Calcium Oxide

APR 5 2002

Crops

Executive Summary

Calcium oxide was petitioned for use as a soil amendment to supply calcium for crops. Calcium oxide is produced by burning various forms of calcium carbonate such as limestone, marble, chalk, oyster shells, and dolomite. It may also be produced as a by-product of industrial processes such as cement production.

The NOSB refined the definition of synthetic in 1995 and considered the combustion of minerals synthetic. Although the NOSB approved use of calcium hydroxide as a component of Bordeaux mix and lime sulfur for fungicide use, it did not approve use as a soil amendment.

Reviewers all agreed that calcium oxide is a synthetic material. Two of the reviewers support continued prohibition, due to availability of non-synthetic alternatives, concerns about worker safety, effect on soil microorganisms, and possible contaminants. One reviewer supports allowance with restrictions on formulated products, but did not provide any support for validity of these measurements, which were found to be without basis by a research chemist.

Summary of TAP Reviewer's Analyses[1]

Synthetic/ Nonsynthetic	*Allow without restrictions?*	*Allow only with restrictions? (See Reviewers' comments for restrictions)*
Synthetic (3) Nonsynthetic (0)	Yes (0) No (3)	Yes (1) No (2)

Identification

Chemical Names: Calcium oxide, CaO

Other Names:
Lime, burnt lime, burned lime, quicklime, calcium monoxide; pebble lime; unslaked lime; fluxing lime; Calcia.

CAS Number: 1305-78-8

Other Codes:
RTECS EW3100000
ICSC 0409
DOT-UN 1910
EPA PC Code: 075604

Characterization

Composition: 99.9% CaO, Ca 71.47%, O 28.53% . Properly stored commercial lime is 90-95% free CaO (Budavari, 1986). The molecular weight is 56.0794.

Properties:
It is white or gray, odorless lumps or powder, the melting point is 2572 °C, the boiling point is 2850 °C, and it readily absorbs oxygen and water from the air. It is soluble in water, forming calcium hydroxide and generating heat. Contact with water or moisture may generate enough heat to ignite nearby combustible materials. Calcium oxide is a strong caustic (Budavari, 1986; Hardy, 2001; NJDH, 1996).

How Made:
Calcium oxide is produced by burning (calcining) various forms of calcium carbonate such as limestone, marble, chalk, oyster shells, and dolomite. Lime burning was one of the first industries in the American colonies, in kilns dug out of the sides of hills. Stone age kilns used for burning lime have been discovered, and lime plaster in good condition is found on

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[1] *This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act to the best of the investigator's ability, and has been reviewed by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA [7 USC 6517(m)]. The information and advice presented to the NOSB is based on the technical evaluation against that criteria, and does not incorporate commercial availability, socio-economic impact, or other factors that the NOSB and the USDA may want to consider in making decisions.*

Egyptian pyramids that are 4500 years old. The Greeks, Romans, Etruscans, Arabians, and Moors used lime plaster and mortar extensively in construction (Kirk-Othmer, 1991b).

The term "lime" is technically used only for burned forms of limestone such as quicklime or hydrated lime. However, the term is often broadly used to refer to limestone, which is primarily composed of calcium carbonate, but also may contain various amounts of magnesium carbonate. Other impurities are silica, iron, and aluminum. Limestone is classified by origin, chemical composition, texture, and geographical formation. Different sources of limestone used to produce quicklime result in different grades of purity of the calcium oxide product.

Limestone is quarried (usually in open pits), crushed, and screened. Dust control is a major environmental problem, requiring management from point sources and suppression at multiple points. The stone is then heated in kilns; typically a coal-fired rotary type in the US. The stone must be heated to the dissociation temperature of the carbonates, which is maintained for a certain duration while the carbon dioxide evolved must be rapidly removed. The reversible reaction is:

$$\underset{\text{high calcium limestone}}{CaCO_3} + \text{heat} \leftrightarrow \underset{\text{high calcium quicklime}}{CaO} + CO_2$$

It takes approximately two tons of stone to produce one ton of quicklime, due to impurities and loss from dust. Energy requirements are high, from 5.5- 8 million Btus per short ton, depending on age and capacity of the kiln (Kirk-Othmer, 1991b).

__Specific Uses__:
More than 90% of the lime (burned or hydrated) produced in the United States is used for basic or industrial chemistry. The primary use is for steel manufacture (30%), metallurgy, air pollution control and water and sewage wastewater treatment (24%), cement and mortar, chemical manufacture, manufacture of glass and paper, diluents and carriers of pesticides such as lime-sulfur and Bordeaux mixture, and bleach production and other chemical manufacture (Kirk-Othmer 1991a, b; Budavari, 1986). Beet sugar refineries typically operate on-site lime kilns to provide both calcium oxide and carbon dioxide for the refining process, while cane sugar refining uses quicklime at a lesser rate (Kirk-Othmer, 1991b).

Calcium oxide or calcium hydroxide is used as liming materials for agricultural use, particularly when a rapid change in pH is desired. Calcium oxide may be difficult to use directly, as it immediately absorbs water after soil application, causing it to form flakes or granules that may harden due to re-formation of calcium carbonate. Caking can only be prevented by very thorough mixing when applied (Tisdale, 1985). Calcium oxide is pound for pound the most effective of commonly used liming materials, with a neutralizing value (calcium carbonate equivalent-CCE) of 179%for the pure material. Pure calcitic limestone has a rating of 100%, however most agricultural limestone rate the CCE as 90-95% because of impurities (Tisdale, 1985). More than 90% of the agricultural lime used in the US is calcium carbonate, next is magnesium-calcium carbonates (dolomitic limestone), and a much smaller percentage is calcium oxide or hydroxide (Miller, 1990). This is due to higher cost, lack of stability, caustic nature, and difficulty in handling (Miller, 1990; Parnes, 1990; Troeh, 1993; Brady, 1975; Zimmer, 2000). Burned lime may be used instead of limestone in order to minimize weight (Troeh, 1993).

__Action__:
In water, calcium oxide ionizes readily to form Ca^{++} and OH^-, forming a medium strong base or alkali. This effectively neutralizes acid soil solutions, and the calcium cation replaces aluminum on the cation exchange complex. In humid climates, such as the eastern US, most soils are acid due to leaching of soils and gradual depletion of bases in the soil cation exchange complex (Troeh, 1993; Engelstad, 1985). A neutral soil pH is desirable for most crops in order to tie up aluminum and iron, which can be toxic to plants at low pH. Other nutrients such as phosphorous and trace elements are more available at neutral pH (Parnes, 1990). Bacterial conversion of ammonium nitrogen to plant available nitrate forms is also stimulated by increased amounts of exchangeable base cations (Brady, 1975). Biological activity is also improved at neutral pH (Parnes, 1990; Brady, 1974; Pankhurst, 1997). Calcium is also an important plant nutrient, aside from its role in pH modification. Calcium is needed in cell membranes and growing shoots and root tips.

__Combinations__:
Calcium oxide (quicklime) used for agricultural applications is rarely in pure form; more commonly it is found in various combinations depending on the source of the parent material. Other minerals that may be present include magnesium (MgO), silica (SiO_2), iron (Fe_2O_3), and aluminum (AlO_3). "Air-slaked lime" contains a mixture of the oxide, hydroxide and carbonate of calcium or calcium and magnesium, derived from the exposure of quicklime (AAPFCO, 2000). Limestone parent materials may also include clay, in the form of alumina-silicates (Kirk-Othmer, 1991b). Kiln dust is a by-product of cement or burnt lime manufacture and contains calcium oxide and calcium hydroxide as well as some potassium and sulfur (Zimmer, 2000).

Slags are a group of industrial by-product materials and are used for their liming properties. Blast furnace slag is a by-product of pig iron, produced by reduction of iron by calcium carbonate, which produces calcium oxide. This calcium oxide combines the molten silica impurities from the iron to form a calcium silicate ($CaSiO_3$) that is cooled and ground. Another type of slag is know as basic or Thomas slag, and is the product of open hearth steel making from high phosphorus iron ores. Lime (calcium oxide) is used to flux the impurities of silica and phosphorous, and is usually applied for phosphorus content as well as liming qualities. Electric furnace slag is produced when phosphate rock is reduced to produce elemental phosphorous, and calcium oxide and silica fuse to produce a calcium silicate (Tisdale, 1985). Fly ash from coal burning power plants is produced when crushed coal and finely ground limestone are suspended and burned, so that the sulfur in the coal reacts to form gypsum ($CaSO4$). The ash residue is a granular mixture of calcium oxide, calcium sulfate, and small amounts of metal oxides. Other industrial by-products that contain calcium oxide include flue dust from cement manufacturing, pulp mill lime, carbide lime, and by-products from the tanning industry (Tisdale, 1985; AAPFCO, 2000).

