LIME AND LIMESTONE

1. Introduction, History, and Terminology

Limestone [1317-65-3] is a naturally occurring mineral that consists principally of calcium carbonate [471-34-1]. It generally contains some magnesium carbonate [546-93-0] as a secondary component. Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation (1). Deposits are distributed widely throughout the world. Limestone is an essential raw material for many industries, including lime production. Its suitability for a particular application depends profoundly on its physical and chemical properties.

Quicklime is produced by the thermal decomposition of limestone. It consists mainly of calcium oxide, with magnesium oxide as a secondary component. As the most readily available and cost-effective alkaline chemical, quicklime plays an essential part in a wide range of industries. Its suitability for a particular process depends on many factors, including physical properties, reactivity to water, degree of sintering, and chemical composition.

Slaked limes are produced by reacting quicklime with water to produce either hydrated lime (a dry calcium hydroxide powder), milk of lime, or lime putty (aqueous dispersions). Slaked limes consist mainly of calcium hydroxide [1305-78-9] and are widely used in aqueous systems as low cost alkaline chemicals.

Commercial lime products fall into three main groups.

Calcium limes, which contain relatively low levels of the oxides of magnesium, silicon, aluminium and iron.

Hydraulic limes, which contain calcium silicates that give the products cementitious (or hydraulic) properties, which enable them to set under water.

Dolomitic limes, which contain relatively high levels of magnesium oxide.

Calcium limes include "*high calcium*", or "*chemical quality*" limes, which are particularly pure (eg., >94% available lime and >97% neutralizing value). They are widely used in the chemical and related industries.

1.1. History.

There is evidence of the widespread use of quicklime and hydrated lime for building by many civilizations by ~1000 BC, including the Greeks, Egyptians, Romans, Incas, Mayas, Chinese, and Mogul Indians. The Romans employed hydraulic lime in many construction projects, including the Appian Way.

Lime was also well known to the Romans as a chemical reagent. In 350 BC, Xenophon referred to the use of lime for bleaching linen. The medical use of limewater was recorded by Dioscorides in 75 AD.

The burning of limestone in kilns was mentioned by Cato in 184 BC. Pliny the Elder (~70 AD) in his *Chapters on Chemical Subjects* described the production, slaking, and uses of lime, and stressed the importance of chemical purity.

The use of lime as a component in mortar for building spread throughout Europe in the 1400s.

In the 1700s, Joseph Black gave the first sound technical explanation of the calcination of limestone, including the evolution of gaseous carbon dioxide. Lavoisier confirmed and developed Black's explanation. In 1766, de Ramecourt published a detailed account of *The Art of the Lime Burner*, which covered the design, operation, and economic aspects of lime kilns.

1.2. Terminology. The lime and limestone industries have generated many traditional expressions, which frequently cause confusion. In particular, the term "lime" generally refers to quicklime and, less frequently, to hydrated lime or slaked lime. However, it is sometimes used incorrectly to describe limestone. The following definitions cover the most common terms. For a more comprehensive list see (1).

Air limes consist mainly of calcium oxide or hydroxide, which, when incorporated into a mortar mix, slowly harden by reacting with atmospheric carbon dioxide.

Air-slaked lime results from excessive exposure of quicklime to the atmosphere. The resulting partial hydration and recarbonation makes the lime unsuitable for most uses.

Agricultural lime is a term, that includes any limestone, quicklime, or hydrated lime product used to neutralize soil acidity.

Argillaceous limestone contains considerable amounts of clay or shale. It has relatively high silica and alumina contents.

Autoclaved lime—see Type S hydrated lime.

Available lime is an analytical term for the calcium oxide–hydroxide content of quicklime or hydrated lime that is able to react with sucrose under specified conditions.

Building limes are lime products, that have the chemical and physical properties necessary for their use in building and construction. They include quick- and slaked limes, calcium, dolomitic, and hydraulic limes.

Calcitic limestone is generally used by agronomists to denote a high calcium stone.

Carbide lime is a by-product from acetylene production from calcium carbide. It is principally calcium hydroxide and occurs either as a wet sludge, or a dry powder of varying degrees of purity and particle size.

Carbonaceous limestone contains organic matter as an impurity. It is often dark gray and has a musty odor.

Chalk is a limestone that has been partially consolidated and therefore has a high porosity. It is generally relatively soft.

Cementstone is an impure stone, that contains sufficient amounts of silica, alumina, and iron oxide for it to be converted into a cement, when fired at sufficiently high temperature.

Chemical-grade (or -quality) limestone is a high purity high calcium or dolomitic limestone containing of at least 95% m/m of total carbonate ($CaCO_3 + MgCO_3$).

Chemical quality lime is a high calcium lime (see below) with low levels of impurities, which meets the quality requirements of the chemical industry.

Compact limestone has a low porosity (typically $<5\%$ by volume). It is generally fine-grained, homogeneous, and hard.

Dead-burned dolomite is a highly sintered form of dolomitic quicklime, that is used as a basic refractory. Some grades contain added iron oxide, which acts as a fluxing agent.

Dolime refers to calcined dolomite.

Dolomite is strictly speaking the double carbonate containing 54–58 % of $CaCO_3$ and 40–44 % of $MgCO_3$. The term is, however, frequently used to describe dolomitic limestone.

Dolomitic limestone is generally understood to contain 20–44 % of $MgCO_3$.

Fat lime is used to describe a quick- or hydrated lime, which has a high volume yield and produces a plastic putty. It is also used for relatively pure quick- or hydrated as opposed to impure and hydraulic limes.

Fine quicklime generally refers to screened products with top sizes of 6 mm or less.

Finishing lime is a type of refined hydrated lime suitable for the finishing coat in plastering.

Free lime is an analytical term for the calcium oxide component of quicklime or hydrated lime. It excludes calcium oxide in $CaCO_3$, $Ca(OH)_2$, and calcium silicates.

Ferruginous limestone contains sufficient iron oxide to color the stone yellow or red.

Fluxing lime is a type of chemical lime used as a flux in steel and nonferrous metal production.

Fluxstone (or metallurgical-grade limestone) is a high purity carbonate rock used in metallurgical processes to flux solid impurities.

Fossiliferous limestone contains fossils that are readily visible to the naked eye.

Granular quicklime usually refers to screened products with a top size of 0.5–2.5 cm.

Ground quicklime refers to powdered products produced by milling.

Hard-burned quicklime is a sintered form of quicklime with a low reactivity to water.

High-calcium quicklime is a general term for products consisting mainly of CaO, and having not $< 2–5\%$ of MgO.

Hydrated lime is a dry powder produced by reacting quicklime with controlled amounts of water.

Hydraulic lime is an impure hydrated lime, containing calcium silicate, which gives the product cementing (or hydraulic) properties, and enables it to set under water.

Iceland spar is a rare and very pure form of calcite. It is transparent and has been used for optical instruments.

Light-burned quicklime is quicklime that is lightly sintered and has a high reactivity to water.

Lime putty is a viscous dispersion of calcium hydroxide in water.

Lime slurry—see milk of lime.

Lump quicklime usually refers to screened products with a top size >6 cm.

Magnesian quicklime is generally understood to contain 5–20% of MgO.

Marble is a highly crystalline metamorphic limestone, that may be calcitic or dolomitic limestone. It occurs in many colors with veined and mottled markings.

Marl is impure, soft, earthy rock, that contains 5–65 % of clay and sand. If it contains >50 % of calcium plus magnesium carbonates, it may be classified as a limestone.

Masons' lime is a hydrated lime used in mortar.

Milk of lime is a fluid dispersion of calcium hydroxide in water.

Neutralizing value is an analytical term for that proportion of limestone, quicklime, or hydrated lime (expressed as CaO) that is capable of reacting with hydrochloric acid under specified conditions. It includes the contribution of $CaCO_3$, CaO, $Ca(OH)_2$, MgO, $Mg(OH)_2$, and the acid-soluble fractions of the calcium silicates, aluminates, and ferrates.

Oolitic limestone (or ooliths) is composed of ooids cemented in calcite. (Ooids are spherical, accretionary grains of calcium carbonate of up to 3 mm in diameter, precipitated by algal action in turbulent waters.)

Oyster shell is one of the many forms of fossiliferous limestones. They are generally high in $CaCO_3$.

Pebble quicklime usually refers to screened products with a top size of 1.5–6 cm.

Phosphatic limestone is derived from invertebrate marine creatures and contains significant levels of P_2O_5 (typically up to 5%).

Precipitated calcium carbonate (PCC) is produced by blowing carbon dioxide into milk of lime, thereby precipitating finely divided calcium carbonate with a mean particle size in the range 0.02–0.2 μm.

Reactivity of quicklime is a measure of the rate at which it reacts with water. There are many reactivity tests (see Sections Chemical Properties and Physical Testing).

Refractory lime—see dead-burned lime.

Slaked lime generally describes an aqueous suspension of calcium hydroxide. It includes milk of lime and lime putty. The term is sometimes used to include hydrated lime.

Soft-burned quicklime—see light-burned quicklime.

Solid-burned quicklime—see hard-burned quicklime.

Stalactites and stalagmites are icicle-like deposits of $CaCO_3$ that form on roofs and floors, respectively, of limestone caverns. They are formed by crystallization from groundwater.

Total lime is an analytical term for the total CaO plus MgO content of a limestone or lime, expressed in terms of CaO equivalent. It includes the carbonates, oxides, hydroxides, silicates, aluminates, and ferrates.

Travertine is a crystalline form of $CaCO_3$ formed at hot-water springs by the evaporation of carbon dioxide from calcium bicarbonate solutions.

Type N or "normal" hydrated lime is defined in ASTM specification C-207 (2). It is generally produced by hydrating high calcium quicklimes at $\sim 100^\circ C$.

Type S or "special" hydrated lime is also defined in ASTM specification C-207 (2). It is produced by hydrating high calcium or magnesian quicklime in an autoclave at $\sim 180^\circ C$, and may contain up to 8% of unhydrated oxide.

Unslaked lime is any form of quicklime.

Whiting is a finely divided product made by milling and classifying limestone (generally chalk). The nominal top size varies from 10 to 75 μm.

2. Limestone

2.1. Formation, Classification and Occurrence. *Formation of Limestone Deposits.* Calcium carbonate has been produced since the Precambrian era (>600 million years ago) by reaction of carbon dioxide with dissolved calcium ions (1). The sedimentation of calcium carbonate occurs by two mechanisms—organic and inorganic. The organic route involves a wide variety of organisms, which build shells, skeletons, or secrete carbonate. The inorganic route involves the direct precipitation (or crystallization) of carbonate.

Most commercially viable deposits of carbonate were formed by the organic route. The factors that control the rate of carbonate production (Ca^{2+}, Mg^{2+}, and CO_2 concentrations, temperature, salinity, water depth, and turbidity) have resulted in most of the thick deposits being produced in shallow seas between 30° north and 30° south of the equator. Such deposits may now be found outside that band as a result of climate change and continental drift.

Some organic species produce aragonite structures, while other make calcite. The former are generally very low in $MgCO_3$ (typically <0.5%). The percentage of $MgCO_3$ in the calcite deposits depends on the water chemistry and tends to be either <4% or between 11 and 19%. As the carbonate-producing organisms only flourished in waters with low turbidity (ie, remote from rivers carrying significant amounts of silt), many carbonate deposits are remarkably pure, with >98% of calcium plus magnesium carbonates.

Inorganic precipitation of calcium carbonate occurs in both sea and inland waters. It has resulted in some commercially significant deposits, the most common of which are oolitic limestone and travertine.

Most carbonate sediments were formed in situ, in shallow water, accumulating where the grains were formed, or were subjected to limited transport (eg, down a gently sloping subtidal shelf). The variety of environments (which includes beaches, tidal, and subtidal flats, lagoons, reefs, shelves, slopes, and deep basins) gives rise to many types of deposit.

Diagenesis is the conversion of sediments into rock by organic, physical, and chemical processes. Six main processes have been identified for limestone—microbial micritization, cementation, neomorphism, dissolution, compaction, and dolomitization. Dolomitization involves the replacement of calcium ions in the crystal lattice by magnesium. This occurs when water rich in dissolved magnesium salts percolates through porous $CaCO_3$ deposits. As the magnesium has a smaller ionic radius than calcium, the crystal lattice contracts, and increases the porosity. Under suitable conditions, up to 50% of the calcium ions may be replaced.

Frequently, the process of sedimentation was interrupted, eg, by falls of volcanic ash. Diagenesis converts such deposits into thin clay seams known as bedding planes. As a limestone deposit is bent and displaced, faults are formed at which the continuity of bedding planes can be disturbed by tens of meters. Faults are generally filled with clay and other minerals.

Classification of Limestones. Limestones are classified in several ways (1). One geological classification includes the following types: biosparites (the most widespread type of massive, well-bedded limestones), micrites, biomicrites, reef, algal, oolitic, dolomitic, chalk, marble, travertine, and tufa. Others are based on grain size, microstructure, texture, and on the principal impurities.

The classification most commonly used in the limestone industry is based on the carbonate content, namely,

Occurrence of Limestones. Limestone deposits cover ~10% of the earth's land surface, and are found in the majority of countries. Three major interrelated factors have had a major influence on the occurrence of limestones around the world, namely, climate, geotechnics, and sea level.

The effect of climate is mentioned in the section on Physical Properties. Geotechnics have had a direct effect on the occurrence of limestones in four ways—continental drift, regional subsidence, regional up-lift, and the volume of the mid-ocean ridges, which in turn have affected sea level. The sea level has had a marked effect on the area of shallow seas around the globe. In the past, levels have been considerably higher than at present (possibly >100 m higher in the Cretaceous period) and the area of shallow water capable of sustaining carbonate producing organisms was considerably greater than at present.

2.2. Physical and Chemical Properties and Impurities. The physical and chemical properties of limestones vary widely depending on the route by which they were formed, the sedimentary environment and the changes brought about by diagenesis (see the section Formation of Limestone Deposits). For this reason, many of the properties given below should be regarded as being typical.

Physical Properties.

Color. The Color of limestone reflects the levels and nature of the impurities present. White deposits are generally of high purity. Various shades of gray and dark hues are usually caused by carbonaceous material and/or iron sulfide. Yellow, cream, and red hues are indicative of iron and manganese. Impurities in marble often produce a variety of colors and patterns.

Odor. Limestone generally has a musty or earthy odor, which is caused by its content of carbonaceous matter.

Texture. The texture of limestones varies widely. All limestones are crystalline, with average grain sizes ranging from <4 μ to ~1000 μm. The distribution of grain sizes affects the texture and ranges from mudstone (mainly calcitic mud with few coarse grains) to grainstone (mainly coarse grains with little mud cement).

Crystal Structure. Calcite and dolomite have rhombohedral structures, while aragonite is rhombic.

Specific Gravity. The specific gravities of the crystalline forms of calcium carbonate and dolomite at 20°C are calcite 2.72 g/cm^3, aragonite 2.94 g/cm^3, and dolomite 2.86 g/cm^3 (3) The specific densities of limestones depends on their porosity.

Porosity. The porosity of limestone varies considerably depending on the degree of compaction and the structure. Typical values (by volume) are 0.1–2% for marble, 0.1–30% for limestones, 15–40% for chalks, and up to 50% for marls. The porosity of dolomites is generally in the range 1–10% (4).

Apparent Density. This is a function of the porosity, the crystal density and the amount of water in the pores. For limestones dried at 110°C, typical values are 1.5–2.3 g/cm^3 for chalk, up to 2.7 g/cm^3 for dense high calcium limestones, and 2.7–2.9 g/cm^3 for dolomite.

Bulk Density. The bulk density depends on the apparent density of the limestone, the particle size distribution, the particle shape, and the amount of water within the pores and between particles.

Crushed and screened limestone with an apparent density of 2.7 g/cm^3 and a ratio of top-to-bottom size of 2:1 typically has a bulk density of 1400–1450 kg/m^3.

Strength. The compressive strength of limestones varies from 10 MN/m^2 for some marls and chalks to 200 MN/m^2 for some marbles. A typical crushing strength for a dense high calcium limestone is 180 MN/m^2.

Hardness. The hardness of limestones generally lies in the range 2–4 Mohs.

