LIME, CALCIUM, AND CALCIUM COMPOUNDS

By Avery H. Reed [1]

Lime is a manufactured product made by calcining limestone or other high-calcium materials. It is never found in a natural state. It is a basic chemical that is used for many purposes and produced all over the world.

The term "lime" is used to describe several phases of the same material. Quicklime is calcium oxide, CaO, with no water of crystallization. Hydrate is hydrated calcium oxide, $Ca(OH)_2$, with 24 percent combined water. Dead-burned lime is calcium oxide, CaO, which has been calcined at a higher temperature. Refractory lime is another name for dead-burned lime. All of these products are called lime. Crushed stone used in agriculture, aglime, is locally called lime.

The United States is one of the leading lime-producing countries, accounting for 18 percent of the world output. In 1974, lime production was a record 21.6 million tons, valued at $476.6 million.

Calcium metal is manufactured in the United States by one company, in Connecticut.

Calcium combines with other elements in many valuable calcium compounds. Calcium fluoride, calcium sulfate, calcium phosphate, and calcium carbonate are discussed in the Fluorine, Gypsum, Phosphate Rock, and Stone chapters, respectively. This chapter includes calcium chloride and other compounds.

INDUSTRY STRUCTURE

Background

Lime has been used since earliest recorded history. Primitive man learned to prepare plaster and mortar. Sandlime mortar was used throughout the Egyptian, Greek, and Roman civilizations, and has persisted ever since.

The industrial revolution required large quantities of lime for use as a chemical reagent in many industrial processes. The building industry required lime for mortar and plaster.

In the United States, the manufacture of lime started in colonial times. Small limekilns were constructed all over the eastern part of the country. The mortar made in colonial times may be seen in the old historic buildings of the period.

As the country developed, large limekilns were built to provide lime for many different uses. As the United States grows, so grows the lime industry.

Organization

The domestic lime industry is a large, well-integrated industry, with large plants all over the country. Most of the lime is made and sold by commercial producers. Some of the large users of lime make their own lime. The lime producers generally mine their own materials.

Leading companies were Marblehead Lime Co., Mississippi Lime Co., Bethlehem Steel Corp., Allied Chemical Corp., Martin-Marietta Chemicals, U.S. Gypsum Co., United States Steel Co., Dow Chemical Co., Diamond Shamrock Chemical Co., and Pfizer, Inc. These 10 companies accounted for 41 percent of the total lime production.

Geographic Distribution

The lime industry is worldwide, with production principally at industrial centers. The United States is the second-leading lime-producing country, with 18 percent of the world total. Other leading countries were the U.S.S.R. (20 percent), Japan (10 percent), West Germany (10 percent), Poland (7 percent), and France (5 percent).

In the United States, lime was produced in 41 States. Production is largely centered around two areas—the Great Lakes region, and the Gulf Coast area. Leading States were Ohio, Pennsylvania, Missouri, Texas, and Michigan. These five States accounted for 53 percent of the total lime output.

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Lime was consumed in every State. Leading consuming States were Ohio, Pennsylvania, Indiana, Texas, Michigan, Illinois, and New York. These seven States used 63 percent of the total lime consumed.

Definitions

All lime is produced from some form of the mineral calcite, $CaCO_3$, or the mineral dolomite, $CaCO_3 \cdot MgCO_3$. The commonest form of calcite used is limestone, although oyster shell, marble, aragonite, or coral may be used.

When calcite is heated to about 2,000° F, it breaks down into quicklime and carbon dioxide. The carbon dioxide, CO_2, goes off as a gas, and the quicklime, CaO, remains. If the temperature were raised to 3,000° F, the quicklime is "deadburned," no longer reactive with water, and very refractory. Dolomite is usually used to produce refractories.

Quicklime reacts with water to produce hydrate $CaO \cdot H_2O$, or $Ca(OH)_2$. Hydrate absorbs carbon dioxide from the air and returns to calcium carbonate. Thus, the process is reversible: calcite plus heat = quicklime, plus water = hydrate, plus air = calcite. Or, $CaCO_3$ + heat = CaO; + H_2O = $Ca(OH)_2$; + CO_2 = $CaCO_3$. This process is demonstrated by the gradual hardening of plaster.

Hydrate, or calcium hydroxide, the dry, white powder, may be used as a paste or putty, as a slurry, or as "milk of lime." Hydration is the process of controlled rapid addition of water. Hydrate may be "regenerated" by drying and heating, to produce quicklime again. The calcium carbonate sludge or byproduct from chemical plants may be regenerated to produce quicklime.

