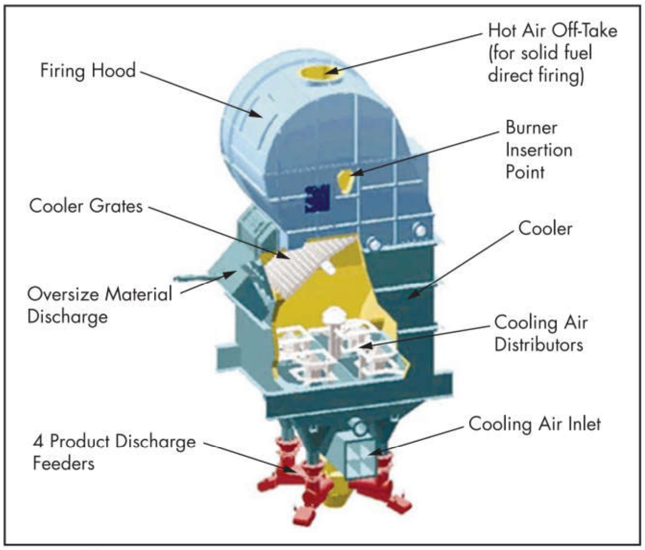
Flash calciners are utilized for cement, gypsum, and alumina calcining among other applications. Gas suspension calciners (GSCs), or flash calciners, such as those from FLSmidth or Calix, utilize a series of high-efficiency cyclones that are low maintenance, have low nitrogen oxide (NO_x) emissions, and can be fueled by natural gas, fuel oil, coal, coke, or alternate fuels. Capacity for the FLSmidth GSC is 1–800 t/h of fine ore (FLSmidth 2013).

Rotary Hearth Calciners

Rotary hearth calciners are sometimes used for coke calcination because they minimize decrepitation and produce consistent coke quality with low energy consumption. Feed enters from the top of the sloped rotating hearth and is moved toward the discharge edge by rabbles.

Calcimatic Kilns

Calcimatic kilns utilize a circular refractory hearth divided into heating zones. This type of kiln is often operated at 25–85 rpm, although these large-diameter hearths can be



Courtesy of Metso

Figure 8 Metso Niems cooler

operated at up to 200 rpm. Fuel choices are limited, as coal cannot be used as a fuel for calcimatic kilns (Boynton 1966).

Fluidized-Bed Calciners

A fluidized-bed reactor is a vertical, usually cylindrical carbon steel vessel that is lined with insulating and refractory firebrick. It has four main sections. The wind box is a plenum that delivers fluidizing gas to the bed through a constriction (or distribution) plate. The constriction plate acts as a distributor for the fluidizing gas, supporting the bed and preventing backflow of solids into the wind box. The third and fourth main sections are the fluidized bed itself, in which the bed may consist of the calcine product; and the freeboard, where larger solids disengage from the upwardly moving gas stream (Downey 2013). A fluidized-bed kiln produces highly reactive soft-burned lime. Fine feed is required for this type of kiln, and it is often used for lime that decrepitates. Fuels that can be utilized in the fluidized-bed kiln are gas, fuel oil, finely ground coal, or fine coke. The Fluo-Solids kiln is an adaptation of a conventional fluidized-bed reactor that has multiple beds (Cimprogetti 2017; Boynton 1966).

Coolers

A rotary cooler with a water quench is typically used for coke calcined in a rotary kiln. Most carbonate kilns utilize a contact cooler such as a Niems. A Niems cooler, shown in Figure 8, has four quadrants. Ambient air is blown uniformly through stainless-steel louvers into the bed of hot lime. Vibratory feeders control the bed level in the cooler by controlling the lime product discharge. Heat recovery efficiencies approaching 90%, with an airflow equivalent to the secondary combustion requirements for calcination are achieved by the Niems cooler (Metso 2018).

Some plants utilize a satellite cooler or a grate cooler. A satellite cooler is the least efficient of the three types of lime coolers. The satellite cooler consists of tubes attached to the kiln in a parallel configuration that rotate with it. Normally, the kiln ID fan provides the air for the cooler. Satellite coolers discharge gas temperatures are low, ~80°C, so they are not usually used for secondary air. Discharge gas for grate coolers is approximately 540°C and is utilized for secondary air, but it produces more than is required for the process, and the high off-gas temperature is problematic for the baghouse or electrostatic filtration systems that are most common (Metso 2018).

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