Specific Heat. The specific heat of calcite rises from 0.191 cal/g°C at 0°C to 0.239 cal/g°C at 200°C (5). A value for dolomite of 0.22 cal/g°C has been reported for the temperature range 20–100°C (6,7).

Chemical Properties.

Stability. Aragonite is pseudostable with respect to calcite under ambient conditions, and consequently has a higher solubility in water. In the presence of water, aragonite slowly recrystallizes to calcite. It also recrystallizes to calcite at 400–500°C in the absence of water.

Calcite is metastable with respect to dolomite in the presence of seawater (which contains dissolved magnesium). The process of dolomitisation is slow, even in geological terms. It is, however, slowly reversed in the presence of freshwater.

Thermal Decomposition. Calcium carbonate decomposes into calcium oxide and carbon dioxide when heated. The heat of dissociation of $CaCO_3$ is 1781 kJ/kg relative to 25°C, and 1686 kJ/kg relative to 900°C (426 and 403 kcal/kg, respectively). The corresponding values for magnesium carbonate are 1439 kJ/kg $MgCO^3$ relative to 25°C and 1362 kJ/kg relative to 700°C.

The carbon dioxide dissociation pressure for calcite is shown in Table 1. At ∼900°C, the pressure reaches 1 atm (8)—this is generally referred to as the decomposition temperature of calcium carbonate. The decompositions of dolomite and dolomitic limestones are complex and are described in (1).

Solubility in Carbon Dioxide-Free Water. The solubility of calcite in distilled water free of carbon dioxide is 14 mg/L at 25°C, rising to 18 mg/L at 75°C. That of aragonite increases from 15.3 mg/L at 25°C to 19.0 mg/L at 75°C (3). These values are, however, only of academic interest, as most waters contain dissolved carbon dioxide.

Reaction with Carbon Dioxide. The increase in "solubility" of limestones in the presence of carbon dioxide is due to reversible chemical reactions that form calcium and magnesium bicarbonates. For example, at 20°C ∼30 mg/L of calcite will dissolve in distilled water that is at equilibrium with atmospheric carbon dioxide (6).

$$CaCO_3 + H_2O + CO_2 \ Ca(HCO_3)_2$$
$$MgCO_3 + H_2O + CO_2 \ Mg(HCO_3)_2$$

On heating a solution of calcium–magnesium bicarbonates, carbon dioxide is evolved and calcium–magnesium carbonates precipitate (this mechanism accounts for the formation of scale in kettles and boilers in hard water areas).

pH in Water. Calcitic limestones give pH values of between 8.0 and 9.0. Dolomite gives values of 9.0–9.2 (6).

Reaction with Aqueous Acids. In general, limestones react readily with acids and are used for acid neutralization. High calcium limestones react readily with dilute hydrochloric and nitric acids at ambient temperatures, whereas dolomite and dolomitic limestones only react readily when the dilute acid is heated. The reaction of limestone with sulfurous acid (formed by the dissolution of sulfur dioxide in water) is the basis of a flue gas desulfurization process (see the section Uses and Specifications). The reactions with acids, which form insoluble or sparingly soluble calcium salts (eg, sulfurous, sulfuric, oxalic, hydrofluoric, and phosphoric acids), are inhibited by the reaction products.

Heat of Reaction with Acids. The heat of reaction of calcite with hydrochloric acid is 4495 cal/mol, or 18.8 kJ/mol (76).

Reaction with Acidic Gases. Limestones react readily with gaseous hydrogen chloride and hydrogen fluoride, forming calcium chloride and fluoride respectively. Dry sulfur dioxide reacts with limestone at 95°C and above to produce calcium sulfite. Sulfur trioxide reacts with limestone to produce the sulfate.

Impurities. The effects of geological factors on the levels of impurities and trace elements are outlined in (1). The levels have considerable influence on the suitability of limestones for many applications (see the section Uses and Specifications).

Typical levels of impurities and trace elements are summarised in Table 3. They are based on published spectrographic analyses of 25 high calcium American limestones (10) and on information viewed by the author.

2.3. Quarrying, Processing, Storage and Transport of Limestone.

Quarrying. Over 95% of limestone is produced by open-cast quarrying, with <5% being extracted by underground mining and other methods. A simplified flow diagram for a limestone quarry is shown in Figure (1).

The first operation in open-cast quarrying is to remove the overburden (ie, the soil, clay, and loose rock overlying the deposit). Various techniques and types of earth moving equipment are used for this.

The next stage is generally to drill the bed-rock from the top of the burden to just below the quarry floor level at controlled distances behind the quarry face. Measured amounts of explosive (typically 140 g per tonne of stone) are then placed in the holes and fired. The size and spacing of the holes and the amount and placing of the explosive are optimised to produce the required fragmentation of the rock.

Some soft rocks (eg, chalk and marl) are broken using heavy rippers. Other soft deposits, such as those found in lakes and in the sea, are extracted with dredgers.

Processing. The broken rock is generally loaded into dump trucks, using front-end loaders or hydraulic excavators, and transported to the primary crusher. The crusher breaks the larger lumps of rock to a size that suits the needs of the business and the characteristics of the subsequent equipment. In the stone processing plant, the stone is screened, recrushed, and rescreened to produce a range of closely graded products. A fraction of the stone may be pulverized—generally by dry grinding.

Increasingly, where high purity limestone products are required, and where the limestone is fed to lime kilns, part or all of the stone may be washed to remove clay and fine fractions.

The fine fractions, including the tailings from washing, are rich in impurities and may be used for landfill.

Storage and Transport. Screened sizes of limestone are stored in bunkers and in outside stockpiles. Fine and ground grades are generally stored in sealed bunkers.

As most screened limestone is distributed to a large number of sites, generally within 40–80 km of the quarry, it is mainly transported in sheeted tipper road vehicles. It has been estimated that >75% of limestone is transported by road (11). Use of rail or water transport becomes more economically viable as the volume of business to a particular site increases, and as the distance becomes greater. Fine grades of limestone are transported by air pressure discharge vehicles, generally by road, but suitable railroad cars are also available.

2.4. Market Overview and Economic Aspects.

Market Overview. Limestone is a major mineral product. Estimating the level of worldwide use presents problems, as the statistics for some major producing countries are not published and as different bases are used in various countries. It has been estimated (1) that global production is >4500 million tonnes per year. Of that total, in 1994, the United States used ~900 million tpa, Japan ~200 million tpa and the United Kingdom ~120 million tpa. The limited available information for various countries (11–14) is given in Table (4).

Table 5 summarizes the proportions of limestone sold to the main market segments in 1994 in Germany, Japan, and the United Kingdom (15,16).

Economic Aspects. Limestone competes with other hard rocks in the major market of aggregate for concrete and roadstone. In most countries, such rocks are widespread and there is intense competition between suppliers, based more on the delivered prices than on the properties of the aggregate.

The *production cost* of limestone depends on a number of factors. The nature of the deposit can be important: massive deposits with little overburden, horizontal strata and, consistent physical, and chemical properties favor low extraction costs, particularly if linked to a large-scale operation. Selection of appropriate equipment to keep the combined costs of labor, capital charges, and other operating costs to a minimum is important to ensure a strong competitive position (1).

The *cost of haulage* is an important factor, as it can equal the ex-works cost of aggregate at a distance of 50 km. For road transport by tipper wagon, the economic distance may be as low as 40–60 km. Rail transport may extend that distance to 200 km and water transport can extend the distance considerably further.

Wastage can markedly affect the economics of a quarry operation. It can be reduced by having a balanced portfolio of customers, thereby obtaining sales for most of the grades of limestone produced. Wastage can range from as low as 2% in some integrated quarries, to a typical value of 20–30% and to 40–50% in quarries supplying only lime kilns.

Ex-works prices for limestone used as aggregate in construction in the United Kingdom are in the range £2–£5 per tonne. Chemical quality limestone for lime burning, glass manufacture, and flue gas desulfurization typically commands prices in the range £5–£10 per tonne. Specialist ground limestone products, such as whiting, can command prices of £25–£250 per tonne, depending on grade and quality. Precipitated calcium carbonate (PCC) is a specialist product, which sells at £250–£1,000 per tonne.

2.5. Uses and Specifications of Limestone.

Table 6 lists the main use of limestone. In most countries, the major use of limestone is as a crushed rock for construction and building, mainly as an aggregate and filler in concrete and roadstone. The second largest use is generally the manufacture of cement.

> *Construction*. Limestone competes with other hard rock aggregates in this segment. In many countries it is the most widely used crushed rock, although it is generally outsold by sand and gravel.

The quality specifications for construction stone relate mainly to its physical properties (1). Thus the stone must be clean, strong, dense, durable, free from cracks, and have the required particle size distribution. Some specifications limit the amounts of organic matter clay, or water-soluble components (eg, alkali metal salts and gypsum). Specifications for the stone in the top dressing of roads (particularly in the vicinity of junctions) sometimes require a high resistance to polishing—this excludes the use of limestone. Standards for the testing and size distribution of roadstone and construction stone are given in (1).

Limestone can be cut and used as dimension stone, but other rocks are generally preferred.

Cement. The production of cement is the main use for chalk, and a major use for dense, high calcium, low magnesium limestone. The limestone is blended with materials containing SiO_2, Al_2O_3, and Fe_2O_3 (such as clay, shale and pulverized fuel ash). In the kiln, the $CaCO_3$ is converted to CaO, which reacts with the SiO_2, Al_2O_3, and Fe_2O_3 in the feed to produce controlled amounts of calcium silicates, aluminates, and ferrates.

Approximately 1.0 tonne of limestone is required per tonne of cement (this includes cement–limestone blends). For the estimated worldwide production of cement, the consumption of limestone in 1995 was $\sim 1420 \times 10^6$ tonnes.

Limestones with a wide range of both physical and chemical properties can be accepted for cement production, providing the magnesium carbonate does not exceed 4% of the calcium carbonate content (higher levels of magnesium cause expansion after setting and reduced strengths). When the composition of the limestone is variable, elaborate arrangements are made to blend the raw materials to produce kiln feed with a consistent chemical analysis.

Agriculture. Many crops grow best under neutral to slightly acid conditions (ie, pH 6–7). Thus soils that are more acidic than pH 6, generally benefit from the application of limestone. The limestone also helps to replace the calcium and (in the case of dolomite) magnesium removed by crops. Other benefits include an increase in the supply of other chemical nutrients, an increase in the organic content of the soil, an increase in beneficial soil microorganisms, improved soil tilth, an improved supply of trace elements, and an increase in the efficiency with which fertilizers are used by the crop (1).

It is important that the limestone used for agriculture is in the correct physical state: A top size of 0.1 cm is generally required. Agricultural limestone is classified into low magnesia (eg, $<15\%$ MgO) and high magnesia grades.

Limestone is also used in animal feeds and poultry grit, where trace element concentrations may be limited (eg, lead levels <10 mg/kg).

Metal Refining. When limestone is used in metal refining, the furnace temperatures convert it to quicklime, which reacts with acidic oxides (eg, SiO_2, Al_2O_3, and Fe_2O_3) to produce molten slags. Considerable quantities are used in blast furnaces for the production of iron, where the typical usage rate is 200-kg/t pig iron and the slag typically contains 40–50% CaO. Smaller amounts are also used as a fluxing agent in the smelting of copper, lead, zinc, and antimony, and in the extraction of bauxite in the production of aluminium. The quality specifications are as for screened chemical-quality stone with a particle size to suit the process. Some magnesium carbonate is acceptable but not essential.

Quicklime. See the section Raw Materials.

Glass. Both high calcium limestone and dolomite are used in the manufacture of glass, which typically contains 10–15 % of (CaO, MgO). The required particle size distribution of the limestone is typically <1 mm, with a limited amount of dust ($<75\,\mu$m). Most glass producers require high purity limestone. Iron is particularly important, with <0.1 % of Fe_2O_3 being widely specified and 0.02 % being required for colorless glass. Levels of organic carbon, sulfur, and phosphorus are also specified.

Flue Gas Desulfurization. Increasingly, significant quantities of limestone are being used in large-scale flue gas desulfurization plants. The limestone is finely ground to 90% $<45\ \mu$m, dispersed in water, and reacted with flue gases in a scrubber. The resulting calcium sulfite hemihydrate comes out of solution as a finely divided precipitate, which is difficult to dewater and is not saleable. In most installations, the sulfite is oxidized to the calcium sulfate dihydrate using compressed air, and, by controlling the crystal size, marketable gypsum is produced. For the gypsum process, the limestone should be of high purity and contain $<1\%$ of $MgCO_3$.

Other Uses. There are many other uses of limestone (including production of wood pulp, paper, ceramics, mineral wool, fillers, whiting, and coal mine dusts, neutralization of acids, and construction of filter beds). They are described in (1).

3. Lime Products

3.1. Raw Materials.

Limestone. Only a small proportion of limestone deposits has the necessary physical and chemical properties for the production of quicklime. When assessing the technical suitability of a limestone, the following factors need to be considered (1):

1. Strength and abrasion resistance of the stone and the quicklime.
2. Resistance of the limestone to thermal degradation.
3. Rate of calcination.
4. Reactivity of the quicklime to water.
5. Impurities—levels of $CaCO_3$, $MgCO_3$, and minor and trace elements.

Strength and Abrasion Resistance. Both the stone and the quicklime should he sufficiently strong to resist the physical forces to which they are exposed in the kiln and the handling and storage systems. Excessive breakage in the kiln increases the resistance to gas flow and heat transfer. Breakage also reduces the yield of granular products, which are usually at a premium, and increases the yield of fines, which are usually in surplus. Various empirical tests have been developed by kiln manufacturers to quantify these properties.

Limestones that are relatively soft and are subject to thermal degradation, or produce a soft lime, cannot be calcined in shaft kilns, but may be suitable for calcination in certain types of rotary and other designs of kiln (see the sections Rotary Kilns, Other Kiln Designs, and Ref. 1).

Thermal Degradation. Some limestones, particularly highly crystalline ones, are prone to break down as a result of the heating, calcining, or thermal cycling processes within the kiln. Various empirical tests have been developed to quantify these effects.

Size. The ratio of the top-to-bottom sizes in the stone fed to lime kilns should preferably be 2:1, although wider ratios are used. A narrow size range gives an open, porous bed, which offers a low resistance to gas flow and heat transfer. It also helps to limit sintering of the smaller sizes while the larger one are still dissociating. Selection of the size is influenced by the cost and availability of the stone and by the limitations imposed by the design of the kiln.

Shape. While a cubical shape is generally preferred for lime kilns, the slabby shapes produced by jaw and roll crushers are acceptable, providing they do not lead to packed beds with low porosity.

Impurities. When limestone is burned in a kiln, most of the impurities persist in the quicklime. Permissible levels of SiO_2, MgO, Al_2O_3. Fe_2O_3, S, Pb. and F depend on the quality specifications for the quicklime. Heterogeneous impurities (eg, those arising from contamination with clay) tend to concentrate in the smaller sizes of quicklime. Removal of the fines (eg, 6 mm to dust) by screening generally improves product quality. Much of the sodium and potassium compounds and some of the sulfur compounds may be removed during calcination. Sulfur oxides, most of which generally arise from the fuel, are absorbed onto the surface of the quicklime at the start of the calcining zone and tend to concentrate in the fine fraction.

Fuel. In lime burning, the fuel is more than a source of heat. It interacts with the process, and the combustion products react with the quicklime. Many different fuels are used in lime kilns. The most common is coal, but coke, fuel oil, and natural gas are also widely used.

Selection of the correct fuel is important to the lime producer. Its cost per tonne of quicklime can represent 50% of the total production cost. Some fuels cannot be used in certain kilns. Other fuels may markedly affect the heat usage, output, and product quality. Some require different refractory linings to be used.

The choice of a fuel for a new kiln, or a new fuel for an existing kiln, should he made with great care. Most kilns can he operated on more than one fuel, and enable the operator to make the selection, which gives the optimum economic performance. The major factors relating to the performance and acceptability of fuel are discussed briefly below. Further details are available in (1).

Calorific Value. The calorific value coupled with the unit cost of the fuel and the kiln heat usage enables the cost of the fuel per unit of quicklime to be calculated. Some confusion arises between the gross (or upper) and the net (or lower) calorific values. The former includes the latent heat of condensation of the water produced by combustion. It is used in North America and the United Kingdom. The net value more logically excludes the latent heat; it is widely used in, eg, continental Europe and Japan.