Status

Historic Use by Organic Farmers:

Neither calcium oxide nor the related form of calcium hydroxide is generally allowed for fertilizer use in organic farming. The NOSB refined the definition of synthetic in 1995 to declare that, "Heating and combustion of plants, animals, and microorganisms shall not be considered synthetic unless expressly prohibited in the National List. The combustion of minerals shall be considered synthetic and reviewed for compatibility under OFPA Sec 2119(m)(1-7)" (NOSB, 1995c). At the meeting in April 1995, the NOSB approved use of calcium hydroxide as a component of Bordeaux mix and lime sulfur, for fungicide use only (NOSB, 1995a). In November of 1995, NOSB approved use of hydrated lime for livestock with a suggested annotation that: "not permitted for soil application or to cauterize mutilations or deodorize animal wastes" (NOSB, 1995b).

OFPA, USDA Final Rule:

OFPA states in Sec. 6508(b):

"Soil Amendments. For a farm to be certified under this chapter, producers on such farm shall not

1) use any fertilizers containing synthetic ingredients or any commercially blended fertilizers containing materials prohibited under this chapter or under the applicable State organic certification program; or
2) use as a source of nitrogen, phosphorus, lime, or potash or any materials that are inconsistent with the applicable organic certification program."

Calcium oxide is not specifically listed anywhere in the NOP final rule. The NOP rule allows hydrated lime at 205.601(i)(3) and lime sulfur at 205.601(i)(5) for plant disease control. Lime sulfur is also listed as an insecticide at 205.601(e)(4). The NOSB voted in October 2001 that synthetic sources of calcium chloride (non-brine sources) are prohibited for crop use, and that nonsynthetic sources from the brine process may be used only as a foliar spray to treat physiological disorders related to calcium uptake. Calcium hydroxide is listed as an approved synthetic nonagricultural substance allowed as an ingredient in organic processed food at 205.605(b)(6).

Calcium oxide is approved by FDA at 21CFR 582.5210 as a substance Generally Recognized as Safe, and permitted for livestock feed, thus it appears to qualify for organic use as a feed additive under 205.603(d)(1), which allows "Trace minerals, used for enrichment or fortification when FDA approved." Technically speaking, calcium is not usually considered a trace mineral but a macro-mineral (Cheeke, 1999).

Regulatory: EPA/NIEHS/Other Sources

EPA: Office of Pesticide Programs Output reporting shows that of the four formerly active registrations, all uses have been cancelled, including tree wash and several forms of pulverized or pebble quick lime (EPA, 2002).
OSHA: legal airborne permissible exposure limit (PEL) is 5 mg/m^3 over an 8-hour workshift.
NIOSH: airborne exposure limit is 2mg/m^3 over 10 hour workshift.
ACGIH: American Conf. of Governmental Industrial Hygienists: threshold limit value 2mg/m^3.
NFPA (National Fire Protection Association) rates as hazardous chemical: health – 1, slightly hazardous, breathing apparatus recommended, non-flammable, reactivity – 1: normally stable but may react with water.
NTP, IARC: not listed as a known carcinogen.
(Sources: MSDS- Mallinckrodt Baker, 1998; NJDH, 1996; Richardson 1993)

Status Among U.S. Certifiers

US certifiers prohibit the use of calcium oxide and calcium hydroxide as fertilizer. This includes OCIA, Farm Verified Organic, Oregon Tilth, MOSA, CCOF, NOFA chapters, MOFGA, QAI, WSDA, TDA (Texas Dept of Ag.), and New Mexico Organic Commodity Commission.

International

IFOAM Basic Standards 2000 – prohibited since not explicitly listed as approved.

EU 2092/91 – Prohibited, as Annex IIA does not list calcium oxide or calcium hydroxide, though it does list basic slag, and "Industrial Lime from sugar production."

Canadian General Standards 1999 CGSB-32.310-99 – prohibited since not listed

Japanese Agricultural Standards – lists "Calcined lime" to be limited for use in Bordeaux mixture as fungicide.

CODEX – not listed. Does permit basic slag.

Section 2119 OFPA U.S.C. 6518(m)(1-7) Criteria

1. *The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.*

   Liming materials are generally considered benign or beneficial when used to improve the soil pH for agronomic use. The basic effect of limestone to raise pH is due to the reactions:

   $CaCO_3 + H_20 \rightarrow Ca^{++} + HCO_3 + OH^-$

   $OH^- + H^+$ (in soil solution) $\rightarrow H_20$

   The rate of this reaction depends on the amount of hydrogen ions (acidity) of the soil.

   When limestone of medium fineness is added to soil, it results in calcium and magnesium being available in three forms: 1) as solid calcium or magnesium carbonates, 2) as exchangeable bases (Ca^{++}) that are adsorbed onto the soil colloids, or 3) as dissociated cations in the soil solution, mostly in association with bicarbonate ions (Brady, 1974). Use of an oxidized material such as calcium oxide produces a more rapid pH change, as it breaks down directly into calcium ion and the hydroxyl anion. This will favor a more rapid effect on the calcium ions in solution and adsorbed on the soil colloids. Both of these forms are subject to leaching. The reverse reaction is also possible: calcium oxide will readily hydrate in solution to form calcium hydroxide, which reacts with carbon dioxide in the soil to form calcium carbonate and bicarbonate. So, although calcium oxide will affect a rapid pH change, it is not stable and depending on soil conditions may eventually revert to insoluble forms (Brady, 1974; Parnes, 1990). Early studies comparing rates of reaction for different liming materials concluded that while hydrated lime reacted more quickly than high calcium limestone, differences largely disappeared after two months (Metzger, 1933).

   Detrimental effects may occur due to difficulties in mixing, resulting in uneven concentrations, and the possibility of overliming. Excess lime can tie up available nutrients such as manganese, copper, zinc, and phosphorous. It also ties up boron. Rapid pH changes can also affect plants and microorganisms negatively when they cannot adjust quickly. For this reason, a well-buffered soil is considered more desirable (Brady, 1974). Overliming is possible where diverse soil conditions exist within a field, and in sandy conditions that may be deficient in micronutrients that will be further reduced in availability at high pH (Troeh, 1993).

2. *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.*

   Sub-acute toxicity data: for rats: at repeated exposure inhalation at 413 mg/m3 or single exposure of 1026 mg/m3 found no deaths, no marked change in behavior or food intake (Richardson, 1993). It is not classed as a carcinogen by NIEHS/NTP.

   It is reactive in soil, as it rapidly hydrolyses to calcium hydroxide, solubilizes into ionic form, or re-carbonates into calcium carbonate (Tisdale 1985; Brady, 1974). Some potential exists for leaching; this is similar to natural leaching of calcium from the soil complex.

   Both calcium carbonate and calcium hydroxide applications to freshwater lakes suffering from eutrophication resulted in reduction of total phosphorus and macrophyte biomass resulting in improved water quality (Prepas, 2001). Treatments of ponds and canals with relatively high levels of slaked lime (210 mg/l for 65 hours) eliminated aquatic plants a month later. This result could not be reproduced in laboratory studies, and researchers theorized that the decline in biomass was due to short-term rise in pH in warm water, which resulted in low concentrations of free CO2 and bicarbonate for biosynthesis (Chambers, 2001).

3. *The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.*

   Calcium oxide is produced by heating mined calcium carbonate, requiring a large amount of energy. Dust is the major problem that must be closely monitored at various stages of mining and processing (Kirk-Othmer, 1991). Combinations found in by-product sources such as flue ash may be contaminated with iron, copper, lead, or other heavy metals (Stout, 1988; Pichtel and Hayes cited in Pankhurst, 1997).