USES

Lime was consumed in every State in 1974. Leading consuming States were Ohio, Pennsylvania, Indiana, Texas, Michigan, and Illinois. These six States, each of which consumed more than 1 million tons, accounted for 58 percent of the total lime consumed.

Leading quicklime-consuming States were Ohio, Pennsylvania, Indiana, Michigan, Texas, and Illinois. These six States consumed more than 1 million tons each and accounted for 59 percent of the total quicklime consumed.

Leading hydrate-consuming States were Texas, Pennsylvania, Ohio, Illinois, and Louisiana, each of which consumed more than 100,000 tons. These five States accounted for 52 percent of the total hydrate consumed.

Table 1.—World Lime production and capacity, 1973

(Thousand short tons)

	Production	Capacity
North America:		
Canada	1,891	2,000
United States	21,132	25,000
Other	379	500
Total	23,402	27,500
South America:		
Brazil	2,200	2,500
Colombia	1,100	1,500
Other	92	100
Total	3,392	4,100
Europe:		
Austria	874	1,100
Belgium	3,770	4,000
Bulgaria	1,026	1,100
Czechoslovakia	2,904	3,000
France	5,461	6,000
Germany, East	3,339	4,000
Germany, West	12,386	14,000
Italy	2,478	5,000
Poland	8,483	9,000
Romania	2,858	3,000
U.S.S.R.	24,000	25,000
Yugoslavia	2,061	1,200
Other	3,197	5,000
Total	72,837	81,400
Africa:		
South Africa, Republic of	1,460	1,500
Other	772	800
Total	2,232	2,300
Asia:		
Japan	13,024	15,000
Iran	1,100	1,200
Other	1,357	1,400
Total	15,481	17,600
Oceania	853	600
Grand total	118,197	133,500

Lime sold by producers was used for chemicals (81 percent), construction (10 percent), refractories (8 percent), and agriculture (1 percent). Captive lime used by producers was 32 percent of the total, compared with 32 percent in 1973 and 34 percent in 1972. Captive lime was used mainly for alkalies, (37 percent), BOF steel furnaces (24 percent), and sugar refining (10 percent).

Leading individual uses were BOF steel furnaces, alkalies, water purification, refractories, and paper and pulp, which together accounted for 63 percent of the total consumption.

Lime for chemical and industrial use increased 4 percent to a record 18.8 million tons. Lime for refractory dolomite increased 2 percent. Lime for construction decreased 9 percent, and lime used in agriculture declined 22 percent.

Leading States for finishing lime were Ohio (41 percent), Nevada (23 percent), and Missouri (18 percent). The leading States for mason lime were Pennsylvania (21 percent), Wisconsin, and Ohio (13 percent). Lime for soil stabilization was used in Texas, which consumed 68 percent of the total, and other States.

Leading States for lime used in agriculture were Pennsylvania (34 percent), Maryland (21 percent), and Virginia (11 percent). Dead-burned dolomite was used in Ohio (58 percent), Pennsylvania (17 percent), Illinois (10 percent), and other States.

Of the main chemical and industrial uses, lime for BOF steel furnaces was consumed in Ohio (27 percent), Indiana (14 percent), Pennsylvania (14 percent), Illinois (10 percent), and other States. Lime for alkalies was used in Michigan (24 percent), New York (23 percent), Louisiana (19 percent), and other States. Lime for water purification was used in Missouri (31 percent), Pennsylvania (16 percent), Texas (8 percent), Alabama (7 percent), and other States. Lime used for paper and pulp, excluding regenerated lime, was consumed in Alabama (36 percent), Texas (14 percent), Virginia (10 percent), and other States. Lime for electric steel mills was used in Missouri (16 percent), Texas (14 percent), Pennsylvania (14 percent), Ohio (12 percent), and other States.

RESERVES-RESOURCES

Lime is made from a variety of calcareous materials, such as limestone, marble, dolomite, shell, coral, aragonite, or byproduct sludge from paper mills, carbide plants, or other industrial plants.

Resources of these materials are plentiful all over the world in vast deposits.

TECHNOLOGY

Lime is a manufactured product prepared by calcining limestone or other calcareous material. Calcining is performed in rotary kilns, vertical or shaft kilns, rotary hearth or "calcimatic" kilns, or fluosolids kilns.