Sulfur. Some of the most important markets for quicklime, notably steelmaking, require low sulfur levels. Sulfur from the fuel is absorbed by quicklime in the cooler part of the calcining zone of lime kilns as calcium sulfate. In the more efficient kilns (eg, shaft kilns) most of this sulfur is retained in the quicklime. In the less efficient units (eg, some rotary kilns) much of the sulfur from the fuel may be eliminated from the kiln in the kiln gases by operating the calcining zone with low levels of excess air and high temperatures and by limiting contact between the kiln gases and the quicklime in the preheating zone.

Combustion Characteristics. The combustion characteristics of fuels vary markedly. Pulverized coal tends to burn with a short, hot, and highly (infrared) emissive flame. Natural gas and wood burn with longer, cooler flames that have lower emissivities. These differences can affect many aspects of quality, and particularly the relationship between the residual $CaCO_3$ content and the reactivity to water.

Other Properties. Solid fuels should he of the correct particle size. In some cases they need to have adequate strength. Their coking properties may he critical, as may be the amount of volatile matter. The ash generally contaminates the lime to some degree with silica, iron oxide, and alumina. It may cause bridging between particles, and can also combine with lime dust and with volatile alkalis (sodium and potassium) to form troublesome deposits. The properties of the fuel ash can have a marked effect on the acceptability of the fuel. Key properties include the *ash content* of the fuel, the *ash fusion temperature* (which is affected by lime dust and by the concentrations of oxygen and carbon monoxide in the atmosphere), and the level of *alkalis*.

3.2. Physical and Chemical Properties of Lime Products.

Quicklime. *Physical Properties.*

Color. Most quicklimes are white. Impurities can result in gray, brown, or yellow tints. When solid fuel is used to calcine quicklime, it produces a gray surface contamination.

Odor. Quicklime has a slightly earthy odor.

Porosity. The porosity of commercially produced quicklime can be as high as 55%, if a porous limestone is lightly burned. Exposure to elevated temperature results in a progressive sintering process (Fig. 2), which can reduce the porosity to <25%. Dead-burned dolomite has a porosity of ~10%.

Density of calcium oxide is ~3.3 g/cm^3. The apparent density of lumps can be as low as 1.4 g/cm^3 for highly porous quicklime. This can rise to over 2.3 g/cm^3 after sintering (Fig. 3).

Calcined dolomite is generally denser than calcium quicklime, if given the same heat treatment. Dead-burned dolomite has an apparent density of $\sim$3.2 g/cm^3.

Bulk density depends on the mean apparent density of the particles and on the voidage between them. The latter is related to the particle size distribution and the particle shape. Most screened commercial quicklime products have compacted bulk densities of 900–1200 kg/m^3. Inclusion of fines can increase the bulk density by up to 30%

Hardness. Most commercial quicklime products have a hardness of 2–3 Mohs. The value for dead-burned dolomite is in the range 3–5 Mohs.

Melting points of CaO and MgO are 2580 and 2800°C, respectively. The value for calcined dolomite is $\sim$2400°C.

Angle of repose for cubical, well-graded quicklime is $\sim$35°. This value increases with increasing fines content. For bunker design, valley angles of not $<$60° are advised.

Chemical Properties

Heat of Hydration. The heat liberated by the reaction of quicklime with water is 1140 kJ/kg of CaO. The value for dolime is 880 kJ/kg of CaO.MgO.

Reactivity to water may be measured by the rate of release of the heat of hydration, or by the rate at which an aqueous suspension reacts with hydrochloric acid (see the section Physical Testing). Reactivity is related to the mean apparent density (Fig. 4).

The low reactivity of calcined dolomite probably arises mainly from the low solubility of $Mg(OH)_2$ in water. Sintering of MgO, which forms at lower temperatures than CaO, may also be a factor.

Affinity for Water. Quicklime has a high affinity for water and is a more efficient desiccant than silica gel. Care should therefore be taken to minimize exposure to the atmosphere.

Relatively small amounts of “air slaking” (eg, 1.5% of combined water) can reduce reactivity to water significantly. The hydration of quicklime is associated with an increase in volume by a factor of at least 2.5 times. This can lead to expansion of products that contain lime that is not fully hydrated.

Reaction with Carbon Dioxide. In the absence of calcium hydroxide, quicklime only reacts with carbon dioxide above $\sim$300 and below $\sim$800°C, depending on the carbon dioxide partial pressure. However, all commercial quicklimes contain some calcium hydroxide, which is capable of reacting with carbon dioxide at ambient temperatures to produce $CaCO_3$ and water (the water can then react with more CaO).

Acid Neutralization. Quicklime is used extensively to neutralize acid oxides (eg, SiO_2, Al_2O_3, and Fe_2O_3) in high temperature, nonaqueous systems such a steel making. In such processes, temperatures are controlled to ensure that the resulting calcium and magnesium compounds form molten slags.

Slaked Lime. *Physical Properties.*

Color. Most hydrated limes are white. High levels of impurity can result in gray or buff tints.

Density. High calcium hydrated lime has a density of ~2.25 g/cm^3. The values for partially and fully hydrated dolomitic lime are ~2.7 and 2.5 g/cm^3, respectively.

Bulk Density. The compacted bulk density is in the range 450–640 kg/m^3. In the as-poured state, it can be as low as 350 kg/m^3, owing to air entrainment.

Specific surface area may be measured by air permeability, or by surface adsorption of nitrogen (BET surface area). The former method generally gives specific areas of 1000–2000 m^3/kg: the latter gives results, which are some 20–30 times greater.

Angle of Repose. In the fluidized state, the angle of repose is 0°. In the compacted state, and particularly with 1% or more of excess water, the angle of repose can be >80°. With bunker aeration, valley angles of 70° have proved to be satisfactory.

Hardness is between 2 and 3 Mohs.

Solubility in water decreases from ~1.85 g $Ca(OH)_2$/L at 0°C to 0.71 g/L at100°C for most commercial calcium hydroxides, but depends on impurity levels (17).

Some inorganic compounds affect the solubility (18). Calcium sulfate is of particular interest: a 2 g/L solution reduces the solubility to 0.06 g $Ca(OH)_2$/L. Organic compounds can increase the "solubility" of calcium hydroxide. Sugar has the greatest effect, as a result of the formation of calcium saccharate (18).

Magnesium hydroxide is only sparingly soluble in water (~0.01 g/L) (19).

Chemical Properties.

Carbon dioxide reacts with calcium hydroxide at below the dissociation temperature (550°C).

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Acid Neutralization. Hydrated lime, whether $Ca(OH)_2$, $Ca(OH)_2.MgO$, or $Ca(OH)_2.Mg(OH)_2$, reacts readily with aqueous and gaseous acids. The rates of reaction depend in part on the particle size of the hydrate.

Silica and Alumina. Hydrated lime reacts with pozzolans (materials containing reactive silica and alumina) in the presence of water to produce hydrated calcium silicates and aluminates. The reactions may take months to proceed to completion at ambient temperatures (eg, in soil stabilization), but proceed within hours at elevated temperatures and water vapor pressures (eg, at 180°C and a steam pressure of 1 MPa in the production of autoclaved aerated concrete).

pH. Because calcium hydroxide is a strong base, a concentration of 0.1 g $Ca(OH)_2$/L gives a pH of 11.3 at 25°C. A saturated solution at 25°C contains 1.8 g/L and gives a pH of 12.4. The pH of dolomitic hydrate is similar to that of calcium hydroxide.

Thermal Dissociation. Calcium hydroxide decomposes at ~550°C to quicklime and water. The quicklime so produced has an exceptionally high reactivity to water.

Causticization. Hydrated lime reacts with soluble metal carbonates to produce insoluble $CaCO_3$ and the metal hydroxide. This reaction is used in a number of processes to convert sodium carbonate to caustic soda.

3.3. Production of Quicklime. *General.* Quicklime is produced by providing heat at temperatures in excess of 900°C to dissociate calcium and magnesium carbonates into the respective oxides and carbon dioxide. The design of lime kiln should be appropriate for the characteristics of the limestone, and for the quality of quicklime to be produced. The fuel should be selected with care to be compatible with the design of kiln and the required quality of quicklime. The following sections provide a brief description of common types of lime kiln, the fuels used, the ways in which the "run-of-kiln" quicklime is processed, and the various factors that can affect product quality. More details are available in the literature [eg, (1, 4, 6, 20, 21)].

A simplified flow diagram for a lime works is given in Figure 5.

Lime Kilns. Lime kilns may be subdivided into three main groups: countercurrent shaft kilns, shaft kilns with an element of cocurrent flow, and rotary kilns. Each type has specific characteristics and produces different ranges of quicklime quality.

Countercurrent Shaft Kilns. Figure 6 is a schematic diagram of a countercurrent shaft kiln (also called vertical shaft kiln). Limestone (with a typical top size of 6–15 cm) is charged into the top of the kiln and quicklime is drawn from the base of the kiln. Fuel is injected into the calcining zone. Combustion air is drawn into the base of the cooling zone, where it cools the quicklime descending from the calcining zone and in doing so, is preheated. The fuel burns in the preheated combustion air to release heat at temperatures in >900°C, which causes the limestone to dissociate into quicklime and carbon dioxide. The products of combustion are drawn upward from the calcining zone into the preheating zone, and heat the limestone to ~800°C. In so doing, they are cooled before being drawn from the top of the kiln.

The major problem with such kilns is obtaining uniform heat release across the shaft. Fuel injected at a wall usually does not penetrate more than ~1 m into a packed bed. For many years, this limited the width (or diameter) of shaft kilns to 2 m. Many designs of kiln have been developed to increase heat penetration, using techniques such as

1. Premixing solid fuel with the limestone before it is charged into the kiln.
2. The use of central burners to inject part of the fuel along the central axis.
3. The use of tuyères to inject the fuel ~1 m into the kiln.

4. Injection of air or recycled kiln gases above the fuel to force it away from the walls of the kiln.

Countercurrent shaft kilns have moderately low heat and electricity usages (see Table 7). Their thermal efficiency is, however, limited by the facts that the limestone can only recover part of the heat in the exhaust gases, and the quicklime leaving the calcining zone can only partially preheat the combustion air (relative to 900°C).

The quicklime produced from countercurrent shaft kilns tends to have a "medium" reactivity to water, because

1. The highest temperatures tend to be at the base of the calcining zone, where the quicklime is most prone to "overburning".
2. Uneven heat release across the shaft means that quicklime in some regions is "overburned" to ensure that quicklime in other areas is adequately calcined.

Nevertheless, large tonnages of quicklime are produced from countercurrent shaft kilns.

Shaft Kilns with a Cocurrent Section. The annular shaft kiln and the parallel flow regenerative kiln were developed to produce uniformly calcined, reactive quicklime at higher thermal efficiencies than can be achieved with countercurrent shaft kilns. Many kilns of each design have been installed around the world during the past four decades.

> *Annular Shaft Kiln.* A major feature of the kiln (Fig. 7) is a central cylinder, which restricts the width of the annulus and ensures good heat distribution. The central column also enables part of the combustion gases from the lower burners to be drawn down the shaft (co-current with the quicklime) and to be injected back into the lower burner chambers. This recycle moderates the temperature at the lower burners and ensures that the final stages of calcination occur at relatively low temperatures. It helps to produce quicklime with a low residual $CaCO_3$ level and a high reactivity. The design includes a heat exchanger to transfer surplus heat in the exhaust gases to part of the combustion air, which increases thermal efficiency by $\sim$10% relative to that of countercurrent kilns (Table 7).
>
> The annular shaft kiln accepts limestone with a top size of 5–11 cm, and can be fired using gaseous, liquid, or solid fuel.
>
> *Parallel-Flow Regenerative Kiln.* The parallel-flow regenerative kiln (Figs. 8 and 9) generally consists of two interconnected shafts. The operation consists of two equal stages, typically of 8 to 15-mins duration at full output.
>
> In the first stage, fuel is injected through lances into shaft 1 and burns with combustion air blown down that shaft. The heat released is partly absorbed by calcining the limestone in shaft 1. Air is blown into the base of each shaft to cool the lime. The cooling air in shaft 1 mixes with the combustion gases,

including the carbon dioxide from calcination. The mixture passes through the cross-duct into shaft 2 at ~1050°C. In shaft 2, the gases from shaft 1 mix with the cooling air blown into shaft 2 and pass upward. In so doing, they transfer much of their heat content to the stone in the preheating zone of that shaft.

During the second stage of the operation, the converse applies. The same amounts of fuel and combustion air are added to shaft 2. The combustion gases plus cooling air pass upward in shaft 1, heating the stone in the preheating zone of that shaft.

The key principles of the above operation are

1. The stone-packed preheating zone in each shaft acts as a regenerative heat exchanger, in addition to preheating the stone to calcining temperature. The surplus heat in the kiln gases is transferred to the stone in shaft 2 during the first stage. It is then transferred from the stone to the combustion air during the second stage. As a result, the combustion air is preheated to ~800°C. This regenerative heat recovery increases thermal efficiency by ~15–25 % relative to the efficiencies of countercurrent kilns (Table 7).
2. The calcination of the quicklime is completed at the level of the cross-duct at a moderate temperature of ~1100°C. This favors the production of highly reactive quicklime, which, if required, may be produced with a low residual $CaCO_3$ content. The kiln is generally designed to accept a feedstone with a top size of 5–12 cm, although some kilns can accept top sizes as small as 2–3 cm with good quality limestone. It can be fired with gaseous, liquid, or solid fuel.

Rotary Kilns (4). There are many designs and variants of the rotary kiln (4). Most use a feedstone with a top size in the range 1–6 cm, although certain designs can process finely divided and powdered limestone. They can be fired with gaseous, liquid, or solid fuels.

In the earliest rotary kilns, stone was fed into the elevated end of the rotating section (generally inclined at between 1.5 and 4°). The stone was preheated by the kiln gases, drawn from the calcining zone at the other end of the kiln, and then calcined as it moved toward and under the flame. The hot lime was then discharged into a pit to cool.

In later designs (eg, Figs 10 and 11), the thermal efficiency of the kiln was improved by

1. Fitting lime coolers, to preheat the combustion air.
2. Fitting raised sections of refractory (ie, dams or mixers) in the calcining zone toimprove heat transfer into, and mixing of the lime/limestone bed.
3. Installing refractory trefoils, metal lifters, or similar devices in the preheating zone of the rotating section.
4. Using a stone preheater and a shorter rotary section.

Rotary kiln heat usages are generally higher than those of shaft kilns (Table 7). Their capital costs also tend to be higher. These adverse factors are offset by their ability to calcine smaller stone and to produce high quality quicklime with low % $CaCO_3$ and high reactivity. A particular advantage of rotary kilns without preheaters is that they can be used to make low sulfur quicklime with less expensive high sulfur fuels (subject to any constraints imposed by sulfur dioxide emission limits).

Many producers have found that rotary kilns complement shaft kilns because they use different sizes of feedstone and produce quicklimes with different characteristics, thereby increasing the utilisation of limestone and meeting a wider range of quality requirements.

Other Kiln Designs. For information about other designs of kiln, see Ref. 1.

Processing of Quicklime. The major demand for calcium quicklimes is as screened grades in the size range 0.5–4 cm. To obtain the maximum yield of those sizes, it is generally necessary to crush the lime discharged from the kilns. Rolls and jaw crushers are widely used because they produce a higher proportion of granular products and fewer fines than other designs.

The crushed quicklime is screened into narrow size ranges (eg, 2.0–4.0 cm, 1.0–2.0 cm, 0.5–1.0 cm, and 0.5 cm to dust). Surplus grades (and particularly the fine fraction) are often used for the production of ground quicklime and hydrated lime.

Calcined Dolomite. Calcined dolomite is produced in both shaft and rotary kilns. Four qualities of calcined dolomite are produced—half-, light-, hard-, and dead-burned. Half-burned dolomite ($CaCO_3 \cdot MgO$) is produced in small quantities in Germany using (it is believed) rotary kilns. Light-burned dolomite is produced in both rotary and shaft kilns. Hard-burned dolomite is generally produced in mixed-feed shaft kilns, operating under reducing conditions.