4. *The effects of the substance on human health.*
Calcium oxide can severely irritate and burn the eyes and skin. Breathing the dust can irritate the lungs, causing coughing and shortness of breath. Higher exposures can cause fluid build-up in lungs and severe shortness of breath. Long-term exposure can irritate the nose, causing a hole in the inner nose, brittle nails, and cracking of the skin (NJDH, 1996). If ingested, it causes a burning sensation, abdominal pain, vomiting, and diarrhea (NIOSH, 1993). Contact with skin or mouth can cause thermal and caustic burns; eye contact causes dangerous clumps in the conjuctival sac (Gosselin, 1984). It can also cause severe irritation to eyes, blurred vision, ulceration, and loss of vision. Fatal burns and deaths from asphyxia have been reported after massive exposure (Richardson, 1993).

5. *The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock.*
Soil pH has a significant effect on the range and composition of soil organisms. Early researchers noted that low pH was injurious to some bacteria, especially the nitrifying bacteria, but favorable to development of fungi (Waksman, 1952). Addition of lime in the form of calcium carbonate was found to stimulate the increase in soil bacteria and increased decomposition of organic matter. Waksman noted that excess calcium carbonate could become injurious to soil bacteria, although no empirical studies were cited.

Earthworm populations are affected by pH, and are mostly absent from soils with extreme pH - over 8 or under 4 (Pankhurst, 1997). The addition of fertilizers such as ammonium salts was found to result in absence of earthworms, but specific comparison of liming materials was not reviewed. Different species of earthworms were found to favor different pH ranges between 5-8. The use of fertilizers is one of many agricultural practices that may have a large impact on population fluctuations of earthworms (Fraser 1994, cited in Pankhurst, 1997).

Use of fly ash as a liming material was found to have a negative impact on dehydrogenase enzyme activity, indicating suppression of overall microbial population. This was attributed to heavy metal contaminants in this material (Pichtel and Hayes, cited in Pankhurst, 1997). Changes in soil pH cause a rapid effect on protozoan populations, which respond positively to lime applications. Nematode populations also increase with liming (Pankhurst, 1997).

The TAP Review document prepared for NOSB in 1995 for hydrated lime states, "In direct soil application, however it would create a strong imbalance of soluble calcium which would negative affect soil microbes and cause rapid oxidation of other soil nutrients" (NOSB, 1995d). While extensive reviews in Pankhurst did not directly consider effect of calcium oxide on microbes, extreme pH levels were found to generally reduce population levels. Other texts note the generally beneficial impact of lime on earthworms and microbes when pH is adjusted to optimal levels (Brady, 1974; Tisdale, 1985). An early study on the impact of limestone applied at different mesh sizes compared to hydrated lime in regards to nitrification rate found that both forms stimulated nitrification, with hydrated forms giving greater results (Walker, 1935).

The petitioner submitted data from experimental work with a proprietary complex containing calcium oxide and calcium hydroxide in combination with other materials to show that this complex did not negatively impact microbial degradation of cotton test strips as compared to a control, limestone application, or burnt lime treatment. Results were highly variable depending on site. Only one of three test sites showed a reduction in degradation rate due to application of burnt lime.

6. *The alternatives to using the substance in terms of practices or other available materials.*
The petitioner requested use of this material not as liming material but as calcium source for crop nutrition (Preston, 2001). Usually calcium deficiencies are associated with low pH soils and soils with a low cation exchanges capacity, such as a leached sandy soil. A standard remedy is to add limestone and build up soil organic matter (Magdoff, 2000). Mined sources can and do provide adequate available calcium to soils and plants in organic farming systems. The principle sources used by organic farmers are limestone, gypsum, and rock (tricalcium) phosphate. Rotations and compost can serve to increase the availability of these amendments. Wood ash and poultry manure also have readily available calcium (Parnes, 1990).

Gypsum (calcium sulfate) is widely used to supply calcium at neutral or higher pH (Tisdale, 1985; Troeh, 1995; Parnes, 1990; Brady, 1974). Gypsum ($CaSO_4$-$2H_20$) has been used as a fertilizer since early Greek and Roman times. Deposits are found at several locations in the US and Canada, and elsewhere in the world (Tisdale, 1985). Gypsum is widely used on saline-sodic soils to replace sodium on the soil colloids with calcium. The sulfur in the gypsum then precipitates with sodium and can be leached out of the soil. Gypsum is not a liming agent and has little effect on soil pH, but also provides sulfur, a necessary plant nutrient (Tisdale, 1985).

In non-organic systems, calcium fertilizers such as superphosphate and triple superphosphate contain 12-18% calcium. Calcium chelated materials may also be applied as foliar sprays.

Normally the large amount of exchangeable calcium on the colloidal complex satisfies the calcium needs of most crops (Mortvedt and Cox in Engelstad, 1985; Troeh, 1995). Some crops have shown calcium deficiency when soil acidity is not a problem; these are usually localized in fruits, storage organs, or shoot tips. Examples include poor kernel formation in peanuts, bitter pit in apples, blossom end rot in tomatoes, tipburn in lettuce, and black heart of celery (Mortvedt, in Engelstadt, 1985). Gypsum applications are effective at supplementing calcium in peanuts (Tisdale, 1985). Foliar applications of calcium chloride are effective when translocation of calcium is a problem to actively growing shoots and fruits (see 2001 TAP review of calcium chloride).

Calcium ions on the soil exchange surfaces are not very mobile, and the plants take up calcium ions more readily from the soil solution (Troeh, 1993). Calcium in solution is in dynamic equilibrium with the exchangeable form, so that when calcium is removed by plants or by leaching, there is replacement by the adsorbed phase (Tisdale, 1985). If there is a sudden addition to calcium in solution, then more adsorption on to the exchange complex can also be expected. Factors determining calcium supply to plants include a number of factors, including total calcium supply, soil ph, CEC, percent calcium saturation of soil colloids, type of soil colloids, and the ratio of calcium to other cations in solution (Tisdale, 1985). A study comparing the effectiveness of different liming materials found that the order of effectiveness in neutralizing acidity was hydrated lime, basic slag, cement kiln dust, and ground limestone. All of these different materials showed increasing response in plant uptake of calcium when applied at increasing rates, based on calcium equivalency, but there was no difference between lime sources (Oguntoyinbo, 1996). Another study comparing liming materials found that efficiency increased with decreased Mg content and that silicates were less effective than carbonates or oxides. Efficiency of carbonate forms increases with fineness of grinding (Gutser, 1987).

Limestone fineness directly affects the rate of solubility of calcium cations (Brady, 1974; Miller, 1990). Where a rapid pH change is desired, use of a more finely ground limestone will effect a quicker change. Limestone can be evaluated for effective calcium carbonate equivalent (ECCE) or effective neutralizing value (ENV) based on a formula derived from the fineness and chemical nature of the liming material (Troeh, 1993). If at least 50% of a limestone will pass through a 100 mesh screen, it is considered fine limestone, and gives good results. Theoretically, if 100% of a ground stone passed through a 100 mesh screen, a pH change would be complete within 3 months (Miller, 1990). Limestone that passes a 60% screen should be completely reacted in soil within three years. Fluid limestone formulations are also available, consisting of finely ground limestone suspended in water with clay (Miller, 1990).

Fertilizer sources of calcium (Parnes, 1990)

	Ca content lbs./ton	lime equivalent, lbs./ton
poultry manures	80	
legume hay	28	
clam and oyster shells	680	1700
wood ashes	700	1750
rock phosphate	420-660	800-1200
calcitic limestone	760	1900
dolomitic limestone	500	1900
gypsum	460	

7. *Its compatibility with a system of sustainable agriculture.*

The Principals of Organic Production and Handling adopted by the NOSB include as goals the "use [of] cultural, biological, and mechanical methods, as opposed to using synthetic materials to fulfill specific functions within the system" and describes an organic systems production system as one designed to:

"Optimize soil biological activity; Maintain long-term fertility;... Recycle materials of plant and animal origin in order to return nutrients to the land, thus minimizing the use of non-renewable resources, (and) Minimize pollution of soil, water, and air" (NOSB, 2001).

The use of nonsynthetic liming materials such as limestone (a nonrenewable resource) is unavoidable in humid climates where soil naturally becomes acid and base cations leach out over time. Increased attention to organic matter additions and use of renewable resources such as poultry manures and wood ashes may be practical in some systems but not all. Use of synthetic calcium oxide contributes indirectly to increased energy use and fossil fuel consumption due to the burning process of manufacture. Natural sources of mined limestone or gypsum are more slowly soluble and contribute to soil fertility and neutralization over a longer term. Some sources of mixed calcium oxides and silicates are usable recycled materials from industrial pollution control systems, iron production, or cement kilns, but these may also contain metal and other contaminants. A neutral pH is beneficial to the soil organisms, but rapid pH changes may cause short term fluctuations and disruptions in population levels.