More than three-quarters of all lime output in the United States is produced in rotary kilns. This is a long, horizontal, rotating cylinder, with raw material entering at one end and fuel at the other. The stone, $CaCO_3$, is heated to about 2,000° F and the carbon dioxide, CO_2, is driven off as a gas with the stack gas. The solid product, quicklime, CaO, is recovered at the end of the kiln.

Vertical kilns are short, wide, vertical cylinders lined with refractory materials. Stone and fuels are fed in at the top and quicklime is drawn off at the bottom.

Calcimatic kilns use a slowly revolving hearth. Stone is placed on the hearth and rotated through a heating chamber.

In the fluosolids kiln, fine-sized stone is dropped through or suspended in a vertical heated chamber.

The quicklime produced in these kilns may either be hydrated or marketed as quicklime. Hydrate is produced as a dry, white powder by adding water slowly to ground quicklime in a vessel known as a hydrator, which mixes and agitates the lime and water.

SUPPLY-DEMAND RELATIONSHIPS

World output of lime in 1974 increased 3 percent to 121.6 million tons. Domestic production increased 2 percent to 21.6 million tons. The United States produced 18 percent of the total.

World production of lime has ranged from 83.1 to 121.6 million tons and averaged 102.1 million tons during the last 10 years. Domestic output during the same period has ranged from 16.8 to 21.6 million tons and averaged 19.4 million tons. During the last decade the United States averaged 19 percent of the world production.

Imports of lime during the last 10 years, mainly from Canada, ranged from 73,000 to 416,000 tons and averaged 221,000 tons. Imports averaged 1 percent of domestic supply. Lime exports averaged only 50,000 tons per year.

BYPRODUCTS AND COPRODUCTS

Some plants recover and use carbon dioxide as a byproduct from a limekiln. Most of these are at sugar plants.

ECONOMIC FACTORS AND PROBLEMS

Raw materials used for lime manufacture are relatively cheap. Limestone is valued at only $1.60 per ton at the quarry. However, the cost of processing is high, and the value of quicklime is relatively high.

Lime requires more energy input per ton than most other industrial materials. Each ton of quicklime requires about 7 million Btu's, which costs about $3.20 per ton of lime. Coal supplies about half and natural gas about half of the energy used in calcining limestone to quicklime.

Transportation is a big factor in the cost of lime, and determines the location of the limekilns.

Table 2.—Lime supply-demand relationships, 1965–74

(Thousand short tons)

	1964	1965	1966	1967	1968	1969	1970	1971	1972	1973	1974
World production:											
United States	16,089	16,794	18,057	17,985	18,637	20,209	19,747	19,591	20,290	21,132	21,645
Rest of world	64,515	66,389	68,013	71,761	75,373	79,087	86,921	90,198	92,233	97,065	99,995
Total	80,604	83,183	86,070	89,746	94,010	99,296	106,668	109,789	112,523	118,197	121,640
Components of U.S. supply:											
Domestic production	16,089	16,794	18,057	17,985	18,637	20,209	19,747	19,591	20,290	21,132	21,645
Imports	123	276	152	81	73	184	202	242	248	334	416
Industry stocks, Jan. 1	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Total U.S. supply	17,212	18,070	19,209	19,066	19,710	21,393	20,949	20,833	21,538	22,466	23,061
Distribution of U.S. supply:											
Industry stocks, Dec. 31	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000	1,000
Exports	30	40	60	52	69	51	54	66	38	37	32
Industrial demand	16,182	17,030	18,149	18,014	18,641	20,342	19,895	19,767	20,500	21,429	22,029
U.S. demand pattern:											
Chemical and industrial	12,333	13,160	14,245	14,527	15,173	16,764	16,870	17,181	17,702	18,428	19,180
Construction	1,481	1,477	1,512	1,433	1,422	1,532	1,510	1,499	1,586	1,611	1,463
Refractory	2,168	2,176	2,193	1,880	1,833	1,866	1,373	1,007	1,075	1,250	1,277
Agriculture	200	217	199	174	213	180	142	80	137	140	109
Total U.S. demand	16,182	17,030	18,149	18,014	18,641	20,342	19,895	19,767	20,500	21,429	22,029