Two types of dead-burned dolomite are produced. The high purity grade, used for the manufacture of refractories, may be produced either by the direct calcination of dolomite, which is then heated to temperatures of up to 1800°C in rotary or shaft kilns, or by sintering pelletized, light burned calcined dolomite at $\sim$1800°C, generally in rotary kilns. The “fettling” grade is produced by heating blended pellets containing finely divided calcined dolomite and iron oxide in a rotary kiln at temperatures of 1400–1600°C.

Natural Hydraulic Lime. Natural hydraulic lime is generally produced in shaft kilns. Typically, the limestone contains 4–16 % of SiO_2, 1–8% of Al_2O_3, and 0.3–6% of Fe_2O_3. Maximum temperatures in the kiln are controlled in the range 950–1250 °C to ensure that much of the silica and alumina react with the lime to produce calcium silicates and aluminates, without excessively sintering the free CaO. The subsequent processing of hydraulic limes is described in the section Hydrated Hydraulic Limes.

3.4. Production of Ground Quicklime and Slaked Lime.

Ground Quicklime. The demand for various grades and qualities of ground quicklime has grown rapidly since the 1950s. Particle size requirements vary from relatively coarse products used for soil stabilization (eg, 99% <2 mm, with 50% $<75\,\mu m$) to very finely divided products for specialist applications (eg, $>99\%$ $<50\,\mu m$).

Additives (eg, water and various organic compounds) may be added during the grinding process to adjust the physical and/or chemical characteristics to meet specific requirements.

The coarser products can be produced at relatively low cost using a beater mill fitted with an integral basket, which acts as a screen. Finer products are generally produced in tube mills and vertical roller mills (1). In the latter case, a variable speed classifier is generally fitted above the mill to control the grading of the product, and to recycle oversized particles. A recent development has been the use of the high pressure roll mill followed by a disintegrator and a classifier. This uses $<60\%$ of the energy required by tube mills.

Hydration Processes. Normal Hydration Process. In this process, calcium quicklimes are reacted with a controlled excess of water at atmospheric pressure and at 90–100°C. This produces Type N hydrate, as defined in ASTM specification C-207 (2), and, if the quality of the quicklime is appropriate, "chemical quality" hydrate. There are many designs of equipment, the choice of which depends on the reactivity and chemical purity of the quicklime, its particle size, and on the requirements for the finished product.

In a typical plant, the quicklime is mixed rapidly with about twice the stoichiometric amount of water in a premixer. It is then passed into the main hydrating vessel, which is agitated and fitted with a weir at the discharge end to give an average solids residence time of 10–15 min. As the hydration proceeds, part of the water boils off and produces a partially fluidized bed. Coarse particles of unreacted quicklime, unburned calcium carbonate, or gritty hydrate are retained behind the weir, while fine particles of hydrate flow over it. In some plants, a purge paddle close to the weir prevents excessive buildup of coarse particles by lifting them over the weir. In others, the coarse fraction is periodically discharged through a purge hole in the weir.

The raw hydrate is then conveyed along one or more tubes, which serve to complete the hydration and evaporate excess water. The hydrate is discharged at $\sim 90°C$, containing $<1\%$ of excess water. It is then fed into an air classifier, in which a recycling air stream removes fine particles and allows coarse particles to fall to the base of the inner feed chamber. The fine particles are conveyed to the finished product bunker. The coarse particles may be rejected as a stream rich in $CaCO_3$. Alternatively, they may be milled, with the product being recycled to the hydrator, reclassified, or blended into the finished product.

The steam generated in the hydrator, together with any air drawn into the process, may be dedusted in a wet scrubber, in which case the milk of lime from the scrubber is fed into the premixer.

Some plants use ageing silos to retain damp hydrate at an elevated temperature for ~ 24 h to ensure that all of the CaO has been converted to $Ca(OH)_2$. Ageing silos are used when the feed quicklime has a low reactivity, for the production of dolomitic hydrate, or when a product with a particularly low expansion potential is required.

Pressure Hydration Process. Type S hydrate, as defined in ASTM specification C-207 (2), is produced by reacting quicklime (generally dolomitic) and water at temperatures of up to 180°C and a steam pressure of up to 1 MPa. After hydration, the product is dried, milled, and air classified.

High Surface Area Hydrated Limes. Two processes have been developed for the production of high surface area hydrated limes for injection into flue gases to remove acid gases. In one, the quicklime is hydrated with an amine–glycol additive in a largely conventional plant (22). Another uses a water–methanol mixture (23).

Hydrated Hydraulic Limes. "Natural hydraulic limes" (see the section Calcined Dolomite) are hydrated with sufficient water to convert the free lime into calcium hydroxide. If the free CaO content is >10–15%, the lime disintegrates on hydration into a powder. Otherwise, the run-of kiln product must be ground before hydration. It may also be necessary to grind the hydrated product to achieve the required properties.

EN 459-1 (24) defines three types of hydraulic limes.

1. *Natural hydraulic limes* (NHL) produced by burning of more or less argillaceous or siliceous limestones with reduction to powder by slaking with or without grinding".
2. *Natural hydraulic limes with additional material* (NHL-Z), which are natural hydraulic limes (NHL) to which suitable pozzolanic or hydraulic materials (up to 20% by mass) has been added.
3. *Hydraulic limes* (HL), which are limes consisting of calcium hydroxide, calcium silicates and calcium aluminates produced by mixing of suitable materials.

Milk of Lime. *Normal Slaking Process.* There are many ways of slaking quicklime to produce milk of lime. They range from simple batch processes to sophisticated continuous slakers.

In the batch processes, water and quicklime are added as required to maintain the milk at ~90°C. With reactive quicklimes, care should be taken to avoid local overheating, which can lead to the formation of particles of gritty calcium hydroxide. With cold water, this technique produces a viscous suspension with 35–40 % solids. Grit arising from uncalcined limestone, unreacted quicklime, and gritty calcium hydroxide settles on the base of the slaker and is removed at intervals.

There are various designs of continuous slakers that produce either milk of lime, or lime putty. Many feature automatic grit removal.

Slaking at ~90°C generally produces the finely divided particles of calcium hydroxide required by most users. If the slaking temperature is allowed to drop (eg, to 70°C), the resulting increase in particle size can reduce the viscosity of the milk and the chemical "reactivity" of the slaked lime.

Ageing milks of lime for ~30 min generally ensures complete hydration, while ageing for a day or more generally increases viscosity and workability.

Production from Hydrated Lime. Hydrated lime disperses readily in water. Both batch and continuous processes are used (25).

Production of Ultrafine Milks of Lime. Two processes have been developed for the production of ultrafine milks of lime (1). One uses hydration at high shear rates (26), while the other mills a conventional milk of lime in a bead mill.

Such milks have the advantage of reacting very rapidly and have handling characteristics that are closer to liquids than typical suspensions.

Lime Putty. Lime putty is generally produced by allowing milk of lime to settle, and drawing off the layer of clear lime water. The putty is then mixed and aged before use.

Lime putty may also be produced by mixing 1 unit (by weight) of hydrated lime with 0.7–1 units of water. Putties made from Type N hydrate should be matured for at least 24 h, while those made from Type S hydrate mature within 1 h.

3.5. Storage and Transport. *Quicklime.* Quicklime should be stored in enclosed bunkers with well-sealed discharge mechanisms to minimize the reaction with atmospheric water vapor and carbon dioxide, and to control dust emission. Storage capacities equivalent to 5–10 days′ use are usually adequate (25).

Screened grades of quicklime (generally 0.5 cm and above) may be transported in tipper trucks. Effective sheeting is essential to minimize atmospheric attack of the quicklime and to control dust emission. Air pressure discharge vehicles are used to transport fine grades of quicklime, and, increasingly, screened grades up to 2 cm. Where available, rail and water transport can significantly extend the economic delivery distance.

A small proportion of quicklime is packaged. Drums, plastic containers, and sacks are used for amounts up to 50 kg. Intermediate bulk containers, both rigid and flexible, are increasingly being used for quantities up to 1 t. There is a small international market for packaged quicklime.

Where totally enclosed bunkers cannot be provided, quicklime should be stored on a concrete base, preferably in a separate bay within a building. It should be used as soon as possible after delivery. Covering the pile with a close-fitting impermeable sheet helps to reduce atmospheric attack. Open reception hoppers should be protected from the elements.

Contact of quicklime with flammable materials should be avoided, especially when there is a risk of water penetration. In the presence of organic matter (eg, wooden floors), the heat of hydration has resulted in fires.

Further details on the delivery, storage, and handling are often available from the supplier.

Hydrated Lime. Bulk hydrated lime is stored in enclosed silos to minimize reaction with atmospheric carbon dioxide and to control dust emission. It is transported in air pressure discharge vehicles, both by road and rail (25).

A substantial proportion of hydrated lime is sold in paper sacks (generally 25 kg), although the use of intermediate bulk containers, holding up to 1 t, is increasing. There is a significant international market for packaged hydrate.

The flow characteristics of hydrated lime are very variable. The angle of repose can vary from 0 to 80°, and depends on the amounts of entrained air, excess water, and other factors. Silos may need to be fitted with devices to cope with bridging of the powder above discharge points and to encourage flow (eg, bin activators, air pads and, in extreme cases, air cannons).

Hydrated lime in paper sacks is generally placed on pallets and stored under cover. By fitting impermeable slip-sheets under the bags and shrinkwrapping a cover over the loaded pallet, hydrate may be stored out of doors for several months.

Further details on the delivery, storage, and handling of hydrated lime are often available from the supplier.

Milk of Lime and Lime Putty. Milk of lime is generally produced on-site and is usually conveyed by pipeline (25). Precautions need to be taken to prevent calcium carbonate scaling and deposition of grit and lime putty. Storage tanks should be agitated and provision made for backflushing the discharge pipe and any other “dead legs”.

Ultrafine milks of lime may be made on site, in which case they are conveyed by pipeline. Otherwise, they are transported by tanker.

Lime putty is either produced on site or delivered in small rigid containers.

3.6. Market Overview and Economic Aspects. *Market Overview.* Global open-market sales of quicklime have been estimated (27) to be 116 million tonnes per year. About 60% of the total is sold in six countries: China, United States, Japan, Germany, the former USSR, and Brazil. Table 8 gives estimates (2000) of lime production for the open market in 25 of the major lime-producing countries, together with estimates (where available) of the percentages used in the chemical industry and in environmental protection (6,28).

Published figures for the sales of lime products generally exclude the many captive producers, whose lime is not sold on the open market, and the multitude of small producers, particularly in the developing countries. The European Lime Association has estimated that, if their contribution were included, the total lime sales could amount to 300 million tonnes per year (29).

The uses of lime products are many and varied. Table 9 lists the main applications.

The pattern of use varies significantly from country to country. Table 10 summarizes the distributions for 9 countries (28,30,31), and Table 11 gives the average distribution in 1998 for sales of 63 million tonnes of lime products in 24 countries (28).

Lime products are subdivided into three main categories, based on chemical composition, namely calcium, dolomitic and hydraulic.

Calcium limes are mainly sold as

A. Screened quicklime products (ie, lump, granular and fine).

B. Ground quicklime products (to various size specifications).

C. Hydrated calcium limes (generally as Type N).

Dolomitic limes are mainly sold as

D. Light-burned screened products.

E. Dead-burned products.

Hydraulic limes

F. Are subdivided in EN 459-1 (24F) into three categories (see the section Hydrated Hydraulic Limes).

An estimate of the proportions of open-market sales of products (A–F) in the European Union is given in Table 11 (29).

High calcium (or *chemical quality*) quicklimes and hydrated limes are a subgroup of calcium limes. In a particular country they may represent from 50 to > 85% of total sales, depending on the quality of limestone deposits and on market requirements.

Economic Aspects. The production of lime products is both energy and capital intensive. In consequence, the price and availability of suitable fuels and electricity, and the choice of kiln are important factors in determining the economic price of lime. For some lime works, the cost of energy represents 40–50% of the production cost (29).

The integration of lime production with the quarry and maximizing the proportions of saleable lime and limestone are also of importance in determining the production cost. The size(s) of stone fed to the lime kilns should complement the sizes of stone that can be sold. Many lime works use shaft kilns to calcine the larger fractions of stone (eg, 40–150 mm) and rotary, or other types of kiln to calcine smaller fractions (eg, 40 mm down to 10 mm and even to dust). Similarly, by integrating lime crushing, screening, grinding, and hydrating plants, surplus screened quicklime fractions can be converted into higher added value ground lime and hydrated lime products.

The ex-works price of screened high calcium quicklime products in Europe is generally in the range £40–£60/t (1998) (1). In the United Ssates, the average ex-works price for high calcium quicklime (mainly screened) was $US 57.4/metric tonne (2000) (27). Ground quicklime and hydrated lime prices are typically some 30–45 % higher than screened lime, reflecting the capital and operating costs of the additional processing stages (eg, in the United States, the ex-works price of calcium hydrated lime averaged $US 80.2/t in 2000). Specialist products, tailored to the needs of individual market segments or customers, generally command higher prices.

Economic haulage distances vary considerably as a result of local factors. Where there are a number of local lime producers, distances of up to 250–400 km may be economic for road deliveries. That range is extended considerably where there is little competition, and where rail or water transport can be used. In southern England, the cost of road delivery of hydrated lime by air pressure discharge vehicle to a customer 150 km from the supplier is equivalent to ~$US 15.

A frequent dilemma for users requiring lime as a milk is whether to purchase screened quicklime, ground quicklime, or hydrated lime. For example, if the delivered prices per tonne of those *products* were $ 74, 91, and 91, respectively, the approximate delivered costs per tonne of *available lime (as CaO)* could be $ 80, 98, and 126, respectively. However, the capital, and operating costs for the equipment required to produce milk of lime are highest for screened quicklime, intermediate for ground quicklime and lowest for hydrated lime.

As a result, customers with large lime requirements (eg, >10,000 tpa on one site) often purchase screened quicklime and install relatively expensive storage, handling, and slaking systems. Customers with intermediate requirements often choose ground quicklime. Customers requiring still smaller tonnages of lime tend to favor hydrated lime. Customers with unmanned processes (eg, water treatment plants) also tend to favor hydrated lime, as the installation tends to be more reliable than the alternatives.

3.7. Uses. *Quicklime (Screened and Ground).*

Iron and Steel. A small amount of ground quicklime is used in the production of iron ore agglomerates from fines. The main advantage of adding 1–6% of lime to the ore is a marked increase in the production capacity of the sinter strand. Ground quicklime is also used for the desulfurization of iron in the ladle before charging into the steelmaking furnace.

The major use of quicklime is in the Basic Oxygen Steelmaking (BOS) process. Screened quicklime 35–70 kg is used per tonne of steel. The quicklime neutralizes the acidic oxides (SiO_2, Al_2O_3, and Fe_2O_3) to produce a basic molten slag. Correct formation of the slag is essential for the refining process. Further information on the role of quicklime and the slag in removing phosphorus and sulfur from steel is given in the literature (32). Calcined dolomite is also added to the BOS vessel to give ~6% MgO in the slag, thereby reducing slag viscosity and attack of the basic refractory lining.

Similarly, the electric arc steelmaking process uses granular quicklime to react with acidic oxides and produce a molten slag.

Screened and ground quicklime are also used in various secondary steelmaking processes. The argon oxygen decarburization process requires screened quicklime with a particularly low residual $CaCO_3$ level ($<0.15\%$ as C).

Calcium carbide is produced by reacting screened quicklime with coke in furnaces, which are heated electrically to 2000°C. It is used to produce acetylene by reaction with water. The by-product is “carbide lime”—an impure form of hydrated lime.

Aerated Concrete. Ground quicklime, with a closely controlled reactivity, is used in the production of aerated concrete blocks, with densities of $\sim 0.7\ g/cm^3$. The quicklime is mixed with an active form of silicon (eg, ground silica sand or pulverized fuel ash), sand, water, aluminum powder and, depending on the quicklime quality, cement. The reaction of quicklime with the aluminium powder generates hydrogen bubbles, which cause the “cake” to rise. At the same time the quicklime reacts with the water, generating heat and causing the cake to set. The cake is removed from the mold and cut into blocks before autoclaving at elevated temperature and pressure.