TAP Reviewer Discussion

Reviewer 1 *[Ph.D. plant pathology, M.S. soil science. Research, consulting, and administrative activities related to waste treatment and reuse of waste as soil amendments and fertilizers. Southeast US]*

Comments on Database

The following information needs to be corrected or added to the database:

Under the Combinations section, the review mentions that kiln dust is a by-product of cement or burnt lime manufacture. In addition to the calcium oxide and calcium hydroxide mentioned in cement kiln dust, there are a variety of other chemicals. Some cement kilns are permitted to burn hazardous waste as a fuel source. The MSDS for cement kiln dust lists a variety of heavy metals that it may contain including lead antimony, arsenic, mercury, and others. The route of exposure for many of these metal is through inhalation or ingestion (Ash Grove Cement Co., 2000).

OFPA Criteria Evaluation

(1) The potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;

The criteria evaluation needs to be corrected or amended as follows:

The petitioner information suggests using calcium oxide as a source of calcium as a plant nutrient. Gypsum is a better source of calcium as a plant nutrient than calcium oxide. Gypsum satisfied the calcium needs of peanuts better than lime and does not modify soil pH (Kamprath and Foy, 1985; Parnes, 1990). Many soils have large amounts of calcium on the exchange complex that are sufficient to supply most crops calcium needs (Kamprath and Foy, 1985).

(2) The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;

I agree with the criteria evaluation.

(3) the probability of environmental contamination during manufacture, use, misuse or disposal of such substance;

Other combination materials may include lime kiln dust, which contains calcium oxide, magnesium oxide, calcium, carbonate, and silica (Peters Chemical Co.). There is increasing interest in the agricultural use of industrial combustion by-products such as fly ash that have a high pH (Pankhurst, 1997). Cement kilns often own limerock mines because limerock is the primary feedstock of cement kilns. Lime kiln dust may come from cement kilns that are permitted to burn hazardous waste, which can be used as a fuel source source (Peters Chemical Co., website; Hansen, 1990).

In 1999, the US EPA proposed management of cement kiln dust under the Resource Conservation and Recovery ACT (RCRA). The US EPA included proposed limitations on various pollutants in cement kiln dust that would be used for agricultural purposes (US EPA, 1999; US EPA, 1998). Cement kilns are also significant point sources for air pollution. Pollutants include carbon monoxide, sulfur dioxide, nitrogen oxides, and particulates.

(4) the effect of the substance on human health;

I agree with the criteria evaluation.

(5) the effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;

The use of nitrogen fertilizers results in an increase in soil acidity, which creates the need for more frequent lime applications (Kamprath and Foy, 1985; Troeh and Thompson, 1993). Waksman (1952) found that calcium carbonate stimulated soil bacteria, which led to an increased decomposition of soil organic matter. The humus fraction of soil organic matter provides long term benefits including pH buffering, increased cation exchange capacity which is pH dependent, and water holding capacity (Bohn et al., 1979; Haynes and Naidu, 1998).

Although this petition is for calcium oxide, the petitioner also submitted information pertaining to a proprietary product called Bio-Cal. Included in this information was research that examined the effects of Bio-Cal, calcium oxide, and calcium carbonate on soil biological activity. Buried cotton strips were used as a bioassay to measure microbial activity. This is an indirect method to assay microbial activity. It was not accompanied by soil assays for target decomposing organisms but rather for broad classes of microorganisms. The results of this field research were statistically quite variable and did not correlate with the Formazan bioassay results for microbial activity. The authors also mention a previous study that showed increased microbial activity with Bio-Cal rather than no difference. At this point in time their results are too variable to draw conclusions about the impacts of different lime materials on microbial activity.

(6) the alternatives to using the substance in terms of practices or other available materials; and

[reviewer corrections incorporated above]

(7) its compatibility with a system of sustainable agriculture.

I agree with the criteria evaluation.

***Reviewer 1 Conclusion** – Summarize why it should be allowed or prohibited for use in organic systems.*

Calcium oxide is a synthetic material due to its production via the combustion of limestone.

Lime to correct calcium deficiency is rarely needed. If calcium is needed, an option is gypsum, which will provide calcium without significantly affecting the soil pH (Tisdale et al., 1985). Poultry manure and legume green manures are also sources of calcium. Lime is predominately used to correct soil pH. The use of inorganic nitrogen fertilizers has increased the need for lime through their acidifying affect (Kamprath and Foy, 1985; Troeh and Thompson, 1993). Current organic standards allow the use of calcium carbonate and dolomite to correct soil pH.

Calcium oxide is also extremely caustic material to handle and causes damage to the respiratory tract. Products used in organic agriculture should strive to reduce risks to farm worker health.

Finally, calcium oxide is also a component of cement kiln dust, which is a by-product of the cement kiln industry (MSDS Ash Grove Cement Co.). Many cement kilns burn hazardous waste and tires for fuel (Hansen, 1990 and 1992). The US EPA has proposed restrictions on various pollutants in cement kiln dust that will be used for agricultural purposes (US EPA, 1998).

Reviewer 1 Recommendation Advised to the NOSB:

The substance is Synthetic

For Crops, the substance should be Not Added to the National List.

Reviewer 2 *[Ph.D. Research chemist, serves on an organic certification committee, Eastern US]*

Comments on Database

I find the database (Characterization and Status) to be reasonably complete and fairly accurate.

OFPA Criteria Evaluation

I agree with the criteria evaluation in the database, and offer additional supporting information.

(1) the potential of such substances for detrimental chemical interactions with other materials used in organic farming systems;

CaO is extremely caustic. Its reaction with water or organic acids (urine) releases a large amount of heat. Addition of water directly to CaO (accidental or otherwise) can generate temperatures as high as 800° C. (NFPA, 78). Ignition of straw and powdered sulfur caused by water/CaO reaction have been reported. Fire fighters are advised to avoid using water on CaO during a fire unless the danger from other burning material is greater than the risks associated with the CaO/water reaction (NFPA, 1978).

The pH of a saturated solution of CaO is about 12.5, which is much higher than that of $CaCO_3$ (9.4) (Weast, 81). It is easy to overlime with CaO, which would tie up plant nutrients like Boron (Parnes, 90), and harm soil biota (see below).

(2) the toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment;

Solid CaO is an irritant causing chemical burns and inflammation of plant or animal tissue (Gosselin et al., 1976). Aqueous CaO [$Ca(OH)_2$] harms organisms primarily through high pH. A study of the use of $Ca(OH)_2$ as a disinfectant against *Cryptosporidium parvum* oocysts in water supplies found that calcium hydroxide only killed oocyst through high pH (Robertson et al., 1992). The hydroxide has no effect on *C. parvum* when the pH is adjusted down to 6. In the Eastern US, $Ca(OH)_2$ will not persist in the soil. Reaction with atmospheric CO_2 and acidic rain water will destroy any hydroxide. This conversion takes some time, however, and local high pH conditions can persist around the lime particles.

(3) the probability of environmental contamination during manufacture, use, misuse or disposal of such substance;

The main environmental problem is dust generated by the kiln firing and powder processing (milling & screening, and packaging). Workers at these plants are advised to wear protective clothing to avoid skin and eye exposure and use a respirator (not single use or quarter-mask respirator) (NIOSH, 1994).

(4) the effect of the substance on human health;
Irritation of skin and eyes, and inflammation of mucus membranes and lungs are the main immediate health effects of CaO exposure. The NIOSH 10 hour time-weighted average human exposure is 2 mg/cu meter and the immediate health danger limit is 25 mg/cu m. (NIOSH, 1994).

(5) the effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock;
Little literature exists on the effect of CaO and $Ca(OH)_2$ on soil organisms. The aqueous hydroxide of calcium is used as an antimicrobial and there exists an extensive literature on its effect on microbe pathogens. $(OH)^-$ ions are antimicrobial at pH > 9 and will inhibit most bacteria and many viruses (Aiello, 1998). CaO soaked in water [$Ca(OH)_2$] is also used to disinfect premises (Aiello, 1998).