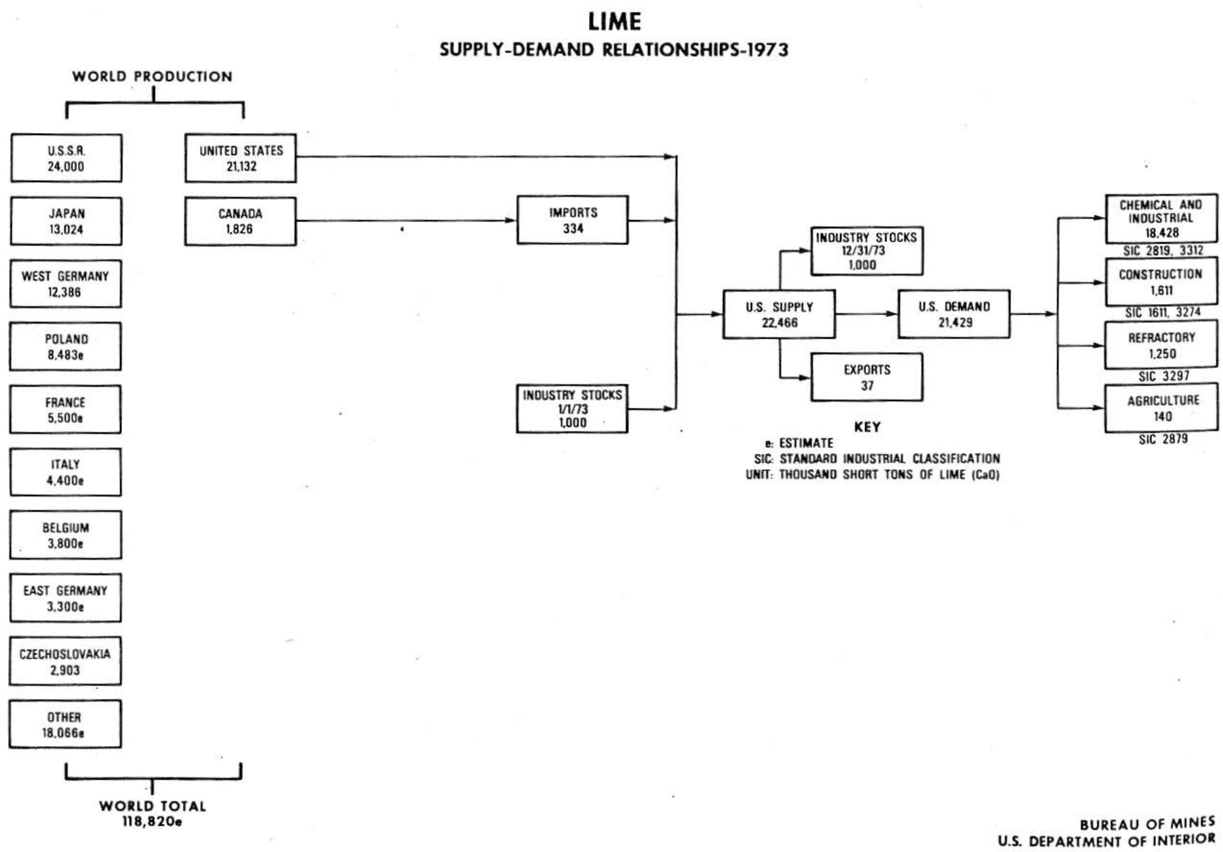

Figure 1.—Supply-demand relationships for lime, 1973.

The average value per ton of lime has increased 82 percent in the last 20 years, from $12.13 to $22.02. In the last 10 years, the average value has gone up 59 percent. The value of hydrated lime averages about $3 more per ton than quicklime. Also, the value of dead-

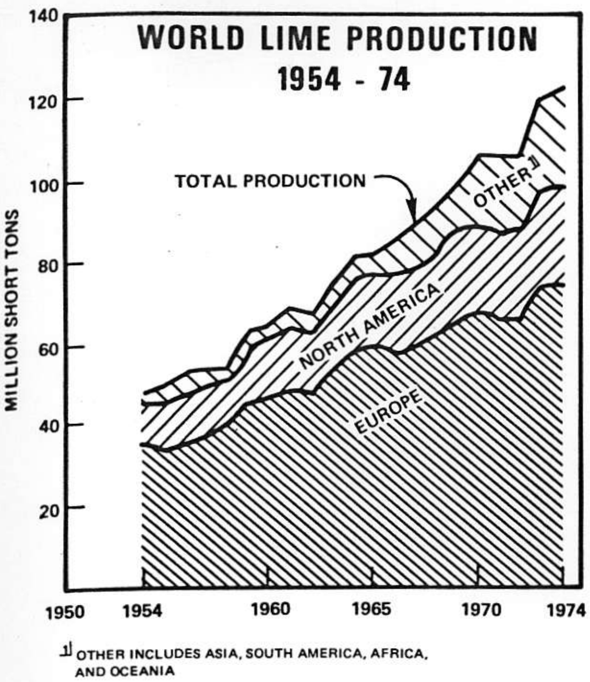

Figure 2.—World lime production 1954–74.