Soil Stabilization. Quicklime and hydrated lime can considerably increase the load-carrying capacity of clay-containing soils. They do this by reacting with finely divided silica and alumina in the soil to produce calcium silicates and aluminates, which possess cementing properties. Quicklime has the advantage over hydrated lime of drying out the soil. It does this by absorbing 30% of its own weight of moisture and also by generating heat, which accelerates evaporation.

Soil stabilization is used in road and rail construction to strengthen subgrades, thereby reducing construction depths. It may also be used to produce a sub-base in place of aggregate. It is used on clay-rich construction sites for placement and compaction of on-site material. In some countries, lime piling is used to pin unstable soils and to provide support for building slabs.

Other Uses. Small quantities of quicklime are used in other processes (1), eg, in metal refining and the production of glass, calcium aluminate cement, and organic chemicals. The largest use of quicklime, however, is in the production of slaked lime (see the section Slaked Lime).

Slaked Lime (Hydrated Lime, Milk of Lime and Lime Putty). There is little reliable information about the proportion of quicklime that is slaked before use. For the European Union, the proportion has been estimated (1) at roughly 50%, of which ~17% units are initially converted into dry hydrated lime (much of which is used as an aqueous dispersion) and 33% units are initially slaked to milk of lime or lime putty.

Slaked lime is used in a large number of processes. The more important ones are described briefly below. More detailed information is available in the literature (1).

The Solvay Process. A key step in the Solvay (or ammonia-soda) process (for the production of soda ash and sodium hydrogen carbonate) is the recovery of ammonia from an ammonium chloride solution by reaction with milk of lime.

$$2\,NH_4Cl + Ca(OH)_2 \rightarrow 2\,NH_3 + CaCl_2 + H_2O$$

Causticiation. Caustic soda is produced by reacting sodium carbonate with milk of lime. Before the development of the electrolytic cell, this was the normal method of production of caustic soda.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2\,NaOH + CaCO_3$$

In addition to its use in the Bayer alumina process (see below) this reaction is used for the regeneration of caustic soda in wood pulp plants for the production of kraft or sulfate paper.

Nonferrous Metallurgy. Slaked lime is used in the production of alumina by the Bayer process to regenerate sodium hydroxide from sodium carbonate solutions (see above). It is used in flotation processes to beneficiate copper ore and to extract gold and silver. It is an essential chemical for the extraction of uranium from gold slimes and for the recovery of nickel and tungsten after smelting.

Slaked lime is used in the production of magnesia and magnesium metal. In the seawater processes, a high calcium hydrate is used to precipitate magnesium hydroxide. The Dow natural brine process uses dolomitic milk of lime.

Water Treatment. Slaked lime is used to remove temporary and permanent hardness. Calcium hydroxide reacts with calcium and magnesium hydrogen carbonates to produce insoluble calcium carbonate and magnesium hydroxide.

$$\mathrm{Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\,CaCO_3 + 2\,H_2O}$$
$$\mathrm{Mg(HCO_3)_2 + 2\,Ca(OH)_2 \rightarrow Mg(OH)_2 + 2\,CaCO_3 + 2\,H_2O}$$

Permanent hardness caused by calcium and magnesium chlorides and sulfates can be removed by adding hydrated lime and sodium carbonate.

$$\mathrm{CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4}$$
$$\mathrm{MgSO_4 + Ca(OH)_2 + Na_2CO_3 \rightarrow Mg(OH)_2 + CaCO_3 + Na_2SO_4}$$

Water can be purified by raising the pH to >11 for 1–2 days, followed by recarbonation to pH 8–9. In addition to killing bacteria, this treatment removes temporary hardness. Acid water may be neutralized by the addition of lime.

Sewage Treatment. Treatment of sewage sludge with slaked lime in conjunction with ferrous sulfate is an effective way of removing solids and phosphorus compounds, and for destroying pathogens. It produces a sludge, which dewaters well and can he used as a fertilizer.

Industrial Wastes. Slaked lime is used to neutralize acid wastes and precipitate heavy metals in effluents from a wide range of industries. In some cases it is also used to assist with the clarification process.

Flue Gas Desulfurization. Of the many flue gas desulfurization processes, three use slaked lime (33).

1. In the *wet scrubbing* process, milk of lime is sprayed through the gases. The product is a suspension of calcium sulfite, which may he oxidized to produce saleable gypsum. Up to 95% removal of sulfur dioxide has been reported, with $>90\%$ utilization of the hydrated lime.
2. In the *dry scrubbing* process, milk of lime is fed into a spray drier the product from which is a dry powder consisting of calcium sulfite and hydrated lime. Up to 85% removal of sulfur dioxide and 40–60% utilization of the hydrated lime have been obtained.
3. In the *hydrate injection* process, sulfur dioxide is removed by injection of hydrated lime either into, or downstream from the boiler. The reaction products are collected with the fly ash for disposal. Only 50–60% of the sulfur dioxide is removed, and the lime utilization is normally $<40\%$. Hydrated lime products, with higher specific surface areas than those of normal hydrate, have been developed to raise the process efficiencies.

Sugar Refining. In the refining of sugar beet, the crude solution of sugar is treated with milk of lime to precipitate calcium salts of organic and phosphoric acids. After filtering, the solution is neutralized with carbon dioxide and calcium carbonate is precipitated. The solids are removed by filtration, and a purified sugar solution is produced. As the process requires a large quantity of both lime ($\sim$250 kg/t of sugar) and carbon dioxide, producers of sugar from beet generally operate lime kilns as an integral part of their process. Because raw sugar extracted from sugar cane is purer than that from sugar beet, its refinement requires much less hydrated lime (typically 5 kg/t).

Sand-Lime Bricks. There is a substantial market in Europe for sand lime bricks. These are made by mixing slaked lime with sand, followed by autoclaving for several hours under a steam pressure of ~1 MPa (180°C). In some processes, it is essential that the lime is not expansive. Otherwise, expansion occurs in the autoclave, resulting in the production of oversized bricks.

Mortars. Slaked lime is used in lime-cement-sand mortars in various proportions. The required compressive strength of the mortar is obtained by adjusting its composition (34). The lime confers several benefits. It increases the plasticity and water retentivity of the wet mortar, and increases the bond strength of the mortar to the masonry. The mortar is more flexible and less prone to cracking.

Soil Stabilization. Both hydrated lime and milk of lime are used in soil stabilization. Hydrate disperses readily when making a soil tilth. Milk of lime has advantages when the soil is dry. It can also he injected under pressure.

Agriculture. The advantages of adjusting soil pH with limestone were described in the section Uses and Specifications of Limestone. Hydrated lime has the additional advantage of being quick-acting.

Bleaching. Chlorine is reacted with hydrated lime to produce a powdered mixture of calcium hypochlorite and calcium chloride, commonly known as bleaching powder.

$$2\,\mathrm{Ca(OH)_2} + 2\,\mathrm{Cl_2} \rightarrow \mathrm{Ca\,(OCl)_2} + \mathrm{CaCl_2} + 2\,\mathrm{H_2O}$$

Calcium hypochlorite solution is used in bleaching wood pulp.

Precipitated calcium carbonate (PCC) is produced by blowing gases containing carbon dioxide through milk of lime. By controlling the conditions, a very finely divided calcium carbonate with a high reflectivity and a median particle size of 0.02–0.2 μm is produced. Some PCCs are coated with compounds, which facilitate their blending with organic substances (eg, plastics and rubber).

Inorganic Salts and Bases. Slaked lime is used in the production of mono-, di-, and tri-calcium phosphates as well as other calcium salts. It is used in the Solvay process to produce calcium chloride as a by-product. Lithium and barium hydroxides are made by causticization.

The brine purification process uses sodium carbonate and milk of lime to remove dissolved calcium and magnesium.

Other Uses. There is a wide range of other uses, including the production of calcium silicate insulation products, plasters, lubricants, pigments, soda lime, organic compounds, and calcium salts. Hydrated lime is also used in the petroleum industry, glass manufacture, solid waste disposal, and leather tanning (1).

3.8. Grades, Specifications, and Quality Control.

Grades. General. Lime producers typically market a relatively large number of grades of lime. Factors affecting product quality include

Chemical and physical properties of the limestone.
Type of lime kiln.
Fuel used in the kiln.
Kiln settings and control parameters.
The ways in which the lime is processed.

As an example, a large works, with three batteries of kiln, a ground lime plant, and a hydrating plant, may produce 30 grades of lime. This enables the producer to offer the product that matches a particular customer's requirements.

Particle Size. Screened quicklime is sold as sized fractions (eg, 40–100 mm, 20–40 mm, 10–20 mm, 5–10 mm, 2–5 mm, 1–2 mm, and a dust fraction, with a maximum particle size of 5 mm).

In most ground quicklime plants, the particle size of the product is controlled by a variable speed air classifier, which enables a number of grades to be made, each designed to meet the requirements of a specific market segment.

Many hydrating plants produce a "chemical quality" product meeting the size (and purity) requirements of both the chemical and building industries. Some plants, however, make a coarser (and less pure) "building quality" hydrate, either as a second grade, or as their only product.

Reactivity/Degree of Burning. Many market segments have differing requirements for the reactivity–degree of burning of quicklime products. By operating various types of kiln and controlling them appropriately, producers are able to match customer requirements by making a particular size of quicklime in two or more grades, each with a different reactivity–degree of burning.

For calcium and dolomitic limes used for building applications, the degree of burning only needs to sufficiently "soft" to ensure that, after slaking, the hydrate–slaked lime is "sound" (ie, contains insufficient CaO to cause expansion). High calcium and dolomitic limes supplied for steelmaking generally need to be relatively soft-burned to ensure that they react sufficiently rapidly in the process. Some niche markets require the reactivity/degree of burning to be controlled within narrow ranges.

The degree of burning of hydraulic limes must such that they set within specified times and pass a compressive strength test.

Chemical Composition. Most lime producers seek to meet the chemical requirements of the major market segments, which, in many countries, are building and steel. The requirements of the latter are generally more demanding in terms of % $CaCO_3$ and reactivity–degree of burning. In addition, the steelmakers' requirements for low sulfur contents, places constraints on the selection of the fuel and/or kiln. As a result, many producers make one quality of quicklime that meets the requirements of both segments. Other producers make two qualities of quicklime—one for each market segment.

While high calcium quicklimes meeting the requirements of the BOS process are also suitable for use in the chemical industry, chemical processes have additional purity requirements. Hydrated limes made from such high calcium quicklimes, are also generally suitable for chemical industry applications.

Some producers make a number of additional grades targeted at niche markets. These generally have particularly low levels of minor and/or trace components (eg, $CaCO_3$, MgO, Pb, Fe, F).

Specifications. General. Until the 1950s, the qualities of most lime products were tailored to the specifications of the building and construction industries.

During the 1960s, the widespread introduction of the BOS process set a new standard for high calcium quicklime quality and resulted in heavy investment in new kilns. The BOS specification was generally compatible with the tightening requirements of the chemical industry.

Currently (2002) European Standards have been adopted for lime and limestone products used in the production of drinking water (35), which could set a new norm for the industry, with particular reference to trace elements.

The particle size requirements often depend on the customers' handling, conveying, and blending systems.

Building Lime. The requirements for building lime are specified in EN 459-1 (24) and ASTM-C5, 141, 206 and 207 (2,36–38). Table 13 gives the classification of building limes in EN 459-1, and Table 14 summarizes the main requirements in EN 459-1 for calcium limes.Hydrated lime for certain sand-lime brick processes should have an expansion <1.0 cm (1) and $<4\%$ MgO (unless it is Type S).

The United Kingdom specification for quicklime used in soil stabilization is given in a Department of Transport publication (39).

Although not essential, high reactivity can be an advantage in soil stabilization.

Basic Oxygen Steelmaking. The requirements for high calcium quicklime and calcined dolomite for use in the BOS Process vary from one works to another. Tables 15 and 16 summarize typical specifications.

Chemical Industry. The most comprehensive summary of specifications for lime used in the chemical industry is given in ASTM-C911 (40). It summarizes the requirements of nine other Standards (41–49). In practice, most high calcium quicklimes that meet the BOS specification also meet the requirements for chemical-grade quicklime. Some chemical processes require particularly low levels of impurities such as silica, iron oxide, magnesium oxide, and fluoride, while others require hydrated lime with a controlled surface area.

Table 17 lists some other applications of lime products in the chemical and related industries for which specifications are given in (1).

Drinking Water. European Standard EN 12518 (35) specifies the quality of high calcium lime products used in the treatment of water intended for human consumption. It includes minor and trace element limits, and is probably the most detailed, and in many respects the most demanding, set of requirements yet published in a lime Standard. Tables 18 and 19 summarize the main requirements.

Quality Control. Sampling. Obtaining a representative sample, particularly with granular products, presents a number of problems and it is essential that a correct sampling procedure be followed. The selection of the sample point is also important. Often, customers believe that the supplier should authorize the product for dispatch on the basis of samples taken ex-bunker. Experience has shown, however, that concentrating sampling effort on the product *before* it is placed in bunkers leads to improved consistency. The information so obtained provides feedback to the kiln control system and helps to improve process control. Providing the quality fed into the bunkers is within specification, there is no need for frequent testing ex-bunker.

When choosing a sample point, several factors need to be considered. Often, the particle size of the quicklime ex-kiln is too large for a routine representative sample to be taken. Where the quicklime is crushed before screening (eg, to <40 mm), it may be practicable to sample that product. Alternatively, it may be more appropriate to sample one of the screened fractions. In that case, correlations should be established between the quality of the sampled fraction and those of the other product streams.

Screened Quicklime. For most lime kilns, the calcining process is controlled on the basis of the residual $CaCO_3$ and the reactivity of the quicklime. The frequency of sampling depends on the response time of the kiln and the variability of product quality. On kilns producing low sulfur quicklime using high sulfur fuel or limestone, it is also appropriate to monitor the sulfur content regularly.

The particle size of the screened fractions should be monitored, either visually, or by sieving, to check the efficiency of the screening process.

Other parameters, such as impurities, reflect the quality of the feedstone, the fuel, or the characteristics of the kiln, and may be monitored less frequently.

Ground Quicklime. For process control purposes, it is generally only necessary to check frequently that the particle size of ground quicklime is within specification, to ensure that the classifier is set correctly. Other parameters need to be monitored less frequently.

Hydrated Lime. For process control purposes, only the free moisture content of the hydrate needs to be monitored frequently. This can be achieved in a number of ways, other than by direct measurement. Monitoring the temperature profile through the hydrator can provide an adequate indication of the moisture content. Visual inspection of the “raw hydrate” by an experienced operator as it is discharged from the hydrator, is a valid technique.

The particle size distribution of the hydrate should be monitored routinely, to ensure that the classifier is operating correctly.

Many designs of hydrating plant remove a $CaCO_3$ rich fraction from “chemical” grade hydrate. In such cases, the residual $CaCO_3$ content should be monitored routinely.

4. Physical Testing and Chemical Analysis

4.1. Limestone.

General. Because most limestone is used locally, many countries have their own standards for sampling, sample preparation, and testing. The following sections refer to European, American, and British standards, to illustrate the principles and procedures involved. In a particular country, the requirements of the most relevant national or international standards should be observed.

The principal uses of limestone are as an aggregate and filler. A description of the procedures for these applications is beyond the scope of this article. Readers interested in those uses should refer to (1) for a summary, to (50) for general details and to the appropriate European (51–55), American (56–60), or national standards for individual procedures.

Sampling and Sample Preparation. It is important to understand the principles of sampling and be aware of the precautions necessary to obtain a representative laboratory sample. They include

1. Adopting a proven procedure for taking increments.
2. Ensuring that each increment is of an appropriate quantity.
3. Taking an appropriate number of increments.

Close attention to each of these points is important, as inadequate sampling practices are a frequent cause of invalid results and discrepancies between laboratories. The sampling procedure adopted will also depend on the required accuracy and precision of the result.

Guidance on sampling granular products is given in EN 932 (51) and ASTM D75 (59) for aggregates, and in ASTM C 50 (57) and BS 6463 Part 101 (63) for limestone. The standards specify the minimum number and size of increments required to obtain a representative sample. Guidance on sampling powders is given in EN 196-7 (62).

The guidance in BS 6463: Part 101 (63) includes sampling from conveyers, bulk containers, packages and silos. It also refers to the use of mechanical samplers.