In human dentistry, $Ca(OH)_2$ is used as an antibacterial agent in root canals (intracanal dressing) and in periodontal work (Estrela et al., 2001; Molander et al., 1999). Stuart et al., 1991, found $Ca(OH)_2$ to be effective in vitro against *Streptococcus mutans*, *Actinomyces viscosus* and *Bacteroides gingivalis.*

Scarification of seeds to enhance germination can favor colonization by pathogenic bacteria. Holliday et al., 2001, found reduction in *Salmonella* and *Escherichia coli* O157:H7 when alfalfa seeds (for sprouts) were treated in 1 % $Ca(OH)_2$. The presence of organic material in the seed did not affect the antimicrobial activity.

Field studies of the effect of liming on soil fauna are difficult to control. Raising soil pH > 6 favors fungi and worm populations over bacteria (Waksmen, 1952; Dick, 1997). pH shifts also alter the availability of nutrients. Nitrogen mineralization can be effected by both pH and changes in the bacteria/fungi populations. Weyman-Kaczmarkowa and Pedziwilk (2000) studied the effect of liming on soil microbes in sandy loam and loose sand soil. They used $Ca(OH)_2$ to increase the soil pH and found that the total microbial biomass (bacteria + fungi) decreased by ~ 50 % when pH was raised from the natural 4.5 to 9.0 in the sandy soil. In the loam (natural pH of 7.7) using $Ca(OH)_2$ to raise the pH to 9.0 decreased the biomass by 30 %, and an increase to pH = 11 decreased biomass by 40%.

A study of different liming materials on soil microbial activity is attached to the petition. This study uses buried cotton strips to measure microbial activity in soils limed with limestone, burnt lime and a brand named product Bio-Cal. Biologic activity is measured by the amount of the strips that decomposed during the 1999 growing season. The study is difficult to interpret. The liming products are not described in enough detail to allow one to assess their relative liming abilities (particle size, CEC). An earlier study in 1998 by the same group used limestone milled much finer than typical field grade lime (Zimmer, 1999). This limestone would have higher Ca availability than field grade limestone and its effect on soil would be more similar to that of the other liming materials tested.

In the 1999 study, four replicates were run for each material in each field. The data scatters badly for all amendments at two sites. At a third site (a garden soil), the scatter drops and the author attempts a Student's t-test of the population means. The results reported show that some of the liming materials can be differentiated at the 2% significance level. A Student t-test to determine if two overlapping populations are distinct assumes that the two populations follow a normal distribution. If limited data suggest that they do have normal distribution, a minimum of five data points for each are usually needed (BBN, 1988). If there is no indication that they are gaussian, then a sample size of 50 is usually indicated. Analysis of the four data points for each liming material using probability and box plots shows no indication that the data are normally distributed. Some of the data visually appear to be outliers, but there are too few data for the box plot routine to flag them as such.

(6) the alternatives to using the substance in terms of practices or other available materials
As stated above, all the basic Ca lime materials affect soil pH and Ca availability the same way. The higher the acid neutralizing power and the calcium solubility are, the faster the effects will be seen in the field. Limestone and gypsum are slower acting than the synthetic calcium oxides but do the same job. Quality pastures with high nutrient grasses are possible using mined limestone and gypsum. Three to five years may be needed to optimize pastures using the mined minerals, however (Nation, 1995). The synthetics work faster, but possible can do harm to soil biota.

(7) its compatibility with a system of sustainable agriculture
Mined liming and Ca field amendments are compatible with sustainable agriculture. The main US limestone deposits are found in the Mid-West, but mineable deposits are found through out the Appalachian and Rocky Mountains (Brobst & Pratt, 1973). CaO is usually produced at limestone quarries. It is synthesized at high temperatures (1000° C.) in open kilns that require large inputs of energy (Vorres, 1991). Since the un-fired limestone is an adequate liming material, the additional processing and energy use seems unnecessary.

A discussion of the petitioned annotation for CaO.

The petition requests that CaO be placed on the National List only if it is in a form that yields less than one degree F [increase in temperature] when mixed with 1:1 vol. water. This request is based on crude caliometry data provided by an analytical testing lab. The lab measured a heat of solution for the product Bio-Cal of 0.6 cal./gm. Assuming that all the material was CaO, the measured heat of solution would be 0.14 kJ/mole, far lower that the traditional CaO value of 63.6 kJ/mole (Kirk-Othmer, 1991b). No controls of known chemistry are reported to validate the test method. 0.6 cal/gm is a much lower heat of solution than any of the Ca liming materials used to make the product.

The heat of solution of a chemical compound is a thermodynamic state function. It is as diagnostic of a specific chemical as the chemical composition or the X-ray diffraction pattern. If CaO were added to the National List of Allowed Synthetics with the annotation "only if it is in a form that yield less than one degree F increase in temperature when mixed with 1:1 vol. water", one would be essentially saying that CaO would be an allowed synthetic only if it does not behave like CaO. If a thermo state property does not define a chemical, then what property does define that compound? How can one prove that a substance on a product's list of ingredients is the synthetic that is on the National List?

Much of the documents attached to the petition pertain to a brand name product, Bio-Cal. Bio-Cal is a processed liming material, which uses feed stocks of kiln dust (CaO + $Ca(OH)_2$), gypsum, and power plant fly ash. Fly ash varies in chemical composition, but is basically a Mg, Fe alkaline earth alumino-silicate (Bone & Himus, 1936). These feed stocks are mixed/milled and heated by a proprietary process to give a final product, which has apparent low heat of solution and high Ca availability (see petition). The pH of 17 lots of Bio-Cal average 12.3 (± 0.4), which is slightly lower than $Ca(OH)_2$. Neither the chemical composition of Bio-Cal nor the processing temperature are given. The final product is probably more than just a mixture of $Ca(OH)_2$, $CaCO_3$ and $CaSO_4$. These phases may exist with reaction rims and precipitated particles of complex hydroxy carbonates and hydroxy sulphates like $Ca_2(H_2O)[SO_3]_2$ (Bassanite) or $Ca(H_2O)_6[CO_3]$ (hexahydrocalcite) (Povarennykh, 1972).

Reviewer 2 Conclusion

CaO is used as an antimicrobial in the medical and food industries. Limited field data suggest that it is harmful to soil biota. All the benefits of CaO additions to soil can be obtained by the addition of mined limestone and gypsum.

Calcium oxide is a crystalline solid. Its crystal structure is Isometric with space group Fm3m. It is generally unstable when moisture is present and exhibits a large exothermic reaction with water to form aqueous $Ca(OH)_2$. The heat of solution in water for CaO is 64 kJ/mole. CaO has a distinct from its precursor $CaCO_3$, which possesses a different chemical composition, crystal structure (Trigonal with space group R3_c), and heat of solution in water (13.1 kJ/mole).

Commercial CaO is synthetic. Natural CaO can form during high temperature contact metamorphism in rock invaded by igneous magma (Berry & Mason 59). It is rare, however, and not commercially exploitable.

CaO is synthetically produced by heating limestone or dolomite in a kiln. Production usually occurs in limestone quarries to minimize transportation costs. CaO is not stable in moist air and will convert to solid $Ca(OH)_2$. Calcium hydroxide has more industrial uses than CaO and most limestone that is fired to lime is further processed to the hydroxide.

The three basic Ca compounds derived from limestone--$CaCO_3$, $Ca(OH)_2$, and CaO--are all used as agricultural field amendments. Limestone can be simply crushed to a desired particle size, while the other two compounds are only used for ag purposes if their powder size or purity are not acceptable for higher value applications.

These basic calcium compounds serve two main purposes as and field amendments. The anion raises the pH of acidic soils. The ability of these compounds to raise pH is determined on the amount of acid each molecule can neutralize (CaO has the highest neutralizing value, Tisdale et al., 1985). The particle size of the liming agent is also important in pH control. Coarse particles have lower surface area than fine ones and take longer to react with soil water and acids. Milling $CaCO_3$ very fine can speed the kinetics of the neutralization and make the limestone behave more like CaO. A mole of $CaCO_3$, however, neutralizes less acid than CaO (Norton & Zhang, 1998), and more limestone would be needed to achieve the final pH of a given amount of CaO. Many ag crops grow best in neutral pH soils. Neutral to slightly basic soil pH binds toxic ions like Al and Fe while releasing other ions needed for plant growth and health (Zimmer, 2000).