burned refractory lime averages about $4 more per ton than other quicklime.

In recent years, many limekilns have closed rather than install expensive antipollution equipment. Other plants, especially new ones, have complied with air pollution regulations.

OUTLOOK

Demand

The U.S. demand for lime in 2000 is estimated at 32,200,000 tons to 44,600,000 tons, with a probable demand of 43,300,000 tons, an annual growth rate of 2.6 percent.

In the rest of the world, demand should parallel the conditions in the United States, and a comparable rate of growth of lime demand is forecast. Accordingly, rest-of-world demand in 2000 is forecast to range from 146 million tons to 203 million tons, with a probable demand of 196 million tons for an annual growth rate of 2.6 percent.

Forecasts of United States and rest-of-world demand for lime in 1985 and 2000 are summarized in table 4. Forecasts of domestic demand by end use are summarized in table 5.

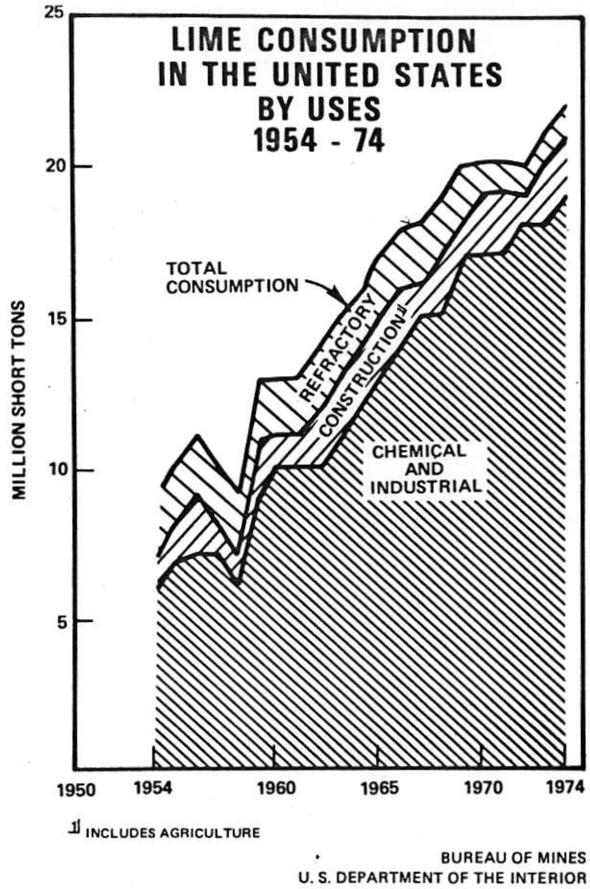

Figure 3.—Lime consumption in the United States by use, 1954–74.

Table 3.—Time-price relationship for lime

Year	Average annual price, dollars per short ton	
	Actual prices	Constant 1973 dollars
1955	12.13	20.59
1956	12.83	21.07
1957	13.17	20.84
1958	13.16	20.31
1959	13.13	19.92
1960	13.35	19.96
1961	13.39	19.75
1962	13.58	19.80
1963	13.73	19.75
1964	13.87	19.67
1965	13.87	19.32
1966	13.27	17.98
1967	13.42	17.61
1968	13.39	16.88
1969	13.94	16.78
1970	14.53	16.59
1971	15.78	17.23
1972	16.78	17.72
1973	17.42	17.42
1974	22.02	19.97
1975	24.30	22.04

Chemical and Industrial.—The forecast base of 35.8 million tons was derived by relating chemi-

Table 4.—Summary of forecasts of U.S. and rest-of-world lime demand, 1973–2000

(Thousand short tons)