(*Note*: it is very difficult to obtain a representative sample from the body of a truck, or from a stockpile. When one of these options has to be used, checks should be made to establish the validity of the procedure.)

Procedures for preparing laboratory samples are given in EN 932 (51), ASTM C702 (58), and 6463: Part 101 (63). They include combining increments and spot samples, drying, blending, reducing, dividing, crushing, and grinding.

Physical Testing. Physical test methods are dominated by procedures developed for aggregates (see the section General). ASTM C110-95 (67) gives the following procedures for limestone: bulk density (loose and packed), dry brightness, pH, grindability, and particle size by sieving and air-jet screening.

Chemical Analysis. EN 12485 (65) specifies a number of test methods for limestone used in the preparation of water for human consumption. Many of them are also relevant to testing limestone for use in limeburning and the chemical industry. They include

1. Principal components (Ca, Mg, and CO_3).
2. Minor components (Al, Fe, Mg, Mn, and Si by flame atomic absorption spectrometry).
3. Trace elements (Sb, As, Cd, Cr, Pb, Hg, Ni, and Se).

ASTM C25 (56) gives methods for Ca, Mg, CO_3, total C, Si, Al, Fe, Mn, P, Sr, free moisture, total S and sulfate, HCl-insoluble matter, and loss on ignition.

EN 196-2 (62) gives methods for loss on ignition, Al, Fe, and Si (by traditional methods).

BS 6463: Part 102 (63) gives methods for neutralising value, total S, Cu, Ag, Sn, and Zn.

4.2. Lime.

Sampling and Sample Preparation. As with limestone, the most common cause of disagreement between laboratories testing lime products arises from the failure to take representative samples. Sampling granular solids of processed, naturally occurring minerals presents particular difficulties. The problem is compounded when, as in the case of quicklime, the quality of the sample is affected by exposure to the atmosphere. In general, if quicklime contains 1.0% or more of combined water, it has not been handled correctly and its reactivity to water will have been reduced.

Guidance on the sampling of lime products is given in ASTM-C50 (64) and BS 6463: Part 101 (63). Samples should be taken from a falling stream whenever possible. Precautions should be taken to ensure that segregation within the stream does not lead to bias. Samples may also be taken from conveyor belts, providing the necessary precautions are taken.

(*Note*: if a sample has to be taken from the body of a truck, the validity of the procedure should be checked.)

In the absence of a proven procedure, each sample should consist of at least 10 increments, and each increment should be of an adequate volume (eg, 10 L for lumps with a maximum size of 10 cm, 2 L for lumps with a maximum size of 1 cm, and 1 L for powders). There are many mechanical aids to sampling, ranging from augers to automatic samplers (63,66).

Some physical tests are performed on the sample as taken. For other physical tests and for chemical analysis, it is necessary to crush, subdivide and pulverize the material to $<300\ \mu m$. This should be done on a separate subsample in such a way as to avoid bias and to avoid excessive exposure to the atmosphere.

All lime samples should be stored in well-sealed containers or bags. When samples are stored for more than 48 h, it is good practice to double-wrap them. As a general rule, quicklime should not be stored in a desiccator because it removes water from some desiccants.

Physical Testing. The most commonly used physical tests are the determinations of the reactivity of quicklime to water and the particle sizes of ground quicklime and of hydrated lime. Test methods are given in EN 459-2 (24), EN 12485 (65), and ASTM-C110 (67). A large number of alternative reactivity tests have been developed: One of the more widely used is the acid titration method described in (68). To facilitate approximate comparisons between the above tests, results obtained for high calcium quicklime, using the above methods, are shown in Figure 12 (*Note:* the results are influenced by the characteristics of the limestone and by the particle size of the sample as tested).

Other physical tests are specified in the above standards (viz, soundness, volume yield, bulk density (24b), and residue on slaking, particle density, specific surface area by porosity, and workability (63d)). They are of particular relevance to the use of lime products in the building and construction industries.

Chemical Analysis. EN 12485 (65) describes test methods for products used in the preparation of water for human consumption, which are also relevant to lime products for use in the chemical industry. They include determinations of minor and trace elements by various atomic spectrometry techniques, combined CO_2, sulfate, water soluble $CaO/Ca(OH)_2$, water insoluble constituents, and Ca and Mg by titration.

BS 6463: Part 102 (63) specifies additional test methods (including total sulfur, insoluble matter in acetic acid, and hydrochloric acids, HCl-extractable fluoride, and minor and trace elements by flame AAS).

EN 459-2 (24) specifies further methods [including ($CaO + MgO$); MgO; combined CO_2; loss on ignition; sulfate; available lime; and Si, Fe, and Al by titration].

Test methods are also specified in ASTM standards C-25 (56), C-1301 (69) and C-1318 (70).

5. Health and Safety Factors

5.1. Limestone. *Health.* Calcium carbonate and calcium magnesium carbonate are nonhazardous substances. As airborne particulates they are generally regarded as "nuisance" dusts and have recommended occupational exposure standards of 10 mg/m^3 for total, and 4 mg/m^3 for respirable dust (71). In common with all dusts, they may irritate the eyes and cause discomfort. They are nonirritant to skin. Exposure to high levels of the dusts can cause discomfort as a result of their drying effect on the mouth and upper respiratory tract. Calcium carbonate is a recognized ingredient of human and animal foodstuffs. It is used as an antacid. The therapeutic dose is 1–5 g. Chronic effects are unlikely to he encountered in industry.

The processing and handling of limestone are not associated with any occupational diseases.

Safety. In the United Kingdom, the quarrying industry has a poorer safety record than general manufacturing. While the use of explosives is generally perceived to be the greatest hazard in quarrying, it is generally well covered by legislation and typically causes $<5\%$ of the deaths and major injuries. However, accidents associated with dump trucks, mechanical shovels, and other mobile equipment (including falls associated with such equipment) are the cause of over 50% of the industry's deaths and major injuries.

In limestone mines, rock falls account for about one-third of deaths and serious injuries, with haulage and transport being the next most significant category. Special electrical precautions (eg, high integrity earthing and use of low voltage portable tools) are essential as water percolates into most limestone mines.

Stone processing involves a number of mechanical operations. The largest category of injuries caused by these generally arises from inadequate guarding of moving machinery and from failure to electrically isolate equipment when carrying out maintenance.

Stone processing generates high noise levels. Measures are taken to reduce or contain the noise at the source, or to exclude it from work areas. Use of television cameras and monitors enable operators to observe critical parts of the process from the control room. Effective personal hearing protection is generally required. In dusty areas, suitable respiratory and eye protection equipment should he used.

5.2. Lime. *Health.* Quicklime and hydrated lime are alkaline in the presence of water (pH 12.4). As airborne dusts, their occupational exposure standards (OES) in the United Kingdom are 2 and 5 mg/m^3, respectively (71). The dusts are irritating to the respiratory tract and may cause inflammation. Contact of lime with the eyes can cause painful irritation and may result in serious damage unless immediate treatment is given.

Both quicklime and hydrated lime are classified as irritant and can cause "chemical burns" of the skin, in the presence of moisture (or perspiration) and when the skin is subject to abrasion. Under the EEC Dangerous Preparations Directive, both products are currently classified by risk phrases R38 (irritating to skin) and R41 (risk of serious damage to eyes). Prolonged and repeated contact may cause the skin to become dry and cracked, and may lead to dermatitis. Ingestion can cause corrosion and damage to the gastrointestinal tract.

Quicklime and hydrated lime are used in the treatment of drinking water. In such cases, limits may be applied to the minor and trace element contents (35).

Safety. In the United Kingdom, the lime industry's safety record is close to the average for general manufacturing. Tripping and falling constitute the largest category of accidents. Lime processing involves a number of mechanical operations: adequate guarding of moving machinery and effective electrical isolation procedures (when carrying out maintenance) are essential.

Both quicklime and hydrated lime are dusty, alkaline products. Not surprisingly, a common injury arises from grit or dust entering the eye. Eye protection should be worn at all times in lime plants and eyewash facilities should be provided. Techniques to control in-plant dust are mentioned in (1).

Advice on first aid treatment can usually be found in the manufacturers' hazard data sheets, or in national standards [eg, (63)].

6. Environmental Issues

6.1. General. The main environmental issues associated with the production of lime and limestone products are usually noise and vibration from quarrying–stone processing, emissions to atmosphere (29) and the usage of energy.

6.2. Noise and Vibration. *Noise.* Quarry blasting can produce powerful impulsive sound waves, which may startle neighbors and cause buildings to vibrate. Under certain atmospheric conditions (particularly temperature inversions) the sound can be focused. Advice has been published on good operating practices to control emissions and avoid the most adverse conditions (72).

Mobile equipment, such as drills, mechanical shovels, and dump trucks, can produce unacceptable noise levels if not adequately silenced. During stone processing, the impact of stone on metalwork can cause complaints and appropriate control measures may be necessary (73).

High pressure and high efficiency fans and blowers, associated with lime kilns, can produce pure tones, which may necessitate the fitting of silencers.

Vibration. The major source of vibration from quarrying is primary blasting. The measurement and control of vibration from this source is well understood. There are established guidelines relating to complaint levels (74) and the risk of damage to property (75).

6.3. Air Pollution. The main emissions to atmosphere are dust, sulfur dioxide, and oxides of nitrogen. The European Commission has published a "best available techniques" reference document for the Lime Industry (29).

Dust Emission. The emission of dust from stone processing, lime kilns, and solids handling is often the major environmental problem associated with the production of lime and limestone products. In many countries, emissions of dust to the atmosphere are limited to <50 mg of solids per m^3 (at $0°C$ and 101 MPa) of exhaust gas.

A variety of techniques are used to control dust emissions from stone processing operations. Dust suppression, which uses water with a wetting agent to cause dust to adhere to larger particles, can be an effective and inexpensive method. It may, however, cause undesirable surface contamination of screened products with fines and increase downstream dust problems.

As the effluent gases from stone processing and local exhaust ventilation systems are generally at relatively low temperatures, bag filters, or high energy wet scrubbers are widely used. The dust collected by bag filters can often be sold as a filler for concrete production.

The temperature of the effluent gases from lime kilns is commonly 200–400°C. In the past, high efficiency multicyclones were widely used to collect the dust. They had the advantage of being relatively inexpensive to install and operate. However, their efficiency is generally no longer adequate in the context of current emission requirements. Electrostatic precipitators can handle gases at the above temperatures. Although their capital cost is high, their operating costs are moderate. Gravel bed filters can he operated at high temperatures. While they are efficient, they have higher capital and operating costs than electrostatic precipitators. Bag filters are widely used when the gas temperatures are $<200°C$. They are lower in capital cost than precipitators, have a high collection efficiency, but have higher operating costs. The reverse-jet method of cleaning the bags has generally been found to be the most effective. Wet collectors are not widely used with quicklime.

The dust collected from lime kilns is generally high in $CaCO_3$ but is contaminated with quicklime and possibly fuel ash. It is usually disposed to landfill.

Wet collectors are generally the preferred method of controlling dust from hydrating plants. The collected milk of lime is fed back to the process. Some hydrators use bag filters designed to cope with the near-dewpoint conditions.

Dust from the grinding, handling, storage, and loading of quicklime and hydrated lime is generally collected in bag filters. The collected dust usually has a high lime content and is sold.

Sulfur Dioxide. Sulfur dioxide emissions from most lime kilns are acceptably low [eg, <500 mg SO_2/Nm^3], as the quicklime captures and retains a high proportion of the sulfur from the fuel and limestone. However, when low sulfur quicklime is produced in rotary kilns and hard-burned calcium lime and dead-burned dolomite is produced in shaft or rotary kilns, most of the sulfur may be emitted with the exhaust gases. In such cases, there may be a need to abate the emission of sulfur dioxide. The only proven sulfur dioxide abatement technique for lime kilns is to use fuels with lower sulfur contents (29) (abatement techniques used in other industries, eg, the injection of calcium hydroxide, have not yet been applied to lime kilns).

Oxides of Nitrogen. Nitrogen oxide emissions from most shaft kilns are acceptably low [eg, <500 mg NO_2/Nm^3], when producing light- and medium-burned quicklime. However, when they are used to produce hard-burned calcium lime and hard- or dead-burned dolomite, higher emissions result. Emissions from rotary kilns producing soft-burned lime are generally acceptable, but increase to >800 mg NO_2/Nm^3 when medium-, hard- and dead-burned products are made. Techniques used in other industries include low NO_x burners, selective noncatalytic reduction, and selective catalytic reduction. The cost-effectiveness of such techniques for lime kilns has yet to be established (29).

Other Substances. Emissions of substances such as volatile organic compounds, dioxins, and furans are reported to be negligible from the vast majority of lime kilns (29). Significant emissions are only likely to occur under exceptional circumstances (29). There is no evidence to suggest that significant emissions of heavy metals can occur from lime kilns.

6.4. Energy Usage.

In a typical lime works, the kilns use ~86% of the total (primary) energy supplied as fuel and a further 6% units as electricity. The remaining ~8% units of energy are used in quarrying and processing of limestone, and screening, grinding, and hydrating of lime.

The decomposition of limestone to quicklime is necessarily an energy-intensive process. Details of the specific fuel and electricity consumption of a few designs of lime kiln are given in Table 7 (1). As the cost of energy is a major proportion of the production cost, considerable efforts have been made by kiln suppliers and operators reduce energy usage per tonne of saleable product, while producing the required product quality.

6.5. Recycling and Disposal.

Recycling.

Limestone, used in concrete and road building, is increasingly being reprocessed and recycled, rather than being disposed to landfill.

Lime Products. Pressures to reduce the amount of waste from lime works have led to increased recycling, or sale of by-products that were formerly used for landfill. Dust removed from kiln exhaust gases and $CaCO_3$ rich "rejects" from hydrating plants are processed and blended with other products to meet the quality requirements of selected market segments (eg, building, acid neutralization, soil treatment, agriculture).

The paper and pulp industry uses large quantities of slaked lime in the sulfate (or Kraft) process to causticize a smelt consisting primarily of sodium carbonate and sodium sulfide. The resulting caustic soda is recycled to the process and the calcium carbonate is removed by filtration. About 90% of the calcium carbonate filter cake may be dried, calcined to quicklime, and recycled to the process. The remaining 10% provides a necessary purge of impurities from the process.

> Calcium carbide is produced by reacting quicklime with coke in a furnace at 1800–2100°C. The calcium carbide is reacted with water in "generators" to produce acetylene. Calcium hydroxide (carbide lime) is a by-product of the process. Where "wet" generators are used, the resulting milk of lime is concentrated by settling and sold into selected market segments. Where "dry" generators are used, part of the carbide lime can be calcined, and the resulting quicklime powder is recycled to the furnace.

Disposal. Quarrying inevitably produces materials that are either too contaminated with clay and/or other impurities, or too fine to be processed and sold. Those materials are generally used for landscaping quarried areas or landfill.

In the past, significant quantities of waste lime products and waste products containing available lime have been disposed to landfill. There are moves in some countries to require waste materials containing significant levels of available lime to be sent to controlled disposal sites, where the run-off water is processed before discharge to watercourses. Some producers have made considerable progress to minimize the production of waste lime products, and to find outlets for those that are made.

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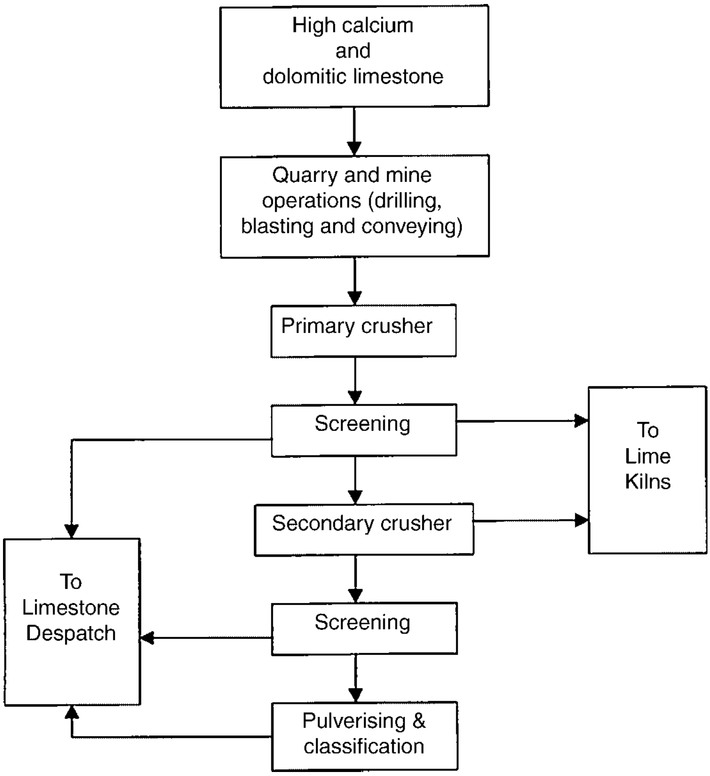

Fig. 1. Flow diagram for a limestone quarry.