Calcium released by solution of the carbonate or hydroxide also competes with Na^{+} and Al^{+3} ions for absorption sites on clay particles. Increasing exchangeable Ca +2 loosens soil structure and facilitates plant uptake of other minerals (Norton & Zhang, 1998; Tisdale et al., 1985). Gypsum ($CaSO_4$) behaves like calcium compounds in its effect on soil texture and plant mineral uptake. The sulfate anion, however, does not change soil pH and does not effect mineral availability in the soil like lime does.

Effective use of gypsum and basic calcium liming materials can have very positive effects on the yield and nutrition of crops and grass forages (Nation, 1995; Zimmer, 2000). Any of the three basic calcium compounds can be used to achieve these effects. The amount of Ca applied and the neutralizing capacity is different for the three compounds, but can be tuned by varying the amount of each compound applied to the soil. The kinetics can also be partially controlled by the choice of particle size used.

Calcium oxide is a synthetic compound. It should be prohibited without annotation for use as a field amendment.

Calcium oxide, which has an unusually low heat of solution, cannot be reviewed due to a lack of consistent properties.

Reviewer 2: Recommendation Advised to the NOSB

The substance is <u>Synthetic</u>
For Crops and Livestock, the substance should be <u>Not Added to the National List</u>.

<u>Reviewer #3</u> [*Organic farmer, organic inspector, advises organic certifier. Western US.*]

Comments on Database

Materials provided with the TAP Review appeared to be consistent and helpful in understanding what the detrimental and positive effects of calcium oxide can be.

This material should be considered synthetic. It is currently allowed for use for disease control as a foliar but is prohibited as a fertilizer. The concern over its use as a fertilizer is that it creates a strong imbalance of soluble calcium, which negatively affects soil microbes and causes rapid oxidation of other soil nutrients.

Producers certified by some chapters of OCIA and OGBA have used these materials in formulations [that meet the proposed restrictions] for many years. In this sense, the materials have previously been accepted for use in organic agriculture… .

<u>OFPA Criteria Evaluation</u>

Alternatives:

There are many existing alternatives for adjusting pH that are currently used in organic agriculture. This particular form and formulation has several significant advantages and mitigates some of the disadvantages.

The approved organic alternatives work well but do not have some of the beneficial properties of this formulation. A distinction needs to be made between the formulation, Bio-Cal, and the generic ingredients, calcium oxide and calcium hydroxide. The Bio-Cal contains several ingredients of which calcium oxide and calcium hydroxide are a part.

The effects of the formulation is different from the effects of each separate ingredient. The request is to allow the generic material to be used in a manner that has effects similar to a proprietary formulation. According to some data [*provided by the petitioner]* this formulation is several times more efficient at providing calcium to plants and soil than either the approved organic alternatives or the petitioned *[generic]* materials.

Is the material compatible with organic production and handling?

With the restrictions requested in the application--specifically the requirements that it be applied in a form that yields less that 1degree Fahrenheit temperature increase when equal volumes of product and water are mixed and that it be part of a managed program to remineralize soils--the negative effects on the soil are mitigated. The material with restrictions is compatible with organic agriculture.

Recent developments and insights into the "soilfoodweb" have developed organic agriculture practices and enhanced our understanding of what developing soil means in terms of microorganisms. Formulations or amendments that increase the activity and number of species of soil microorganisms should be considered compatible with organic agriculture. The restriction that this material be applied to the fields in amounts necessary to raise soil minerals to optimum levels based on soil tests is also likely to increase diversity of microorganisms.

The same material without restrictions has been found to have detrimental effects to the soil. In common terms, it "burns the soil and kills the worms." Some data suggests the effects may not be as harmful for the first applications, instead the harmful effects build up over time and in conjunction with other practices.

The material is synthetic and alternative materials are available to adjust pH and protect plants from disease.

<u>Other considerations</u>

This petition brings up a larger issue with some important implications for considering what materials should be allowed for use in organic agriculture. The larger issue is: if a material that can cause harm when used conventionally can be restricted or reformulated in a manner that does not cause harm, should it be allowed? If it is allowed, what quantitative measurement of harm should it be judged by? … .

The measurement of harm should be based on our increasing understanding of soil and plant microbiology. What it means to "build the soil" can now be defined by measurement of the diversity of microorganisms. Soil building is fundamental to the principals of organic agriculture and specified in the Final Rule in 205.203 (a)" "The producer must select and implement tillage and cultivation practices that maintain and improve.... biological condition of soil… ." Soil building is a method of increasing fertility, pest and disease control for crop production.

If a material is either neutral or increases the diversity of microorganisms, it should be considered beneficial to the soil. A material that enhances the diversity of microorganisms can be considered safe for the environment, producer, field workers, and consumer and therefore allowed for use in organic agriculture… . The significance of using soil microbial components and soil enzyme activities as indicators for monitoring the impact of materials on soil is gaining recognition. It is also very significant to organic agriculture… .

In the case of calcium oxide, one of the main harmful effects of the material is the heating (oxidation) of the soil. An evaluation method that measures the amount of heat a given formulation produces is a valid evaluation method. The restriction that limits the amount of heat produced is appropriate for organic agriculture. Unfortunately, there does not appear to be protocols established as to how to measure this effect. The manufacturer's test has the advantage of being simple to perform at the farm level.

In the petition there were several documented questionnaires from organic growers testifying to their support for Bio-Cal. *[In this reviewers opinion]* long term support for a material from organic growers is significant factor in considering a material's organic status.

The material has long been recommended for use as disease control in "Bordeaux mixture." This mixture is effective for its toxicity and is not usually considered part of a soil building regime or beneficial to microorganisms. It does however show the material has been accepted for other aspects of organic crop production

Reviewer 3 Conclusion

I recommend that it be approved as synthetic-allowed with requested restrictions on its use. *[The proposed]* restrictions protect the soil from excessive oxidation ("burning") that can be caused by using too high a concentration. It also prohibits direct application of the material in raw form. To meet this restriction, the material must be formulated with other materials before being applied to the soil. It can be used as an ingredient, but not directly.

The restriction *[also]* limits the amount of material that can be applied and requires soil testing.*[and]* requires further documentation on its use and limits the amount of material used.

Reviewer 3: Recommendation Advised to the NOSB

The substance is Synthetic.

For Crops and Livestock, the substance should be Added to the National List with restrictions.

Suggested Annotation: It is applied in a form that yields less than 1 degree Fahrenheit temperature increase when equal volumes of product and water are mixed. It is applied to fields in amounts necessary to raise soil minerals to optimum levels based on soil tests. It is applied as part of a managed program to remineralize soils.

[End of TAP Reviewer Comments]

TAP Conclusion:

All three reviewers find calcium oxide to be a synthetic material. Two of the reviewers support prohibition, and find that there are nonsynthetic alternatives, as well as concerns about worker safety, possible effects on microorganisms, and possibility of contaminants. One reviewer supports allowance with restrictions on formulated products proposed by the petitioner, however did not offer any validation or support for this method of determining heat of solution. A research chemist reviewer noted that, "No controls of known chemistry are reported to validate the test method." Calcium carbonate (limestone), gypsum, the use of legume cover crops, and poultry manure are nonsynthetic alternatives widely used in organic soil building programs.

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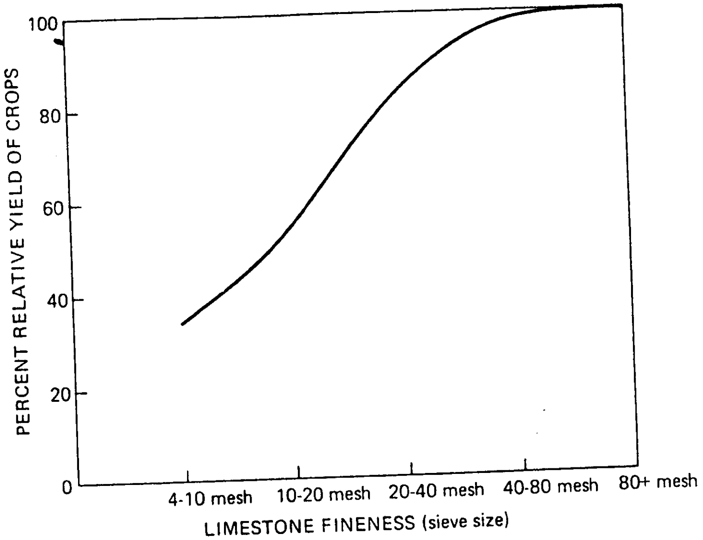

FIGURE 15:3. Relationship between the particle size fraction of limestone and yield of crops in nine field experiments. [*Data from several sources; summarized by Barber* (1).]