	1973	2000 Forecast range		Probable		Probable average annual growth rate 1973–2000, percent
		Low	High	1985	2000	
United States:						
Total	21,429	32,200	44,600	29,300	43,300	2.6
Cumulative	----	719,000	865,000	306,000	849,000	----
Rest of the world:						
Total	97,391	146,000	203,000	133,000	196,000	2.6
Cumulative	----	3,270,000	3,930,000	1,390,000	3,860,000	----
World:						
Total	118,820	178,200	247,600	162,300	239,300	2.6
Cumulative	----	3,989,000	4,795,000	1,696,000	4,709,000	----

Table 5.—Projections and forecasts for U.S. lime demand by end use, 1973 and 2000

(Thousand short tons)

End use	1973	2000 Contingency forecasts for United States: Forecast base	Forecast range: Low	Forecast range: High	Probable
Chemical and industrial	18,428	35,760	30,000	40,000	40,000
Construction	1,611	2,430	2,000	4,000	3,000
Refractory	1,250	420	100	400	200
Agriculture	140	70	100	200	100
Total	21,429	----	32,200	44,600	43,300

cal and industrial lime demand to population growth. However, growth of the use of lime in steel mills has expanded at a higher rate than population, and a high forecast of 40.0 million tons is projected. A low forecast of 30.0 million tons is based on the possible use of substitutes and to the development of new metallurgical processes that may require less lime. Because of the potential growth of lime use in new processes such as sulfur removal from air and water pollutants, the probable demand is selected as the high, 40.0 million tons.

Construction.—The 1973 demand for lime in construction was related to the growth rate of new construction to obtain a forecast base of 2.4 million tons. However, the use of lime for plaster and mortar has been steadily declining. Lime for soil stabilization has shown increasing growth. Balancing these factors, the forecast range is projected at 2.0 to 4.0 million tons. Probable demand is estimated to lie between, at 3.0 million tons.

Refractory.—Demand for refractory dolomite has been steadily declining due to the phasing out of the open-hearth steel furnace. By the year 2000, most of these furnaces will be closed. Thus the forecast range is projected at 100,000 to 400,000 tons, and the probable demand is estimated at 200,000 tons.

Agriculture.—The use of lime in agriculture has not increased substantially. Since crushed limestone is so much cheaper, the use of lime has actually decreased. The demand for lime for agriculture in 2000 is expected to range between 100,000 and 200,000 and average 100,000 tons.

Supply

Supplies of materials for lime manufacture are virtually unlimited throughout the world. In the United States, supplies are more than adequate for any cumulative requirements to 2000.

Possible Supply-Demand Changes.—Domestic production of lime in 1973 was 21,132,000 tons. The total U.S. demand for lime in 1973 was 21,429,000 tons. Therefore, domestic production supplied 99 percent of the total U.S. demand.

The probable demand for lime in 2000 is forecast at 43.3 million tons. If the present percentage met from domestic sources prevails at that time, U.S. lime output in 2000 would be 42.9 million tons.

For speculative purposes, table 6 compares this sum to the quantity of domestic production in 2000 as derived from a projection of the historical trend. A straight-line projection of production during the past 20 years suggests

Table 6.—Comparison of domestic lime production and demand 1954–74, 1985, and 2000

(Thousand short tons)

Year	U.S. demand	Domestic production	
1954	8,592	8,629	
1955	10,438	10,480	
1956	10,536	10,577	
1957	10,259	10,274	
1958	9,191	9,211	
1959	12,482	12,500	
1960	12,906	12,935	
1961	13,256	13,249	
1962	13,811	13,753	
1963	14,605	14,521	
1964	16,182	16,089	
1965	17,030	16,794	
1966	18,149	18,057	
1967	18,014	17,985	
1968	18,641	18,637	
1969	20,342	20,209	
1970	19,895	19,747	
1971	19,767	19,591	
1972	20,500	20,290	
1973	21,429	21,132	
1974 [1]	22,029	21,645	
1985	[2] 29,300	[3] 29,927	[e] 29,000
2000	[2] 43,300	[3] 40,179	[e] 43,000

[e] Estimated.
[1] Preliminary, not used in forecasts.
[2] Probable forecasts from table 4.
[3] 20-year trend.

that lime output in 2000 would be 40.2 million tons.

Cumulative domestic requirements for lime, 1973–2000, will probably be 849 million tons. Domestic reserves of limestone are ample to meet this projected demand.

Little change is foreseen in world lime supply-demand relationships beyond 2000.