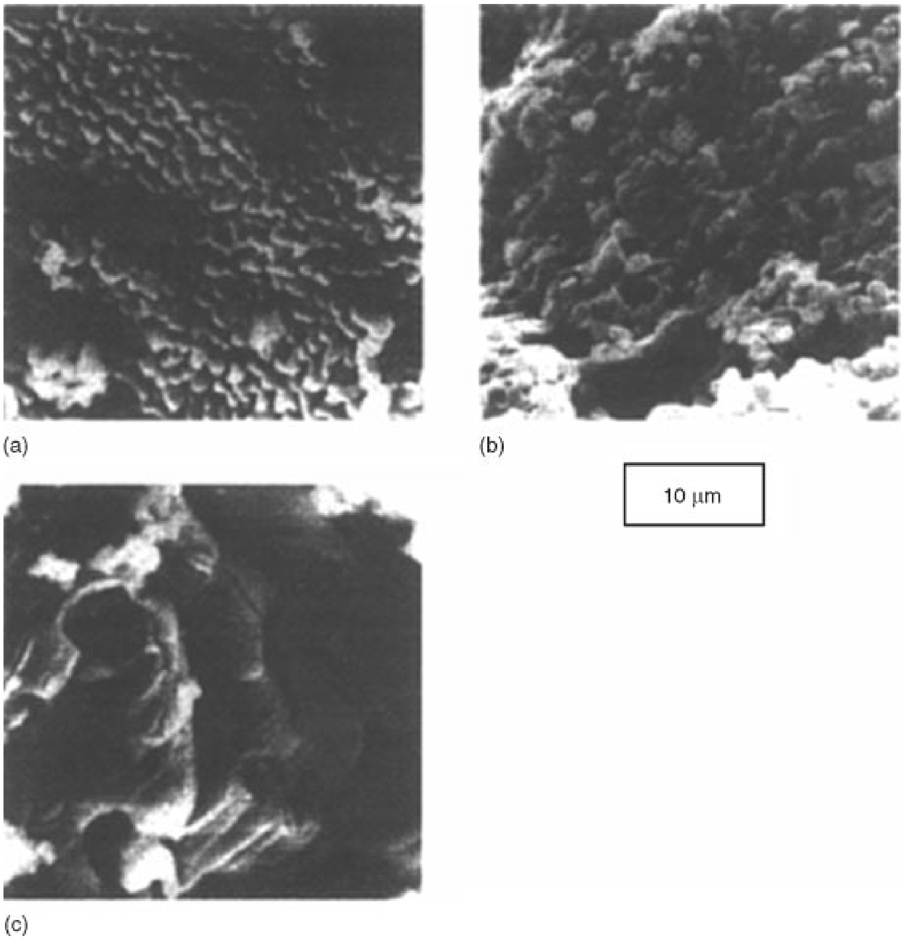

Fig. 2. Scanning electron micrographs of quicklimes with apparent densities. (a) 1.5 g/cm^3. (b) 1.9 g/cm^3; (c) 2.3 g/cm^3. (Courtesy of Buxton Lime Industries Ltd.)

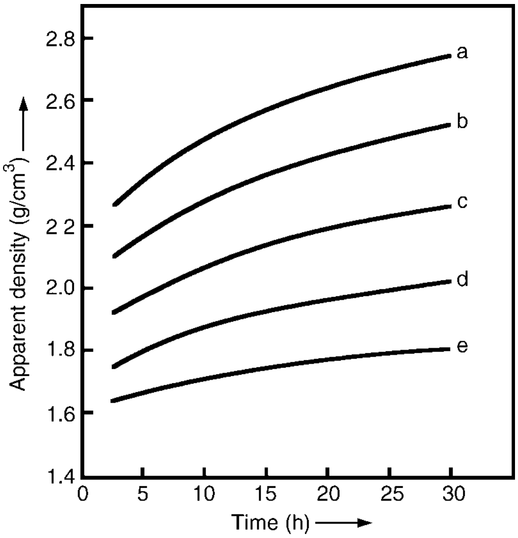

Fig. 3. Variation of apparent density with temperature and time. (a) 1400°C; (b) 1300°C; (c) 1200°C; (d) 1100°C; (e) 1000°C.

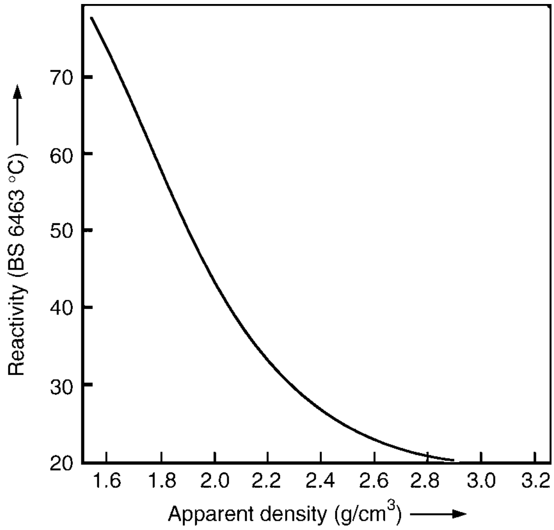

Fig. 4. Relationship between reactivity and mean apparent density for a dense, high calcium quicklime.

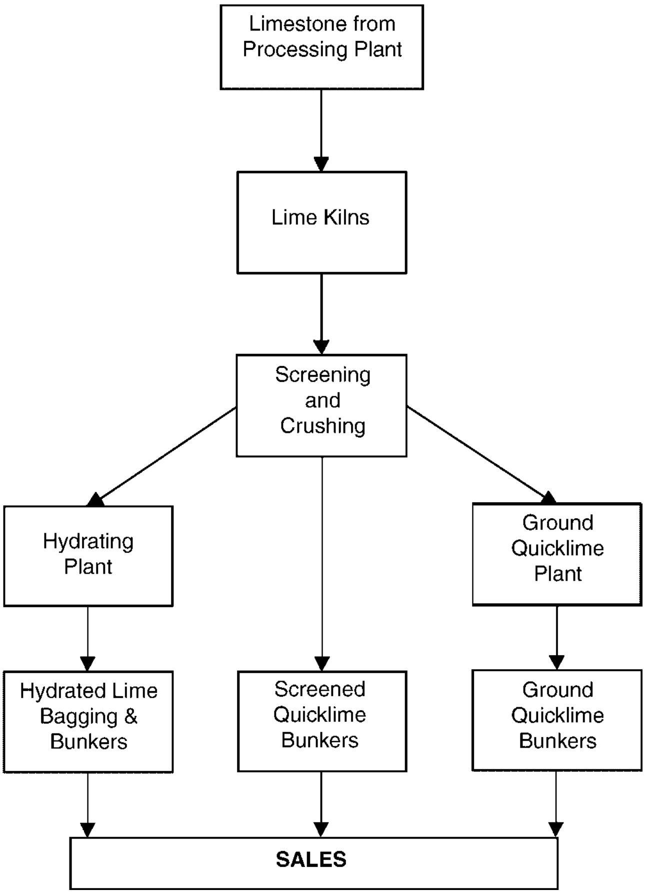

Fig. 5. Flow diagram for a lime works.

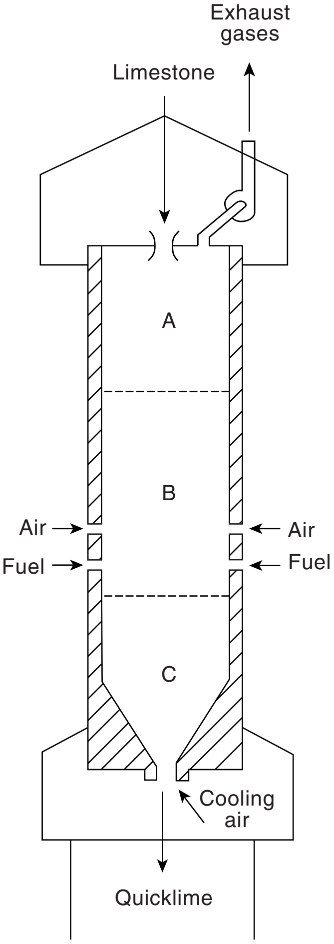

Fig. 6. Cross-section of a vertical shaft kiln. (A) preheating zone; (B) calcining zone; (C) cooling zone.

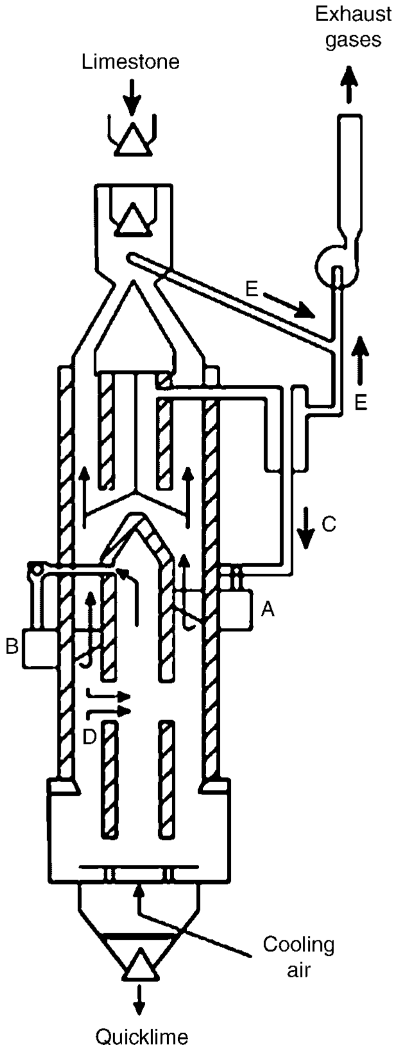

Fig. 7. Cross-section of an annular shaft kiln: (A) upper burners, (B) lower burners, (C) combustion air to upper burners, (D) combustion air to lower burners, (E) kiln exhaust gases.

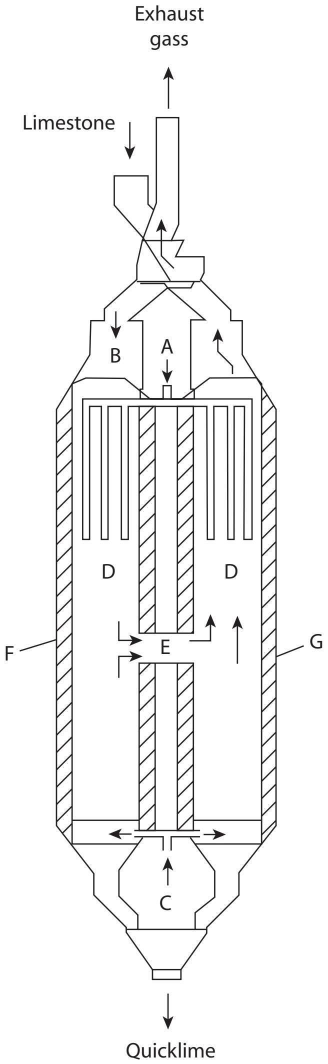

Fig. 8. Cross-section of a parallel-flow regenerative kiln. (A) Fuel, (B) combustion air, (C) cooling air, (D) lances, (E) cross-duct, (F) shaft 1, (G) shaft 2.

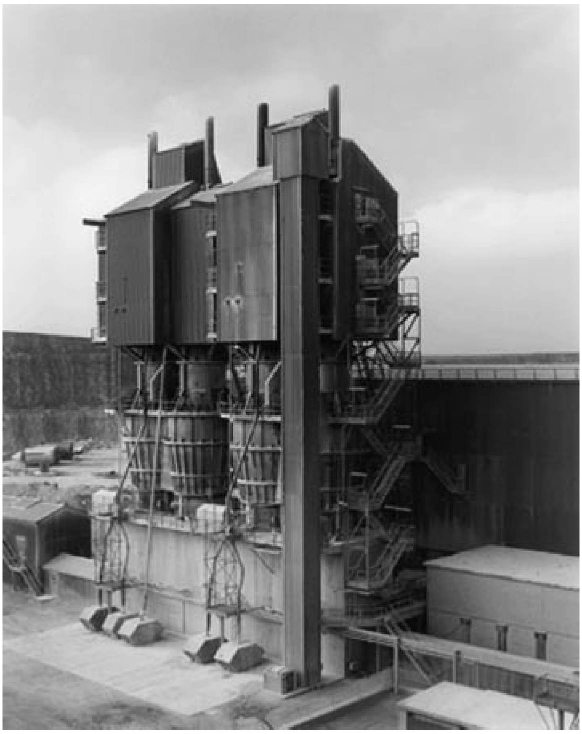

Fig. 9. Two 300 t/d parallel-flow regenerative kilns. (Courtesy of Buxton Lime Industries Ltd.)

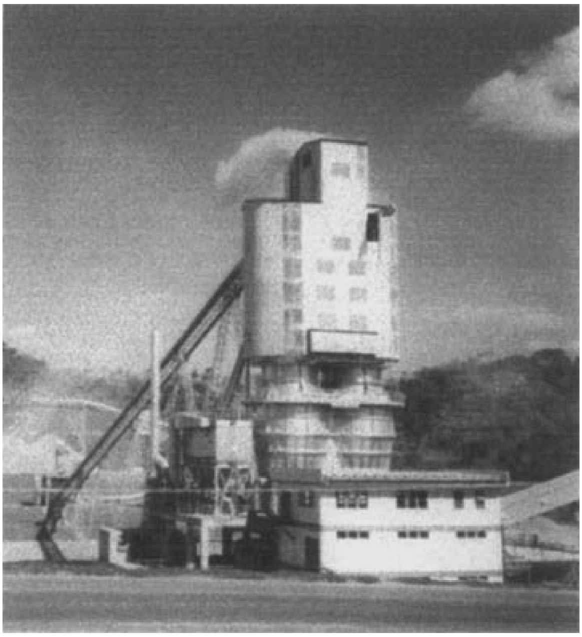

Fig. 10. Cross-section of a long rotary kiln. (a) Limestone, (b) exhaust gases, (c) refractory trefoils, (d) kiln shell, (e) fuel plus secondary air, (f) lime cooler,(g) cooling air, (h) quicklime.

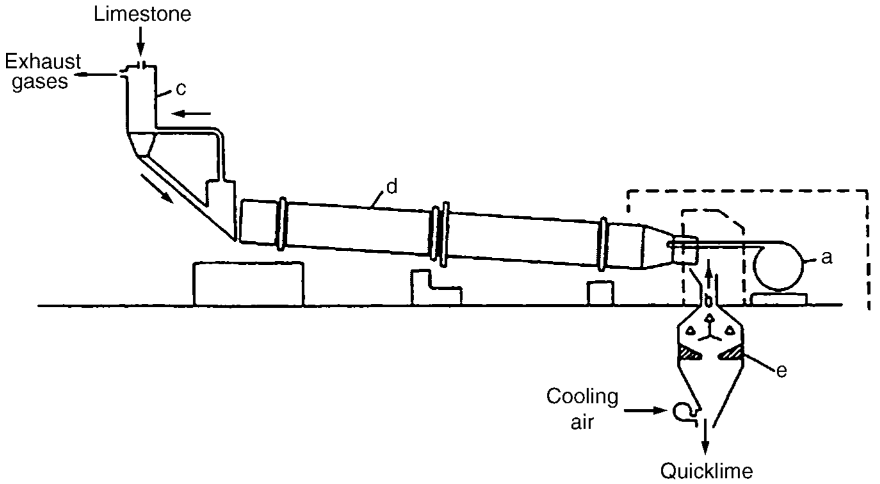

Fig. 11. Cross-section of a preheater rotary kiln. (a) fuel, (b) preheated combustion air, (c) preheater, (d) kiln shell, (e) cooler.