100-mesh sieve, should give excellent results and yet be cheap enough to encourage its use. Such a lime is sufficiently pulverized to rate as a *fine* limestone. Some limestones are finer than this, 50 or 60 percent passing a 200-mesh screen, but the cost of grinding the stone to this very fine condition seldom can be justified. The fine limestone described above has enough of the finer particles to give quick results and yet a sufficient amount of the coarser fragments to make it last over the period of the rotation.

A limestone which does not approximate the fineness designated above should be discounted to the extent to which it falls short. It may be necessary, for example, to consider 3,000 pounds of one limestone as equal to 1 ton of another, even though their chemical analyses are the same. Considerable judgment in the interpretation of fineness guarantee is necessary in order that such an adjustment be made correctly. Much limestone that falls below the standard set above is now being used because, as a by-product, it is very cheap. When the amounts put on the land are properly adjusted, as good results may be expected from the coarser as from the finer limestones and the effects should last considerably longer.

15:4. CHANGES OF LIME ADDED TO THE SOIL

In considering the changes which lime undergoes after it is added to the soil we must always keep in mind that (a) the calcium and magnesium compounds applied undergo solution under the influence of a variable partial pressure of carbon dioxide, and (b) an acid colloidal complex will adsorb considerable amounts of calcium and magnesium ions.

REACTION WITH CARBON DIOXIDE. When lime—whether the oxide, hydroxide, or the carbonate—is applied to an acid soil, the movement as solution occurs is toward the bicarbonate form. This is because the carbon dioxide partial pressure in the soil, usually several hundred times greater than that in the atmospheric air, generally is high enough to cause a reaction with the hydroxide and even the carbonate. The reactions, written only for the purely calcium limes, follow:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

$$Ca(OH)_2 + 2H_2CO_3 \rightarrow Ca(HCO_3)_2 + 2H_2O$$

$$CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$$

REACTION WITH SOIL COLLOIDS. All liming materials will react with acid soils, the calcium and magnesium replacing hydrogen on the colloidal complex. The adsorption in respect to calcium may be indicated as follows:

$$\begin{matrix}H\\H\end{matrix}\boxed{\text{Micelle}} + Ca(OH)_2 \rightleftharpoons Ca\boxed{\text{Micelle}} + 2H_2O$$

$$\begin{matrix}H\\H\end{matrix}\boxed{\text{Micelle}} + \underset{\text{In solution}}{Ca(HCO_3)_2} \rightleftharpoons Ca\boxed{\text{Micelle}} + 2H_2O + 2CO_2\uparrow$$

$$\begin{matrix}H\\H\end{matrix}\boxed{\text{Micelle}} + \underset{\text{Solid phase}}{CaCO_3} \rightleftharpoons Ca\boxed{\text{Micelle}} + H_2O + CO_2\uparrow$$

As the above reactions of limestone proceed, carbon dioxide is freely evolved. In addition, the adsorption of the calcium and magnesium raises the percentage base saturation of the colloidal complex and the pH of the soil solution is pushed up correspondingly.

DISTRIBUTION OF CALCIUM AND MAGNESIUM IN LIMED SOIL. Calcium and magnesium, if supplied by a limestone of average fineness, will exist in the soil at least for a time, in three forms: (a) as solid calcium and calcium–magnesium carbonates, (b) as exchangeable bases adsorbed by the colloidal matter, and (c) as dissociated cations in the soil solution mostly in association with bicarbonate ions. When the calcium and calcium–magnesium carbonates have all dissolved, the system becomes somewhat simpler, involving only the exchangeable cations and those in soil solution, both of which are subject to loss by leaching.

DEPLETION OF CALCIUM AND MAGNESIUM. As the soluble calcium and magnesium compounds are removed, the percentage base saturation and pH are gradually reduced and eventually another application of lime is necessary. This then is the type of cycle through which much of the calcium and magnesium added to arable soils swings in humid regions.

15:5. LOSS OF LIME FROM ARABLE SOILS

Calcium and magnesium are lost from soils in three ways: (a) by erosion, (b) by crop removal, and (c) by leaching. Since these three types of lime loss have already been discussed and evaluated in Chapter 9, it is a simple matter to draw such data together in tabular form (Table 15:3). Although the values shown do not represent losses from soils in general, they are quite significant when used comparatively.

TABLE 15:3. *Lime Losses from Soil*

Values in pounds per acre per year.

Manner of Removal	Calcium		Magnesium	
	CaO	$CaCO_3$	MgO	$MgCO_3$
By erosion, Missouri experiments, 4 percent slope	120	214	48	102
By the average crop of a standard rotation	56	100	50	105
By leaching from a representative silt loam	140	250	33	70
Total		564		277

The data for erosion removals are for a silt loam in Missouri cropped to a rotation of corn, wheat, and clover (see Table 9:6). The acre annual removal by crops was calculated for a standard and representative rotation, assuming reasonable yields (see Table 9:2). The leaching losses are for a postulated representative silt loam under a rainfall of perhaps 36 to 40 inches and cropped to a standard farm rotation. All data are in pounds per acre per year expressed in the conventional *oxide* form and also in the more practical terms of *calcium* and *magnesium carbonates.*

The greater loss of calcium than magnesium no doubt is because the soil colloidal matter almost always carries a much larger amount of the calcium in an exchangeable condition. And since the average liming material supplies several times more calcium than magnesium, this loss ratio will in general be maintained and even accentuated in arable lands as liming proceeds.

This does not mean, however, that the magnesium in lime is of minor importance. Far from it. In fact, judging from the figures of Table 15:3, there should always be at least one third as much magnesium as calcium in the lime applied in order to proportionately meet the outgo of the two constituents. Other things being equal, it is generally wise to select a magnesium-containing limestone.

The figures quoted in Table 15:3 indicate that 500 to 600 pounds of limestone per acre per year may be required to meet the loss from cropped soils in humid regions. This amounts to about 1 to 1.5 tons of carbonate of lime during the period of the average rotation, depending upon the kind of soil and other factors. Such a conclusion verifies the importance of lime in any scheme of fertility management in areas of medium to heavy rainfall.

15:6. EFFECTS OF LIME ON THE SOIL

It has already been emphasized that the changes of lime in the soil are many and complicated. Therefore, the following presentation must necessarily be more or less general in nature. The better known effects of liming are (a) physical, (b) chemical, and (c) biological.

PHYSICAL EFFECTS. A satisfactory granular structure is somewhat encouraged in an acid soil by the addition of any form of lime, although the influence is largely indirect. For example, the effects of lime upon biotic forces are significant, especially those concerned with the decomposition of the soil organic matter and the synthesis of humus. The genesis of the humus as well as its persistence greatly encourages granulation (see p. 58). The stimulating effect of lime on deep-rooted plants, especially legumes, is significant.

CHEMICAL EFFECTS. If a soil at pH 5.0 is limed to a more suitable pH value of about 6.5, a number of significant chemical changes occur. Many of these were described in Chapter 14 and will be outlined here to reemphasize their importance.

1. The concentration of hydrogen ions will decrease.
2. The concentration of hydroxyl ions will increase.
3. The solubility of iron, aluminum, and manganese will decline.
4. The availability of phosphates and molybdates will increase.
5. The exchangeable calcium and magnesium will increase.
6. The percentage base saturation will increase.
7. The availability of potassium may be increased or decreased depending on conditions.

Of the specific chemical effects of lime mentioned, the reduction in acidity is one commonly recognized. However, the indirect effects on nutrient availability and on the toxicity of certain elements are probably more important. Liming of acid soils enhances the availability and plant uptake of elements such as molybdenum, phosphorus, calcium, and magnesium. At the same time, it drastically reduces the concentration of iron, aluminum, and manganese, which under very acid conditions are likely to be present in toxic quantities.

BIOLOGICAL EFFECTS. Lime stimulates the general purpose, heterotrophic soil organisms. This stimulation not only favors the formation of humus but also encourages the elimination of certain organic intermediate products that might be toxic to higher plants.