CALCIUM

Calcium metal is produced at four plants, one in Canada, one in France, one in the U.S.S.R., and one at Canaan, Conn.

Although calcium is the fifth most abundant element, with more than 3 percent of the earth's crust, it is never in a natural state. It is widely distributed in nature as calcium carbonate, chalk, marble, gypsum, fluorspar, and phosphate rock, and as a part of other rocks and minerals.

Chromasco Corp., at Renfrew, Ontario; Plant-Wattohm S.A. in France; and Pfizer, Inc., in Connecticut produce calcium by a thermal reduction method called the "Pidgeon process." To make calcium metal, high-purity quicklime and commercially pure aluminum powder are briquetted and charged into horizontal retorts made of chrome nickel steel. Under vacuum, at a temperature of about 1,200° C, the aluminum reduces the quicklime to form an aluminum oxide slag and calcium vapor. This vapor crystallizes at about 700° C in the condenser section of the retort, which projects outside the furnace wall.

Developments in atomic power and reactor technology have created a demand for rare refractory metals such as beryllium, zirconium, titanium, and tantalum. These metals are separated from their compounds by reduction with calcium. Calcium is also used as a reducing agent in ferrous metallurgy and in the metallurgy of uranium and thorium. As a purifier, calcium removes sulfur, phosphorus, and oxygen from steel, and removes bismuth, antimony, and arsenic from lead. A new and increasing use is in the new solid-state storage battery that never needs more water.

At Canaan, Conn., Pfizer purchased a surplus magnesium metal plant from the Government and converted it to make calcium metal, using the same equipment and the same process. The high-purity limestone for the calcium source is produced by Pfizer in Adams County, Mass. The calcium metal is cut to various sizes and sealed in 55-gallon steel drums. Because calcium reacts explosively with water, releasing hydrogen which ignites, these drums require special handling in shipping. Pfizer supplies customers all over the country with calcium metal. Production figures are confidential.

CALCIUM COMPOUNDS

Calcium combines readily with many other elements to form useful compounds. Some of these are found in their natural state, but many others are manufactured, frequently as byproducts.

Calcium chloride was produced in California from dry lake beds, and in Michigan from brine wells. Synthetic calcium chloride was recovered as a byproduct in New York, Ohio, and Washington. The calcium chloride was used to melt snow and ice from streets, to keep down dust on roads, and as an accelerator in concrete.

Many other calcium compounds were produced or imported, including the following: calcium nitrate, whiting, calcium borate, calcium carbide, calcium cyanide, calcium cyanamid, precipitated calcium carbonate, dicalcium phosphate, calcium hypochlorite, and chlorinated lime.

SOURCES OF CURRENT INFORMATION

U.S. Bureau of Mines publications:

Lime. Ch. in Commodity Data Summaries, annual.
Lime. Ch. in Minerals Yearbook, annual.
Lime. Reported monthly in Mineral Industry Surveys.

Other sources:

Rock Products.
Pit and Quarry.
Company annual reports.
Engineering and Mining Journal.

92 GNW 001 – Middle Point ~ McNaughton Point

Comments: crystalline limestone (8 Km s. of Pender Harbour) few small contorted and faulted beds, which are lenticular + pinch out along strike. The Limestone is closely associated with finely banded siliceous schists.

BCDM Bull 40-97

092 GNW 002 – Salmon Inlet

large body white crystalline limestone is about 2.4 km. up Thornhill Creek which flows into Salmon Inlet (a branch of Jervis Inlet) from the south 12.8 km. east of the arm.

BCDM. Bull 40-97

092 GNW 031 – Penninsula Lime

Limestone + Dolomite are interbedded with meta-sedimentary + metavolcanic rock possibly of the Jervis GP which form a pendant in quartz diorite

BCDM Ann 1971-254

092 GSW 002 Sechelt

Diorite was quarried for dimension stone

BCDM Min 1963 - 139
1964 - 1

092 GSW 008 L+H Swanson Quarry

quarry is on top of rounded knoll of medium to coarse grained light grey ~~granit~~ granodiorite the composition of the rock was essentially quartz and oligoclase + andesine with lesser orthoclase, biotite + hornblende. Similar rock seems to underlie much of the surrounding area.

BCDM 1970 p 492/1 Min

092GSW009 Canada Cement Ltd
" Lafarge Cement Ltd

BCDM 1970 p. 495
1971 p. 459/1/Gem