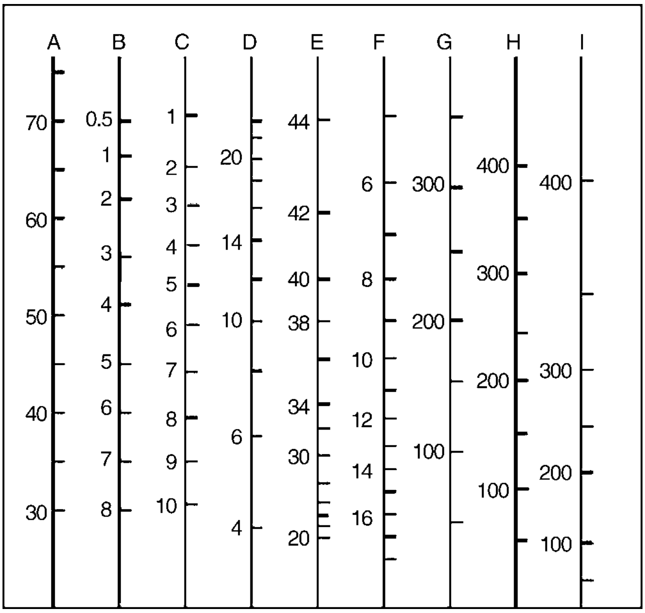

Fig. 12. Comparisons between reactivity tests for a high calcium quicklime. (A) BS 6463°C after 2 min (63); (B) EN 459-2, t_{60} (time to reach 60°C) (24b); (C) EN 459-2, t_u (min) (time for 80% slaking) (24b); (D) ASTM-C110, temperature rise (°C) after 30 s; (E) ASTM-C110, max. temperature rise (°C); (F) ASTM-C110, time to max. temperature (min) (67); (G) acid titration (mL) at 3 min; (H) acid titration (mL) at 5 min; (I) acid titration (mL) at 10 min (68).

Table 1.

Ultra high calcium	$> 97\%\ CaCO_3$
High calcium, or chemical	$> 95\%\ CaCO_3$
High purity carbonate	$> 95\%\ CaCO_3 + MgCO^3$
Calcitic	$< 5\%\ MgCO_3$
Magnesian	$5–20\%\ MgCO_3$
Dolomitic	$20–40\%\ MgCO_3$
High magnesium dolomitic	$40–46\%\ MgCO_3$

Table 2. **Pressure of Carbon Dioxide above Calcite**

Temperature °C	CO_2 Pressure (atm)
600	0.003
700	0.026
750	0.079
800	0.24
850	0.50
900	1.00

Table 3. **Typical Ranges of Impurities–Trace Elements in Commercial Limestones**

	Typical range		
Impurity or trace element	Low	High	Units
silica (as SiO_2)	0.1	2	%
alumina (as Al_2O_3)	0.04	1.5	%
iron (as Fe_2O_3)	0.02	0.6	%
sulfur (as $CaSO_4$)	0.01	0.5	%
carbonaceous matter	0.01	0.5	%
manganese (as MnO_2)	20	1000	mg/kg
antimony	0.1	3	mg/kg
arsenic	0.1	15	mg/kg
boron	1	20	mg/kg
cadmium	0.1	15	mg/kg
chromium	3	15	mg/kg
copper	1	30	mg/kg
fluoride	5	3000	mg/kg
lead	0.5	30	mg/kg
mercury	0.02	0.1	mg/kg
molybdenum	0.1	4	mg/kg
nickel	0.5	15	mg/kg
selenium	0.02	3	mg/kg
silver	0.2	4	mg/kg
tin	0.1	15	mg/kg
vanadium	1	20	mg/kg
zinc	3	500	mg/kg

Table 4. **Estimated Extraction of Limestone in Various Countries (1994)**

Country/region	Estimated total excluding captive usage for cement 10^6 tpa	Estimated captive usage for cement 10^6 tpa[a]	Total including usage for cement 10^6 tpa
Africa		50	
America—United States	800	70	870
—Other		110	
Austria	12	4	16
Belgium	24	8	32
China		420	
Czech Republic	2		
Denmark	1	2	3
Germany	33	33	66
Finland	1	1	2
France		21	
Greece		14	
India		56	
Ireland		2	
Italy		34	
Japan	108	100	208
Luxembourg		1	
Mexico		28	
Netherlands		3	
New Zealand	3	2	5
Norway	1	1	2
Poland	10		
Portugal		8	
Sweden	2	3	2
Slovak Republic	4	28	32
Spain	2	28	30
South Africa	1		
South Korea		50	
Thailand		28	
Turkey	28	31	59
United Kingdom	110	10	120
Former USSR		55	
Estimated world total	3080	1420	4500

[a] The “estimated captive use for cement” is an approximate value, derived from Cembureau data for 1995, on ILA statistics (1994) for noncaptive use, and on an assumed average conversion rate of 1.0 tonne of calcium carbonate per tonne of clinker.

Table 5. **Sales of Limestone to the Main Market Segments (1994)**

	Germany		Japan		U.K.	
Market segment	10^6 tpa	%	10^6 tpa	%	10^6 tpa	%
construction and building						
building materials[a]	5.6	8.5	34.2[b]	16.4[b]	13.2	11.0
building construction	1.6	2.4			39.1	32.5
roads and below grade	16.0	24.3	27.3	13.1	47.0	39.0
cement (including captive)	33.3	51.0	100.5	48.3	10.0	8.3
agriculture	1.4	2.1	1.3	0.6	2.2	1.8
iron and steel	3.1	4.7	22.5	10.8	2.7	2.2
environmental protection	1.3	2.0	3.8	1.8	0.6[c]	0.5[c]
other	3.1	4.7	18.5	8.9	6.3	5.2
Totals	*66*		*208*		*121*	

[a] Excluding cement.

[b] Data for Japan includes both building materials and construction.

[c] Estimated value for 2000. (In the United Kingdom the use of substantial tonnages of limestone for flue gas desulfurization only started in 1994.)

Table 6. **Uses of Limestone**

Application		Application
aggregate	concrete	smelting of ores—copper, lead, zinc, antimony
	roads unbound	alumina extraction from bauxite
	asphalt	glass
	rail track	ceramics
	drainage/filtration	mineral wool
sand for mortars		flue gas desulfurization
armour stone		hydrogen fluoride absorption
cement	ordinary Portland	pulp (sulfite process)
	composite	organic chemicals
	masonry	rock dust for mines
	calcium aluminate	whiting/fillers (see (1))
arable land and pasture		water treatment
fertilizers		sewage filtration
animal feedstuffs		effluent neutralization
poultry grits		sodium dichromate
neutralizing acid rainfall		calcium zirconate
iron		limeburning
steel		

Table 7. **Typical Energy Usages of Some Types of Lime Kiln**

Kiln type	Net heat usage (kJ/kg)[a]	Metered electricity usage (kWh/t)
parallel-flow regenerative	3600–4200	18–25
annular shaft	3950–4600	18–35
countercurrent shaft	4200–5000	20–40
preheater rotary	5000–6000	20–45
long rotary	6500–7500	10–15

[a] The heat of dissociation is 3180 kJ/kg CaO.

Table 8. **Lime Production and Chemical–Environmental Usages in Various Countries (2000)**

Country	Chemical %	Environmental %	Production 10^6 tpa
China			21.5
USA	9	3	19.6
Russia			8.0
Japan	24	9	7.7
Germany	6	14	7.6
Mexico	11	4	6.5
Brazil			5.7
Italy	1.5	13	3.5
Korea	18	4	3
Canada			2.6
Poland			2.5
United Kingdom	15	15	2.5
France	2	1	2.4
Iran			2.2
Austria			2.0
Belgium	3	6	1.8
Romania			1.7
Australia	3	6	1.5
Colombia			1.3
South Africa	12	7	1.3
Czech Republic	4	16	1.2
Bulgaria			1.1
Turkey	12	2	1.1
Chile			1.0
Spain	4	1	1.0
World total (est.)			*116*

Table 9. **Main Uses of Lime Products**[a]

- Steel
  - primary
  - secondary

- Chemicals and Food
  - dyestuffs
  - citric acid
  - glue and gelatine
  - medicinal drugs
  - baking powder
  - oil well muds
  - oil and petroleum additives
  - soda ash
  - soda lime
  - caustic soda
  - calcium carbide
  - precipitated calcium carbonate
  - bleaches
  - resins
  - plastics
  - sugar refining
  - toothpaste

  - apple storage

- Industrial Processes
  - non-ferrous metal production
  - wire drawing
  - leather tanning
  - paper and pulp
  - paints, pigments, and varnishes
  - rubber

- Building materials
  - aerated concrete
  - calcium silicate bricks
  - refractories
  - plasterboard
  - alumina cement
  - building adhesives
  - insulation materials

- Building Trade
  - mortars
  - renders
  - plasters
  - soil stabilization

Environmental Protection

water	purification and clarification softening
sewage	treatment disinfection
flue gas	acid gas removal dioxin/furan/heavy metal removal
effluent	acid neutralization heavy metal removal clarification/settling

neutralization of acid mine drainage

- Agriculture
  - pH adjustment/sweetening of soils
  - animal foodstuffs

  - insecticides and fungicides

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[a] The role of lime products in each of these applications is described in (1).

Table 10. **Use of Lime Products in the Main Market Segments (1994)**

Country	Iron & steel %	Non-ferrous metals %	Building trade %[a]	Building materials %[b]	Chemical industry %	Other industry %	Environmental protection %[c]	Agriculture & food %
Belgium	70		7	6	7	1	8	1
Germany	36		12	27	7	2	14	2
France	58	3			4		20	15
Italy	27		65		2		5	1
Japan	54	1	5	2	23	3	9	3
S. Africa	42	30	7		16	4	1	
Turkey	25	1	53	1	12	7	1	
United States	31	7	8		5	24	25	
United Kingdom	55		7	8	5	5	19	1

[a] Mainly mortar, render, plaster, and soil treatment.

[b] Mainly aircrete, sandlime bricks, other calcium silicate products, and refractories.

[c] Mainly potable water, sewage, liquid effluent, and gaseous effluent treatment.

Table 11. **Average Distribution of Open-Market Sales in 24 Countries (1998)**

Market segment	% of Sales
iron and steel	38
non-ferrous metals	5
building trade	16
building materials	9
chemical industry	11
environmental	15
other industry	6

Table 12. **Estimated Sales of Different Categories of Lime in the European Union (1995)**

Category	% of Total lime sales
screened quicklimes - (*A*) plus (*D*)[a]	30
ground calcium quicklimes (*B*)	50
hydrated calcium limes (*C*)	16
dead-burned dolomite products (*D*)	2.5
hydraulic limes (*E*)	1.5

[a] Product (*E*) probably amounted to 5–10% of total sales.

Table 13. **Classification of Building Limes (24)**

Description	Form[a]	Classification
calcium lime 90	Q, H, P	CL 90
calcium lime 90	Q, H, P	CL 80
calcium lime 70	Q, H, P	CL 70
dolomitic lime 85	H	DL 85
dolomitic lime 80	H	DL 80
hydraulic lime 2	H	HL 2
hydraulic lime 3.5	H	HL 3.5
hydraulic lime 5	H	HL 5
natural hydraulic lime 2	H	NHL 2
natural hydraulic lime 3.5	H	NHL 3.5
natural hydraulic lime 5	H	NHL 5

[a] Q = quicklimes, H = hydrated limes, P = putties/milks of lime.

Table 14. **Specifications for Types CL 70, 80, and 90 limes (24)**

Type	CaO + MgO %	MgO %	CO_2 %	SO_3[a] %	Soundness[b]	Yield[c] dm^3	Fineness[d] %
CL 90	≥ 90	≤ 5[e]	≤ 4	≤ 2	pass	≥ 26	≤ 7
CL 80	≥ 80	≤ 5	≤ 7	≤ 2	pass	≥ 26	≤ 7
CL 70	≥ 70	≤ 5	≤ 12	≤ 2	pass	≥ 26	≤ 7

[a] The SO_3 of content of $>3\%$ and up to 7% is permissible if soundness is demonstrated at 28 days of water curing using a test given in EN 192.

[b] In accordance with clause 5.9 of EN 459-1 (24).

[c] For quicklimes only, in accordance with clause 5.9 of EN 459-2 (24).

[d] For hydrated limes only, % by mass retained on 0.09-mm sieve, in accordance with clause 5.2 of EN 459-2 (24).

[e] The MgO content of up to 7% is acceptable, if a soundness test in EN 459-2 (24) is passed. (*Note*: For quicklimes, the values correspond to the finished product. For all other kinds of lime, the values refer to the mass of product after removal of bound and free water.)

Table 15. **Typical BOS Specification for High Calcium Quicklime**

Parameter	Criterion	Level
neutralizing value (as CaO)	average	$>95.0\%$
	minimum	93.00%
SiO_2	average	$<1.0\%$
	maximum	1.50%
MgO	average	$<1.5\%$
S	average	$<0.03\%$
	maximum	0.04%
loss on ignition (due to CO_2)	maximum	2.5%
reactivity (BS 6463: 1987, 2 min)	minimum	46°C
Grading (ex works)	>44 mm	0%
	$-44+38$ mm	$<10\%$
	$-38+12$ mm	$>75\%$
	$-12+6$ mm	$<10\%$
	<6 mm	$<5\%$

Table 16. **Typical BOS Specification for Light-Burned Dolomite**

Parameter	Level
CaO	54–63%
MgO	34–43%
SiO_2	$\leq$2.0%
S	$\leq$0.06%
“reactivity”	“soft-burned”
passing 5 mm	$\leq$15%

Table 17. **Some Chemical- and Food-Related Specifications**

Application	Typical requirement
sugar refining	<2 mg/kg As
precipitated $CaCO_3$	low MgO, SiO_2, Al_2O_3, Fe_2O_3
calcium phosphates and food-grade chemicals[a]	<7 mg/kg As, <13 mg/kg Pb, <75 mg/kg Zn, <130 mg/kg (Cu + Zn), <75 mg/kg F <70 mg/kg heavy metals (as Pb),
MgO and $Mg(OH)_2$	$<0.2\%$ residual CO_2
glass	$<0.1–0.2\%$ Fe_2O_3 for optical and $<0.5\%$ for standard glass
calcium aluminate cement	low SiO_2 and Fe_2O_3

[a] For example, calcium citrate, lactate, and tartrate.

Table 18. **High Calcium Lime for Use in Water Treatment: Major and Minor Components and Grading (35)**

Parameter[a]	Form of lime[b]	Type 1[c]	Type 2[c]	Type 3[c]
% CaO[d]	G, L	$\geq$87	$\geq$84	$\geq$80
% $Ca(OH)_2$[d]	H, M	$\geq$92	$\geq$87	$\geq$83
% SiO_2	all	$\leq$2.0	$\leq$3.0	$\leq$4.0
% Al_2O_3	all	$\leq$0.5	$\leq$1.0	$\leq$2.0
% Fe_2O_3	all	$\leq$0.5	$\leq$1.0	$\leq$1.5
% MnO_2	all	$\leq$0.15	$\leq$0.4	$\leq$0.5
% $CaCO_3$	all	$\leq$7.0	$\leq$8.0	$\leq$9.0
% >600 μm	G, H, M	$\leq$0.1	$\leq$0.1	$\leq$0.1
% >90 μm	G	$\leq$7.0	$\leq$7.0	$\leq$7.0
% >90 μm	H, M	$\leq$5.5	$\leq$5.5	$\leq$5.5

[a] Test methods are specified in EN 12485 (65).

[b] G = pulverised quicklime; L = granular quicklime; H = hydrated lime; M = milk of lime.

[c] % values are by mass.

[d] The % CaO and % $Ca(OH)_2$ levels refer to the water-soluble values.

Table 19. **High Calcium Lime for Use in Water Treatment: Toxic Substances (35)**

	Upper Limits	
Parameter	Type A mg/kg	Type B mg/kg
antimony	4	4
arsenic	5	20
cadmium	2	2
chromium	20	20
lead	25	50
mercury	0.3	0.5
nickel	20	20
selenium	4	4