Most of the favorable soil organisms, as well as some of the unfavorable ones such as those that produce potato scab, are encouraged by liming. The formation of nitrates and sulfates in soil is markedly speeded up by increasing the pH. The bacteria that fix nitrogen from the air, both nonsymbiotically and in the nodules of legumes, are especially stimulated by the application of lime. The successful growth of most soil microorganisms so definitely depends upon lime that satisfactory biological activities cannot be expected if calcium and magnesium levels are low.

15:7. CROP RESPONSE TO LIMING

Figure 14:9 specifies in a general way the lime levels at which various plants seem to grow most satisfactorily, thereby indicating whether or not a particular crop is likely to be benefited by liming. Of the lime-loving plants, alfalfa, sweet clover, red clover, asparagus, cauliflower, and lettuce are representative. However, a surprisingly large proportion of crop plants is quite tolerant to the conditions presented by moderately acid soils. If such plants respond to lime, it is because of the stimulating influence of lime upon the legume which preceded them in the rotation.

REASONS FOR RESPONSE. When plants are benefited by lime, a number of possible reasons may be suggested: (a) the direct nutritive or regulatory action of the calcium and magnesium, (b) the removal or neutralization of toxic compounds of either an organic or inorganic nature; (c) the retardation of plant diseases, (d) an increased availability chemically of plant nutrients, and (e) an encouragement of microorganic activities favorable in a nutritive way. Since several of these factors undoubtedly function concurrently, crop response to liming is a complicated phenomenon, and only the broadest conclusions may be drawn.

The growth of a number of plants is definitely retarded by liming, prominent among which are cranberries, blueberries, watermelons, laurel, and certain species of azaleas and rhododendrons. It is, therefore, advantageous not only to know the condition of the soil but also to understand the influence of lime on the crop to be grown. Lime is too often used as a cure-all, little attention being paid to the widely differing responses exhibited by various crops.

15:8. OVERLIMING

This leads to the question of *overliming*, the addition of lime until the pH of the soil is above that required for optimum plant growth on the soil in question. Under such conditions many crops that ordinarily respond to lime are detrimentally affected, especially during the first season following the application. With heavy soils and when only moderate amounts of lime are used, the danger is negligible. But on sandy soils low in organic matter and therefore lightly buffered, it is easy to injure certain crops, even with a relatively moderate application of lime.

The detrimental influences of excess lime have been mentioned (see p. 389). Consequently, they are merely outlined here for convenience:

1. Deficiencies of available iron, manganese, copper, and/or zinc may be induced.
2. Phosphate availability may decrease because of the formation of complex and insoluble calcium phosphates.
3. The absorption of phosphorus by plants and especially its metabolic use may be restricted.
4. The uptake and utilization of boron may be hindered.
5. The drastic change in pH may in itself be detrimental.

With so many possibilities and with such complex biocolloidal interrelations to handle, it is easy to see why overliming damage in many cases has not been satisfactorily explained.

The use of lime in a practical way raises three questions. If the first is answered in the affirmative, the other two present themselves in logical sequence. The three questions are: (a) Shall lime be applied? (b) Which form shall be used? (c) What shall be the rate of application?

15:9. SHALL LIME BE APPLIED?

The old concept concerning lime was that of a *cure-all*—that it was almost certain to be beneficial, no matter what the problem. Such an opinion should now be discarded since it may lead to a waste of money and in some cases to overliming. The use of lime must be based on measured soil acidity and on crop requirements.

In determining the desirability of applying lime, the chemical condition of the soil itself should be examined. For this a pH determination commonly is made, either by means of a pH meter or by the less accurate indicator-dye method (p. 393). Representative subsoil as well as surface samples should be examined. The pH is correlated fairly closely with percentage base saturation and is an indicator of the probable activity of the calcium, magnesium, and other elements in the soil. Besides, the test is very easy and the results are quickly determined, two reasons why the test is one of the most popular now available for soil diagnosis.

Before a recommendation can be made, however, the general lime needs of the crop or crops to be grown should be considered. The final decision depends upon the proper coordination of these two types of information. A grouping of crops such as that shown in Fig. 14:8 will greatly aid in deciding whether or not to lime.

15:10. FORM OF LIME TO APPLY

On the basis of the ideas already presented, it is evident that five major factors should be considered in deciding on a specific brand of lime to apply:

1. Chemical guarantees of the limes under consideration.
2. Cost per ton applied to the land.
3. Rate of reaction with soil.
4. Fineness of the limestone.
5. Miscellaneous considerations (handling, storage, bag or bulk, and so on).

GUARANTEE AND COST RELATIONS. By a purely arithmetical calculation based on factors 1 and 2, the cost of equivalent amounts of lime as applied to the land can be determined. These factors will show which lime will furnish the greatest amount of total neutralizing power for every dollar expended.

For instance, the *neutralizing power* ($CaCO_3$ equivalent) of two limes, a hydroxide and a ground limestone, are guaranteed at 135 and 95, respectively. The cost of applying a ton of each to the land (all charges, including trucking and spreading) for purposes of calculation will be considered to be $15.00 for the hydrate and $8.00 for the carbonate. Obviously, it will require only $\frac{95}{135}$, or 0.7 ton of the hydroxide to equal 1 ton of the carbonate. The cost of equivalent amounts of neutralizing power based on 1 ton of limestone will therefore be $10.50 for the hydroxide of lime and $8.00 for the limestone. Unless a rapid rate of reaction were desired, the advantage in this case would definitely be with the limestone. Economic considerations account for the fact that about 95 percent of the agricultural liming material applied in the United States is ground limestone.

RATE OF REACTION WITH SOIL. Burned and hydrated limes react with the soil much more rapidly than do the carbonate forms. For this reason, these caustic materials may be preferred where immediate reaction with the soil is required. In time, however, this initial advantage is nullified because of the inevitable carbonation of the caustic forms of lime.

In comparing carbonate-containing materials, it should be remembered that highly dolomitic limestones generally react more slowly with the soil than do those which are highly calcic. This difference is due to the comparatively slow rate of reaction of dolomite which is supplied along with calcite in dolomitic limestones (see Fig. 15:2). When rapid rate of reaction is not a factor, however, dolomitic limestone is often preferred because significant quantities of magnesium are supplied by this material. Over a period of two or three rotations, soils treated with highly calcic limestone have been known to develop a magnesium deficiency even though the pH was maintained near 7.

The fineness of the limestones under consideration is important, especially if the material is high in dolomite. If it is not sufficiently pulverized to rate as a *fine* lime (see the rule on pp. 409–10), allowance must be made for the lack of rapid acting material by increasing the rate of application.

MISCELLANEOUS FACTORS. Several miscellaneous factors may at times be important. The handling of the caustic limes, even when bagged, is somewhat more disagreeable than working with limestone. The necessity for storage also comes in since sometimes it is desirable to carry lime from one season to another. Limestone has the advantage here since it does not change in storage as the others do.

The question of purchasing the lime, especially the limestone, in bags or in bulk has become increasingly important in recent years. Spreading limestone in bulk by trucks has greatly reduced handling costs (see Fig. 15:4). This method tends, however, to limit the choice of when the material may be applied, since wet or plowed fields cannot be serviced by heavy machinery. The decision as to what method to use should not be finally approved until the nature of the soil and the probable response of the crops have again been reviewed.

15:11. AMOUNTS OF LIME TO APPLY

The amount of lime to apply is affected by a number of factors, including the following:

1. Soil:
    - Surface: pH.
    - Surface: Texture and structure.
    - Surface: Amount of organic matter.
    - Subsoil: pH, texture, and structure.
2. Crops to be grown.
3. Kind and fineness of lime used.
4. Economic returns in relation to cost of lime.

SOIL CHARACTERISTICS. The pH test is invaluable in making decisions because it gives some idea of the percentage base saturation of the soil and the need for lime. The texture and organic matter also are important since they are indicative of the adsorptive capacity of the soil and the strength of

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acetic acid. *Note:* May also exist as calcium dihydroxymalonate.

THERAP CAT: Oral hypoglycemic.

1686. Calcium Methionate. *Methanedisulfonic acid calcium salt.* $CH_2CaO_6S_2$; mol wt 214.24. C 5.61%, H 0.94%, Ca 18.71%, O 44.81%, S 29.93%. $CaCH_2(SO_3)_2$. Prepn: *Beilstein* **vol. 1**, 1st suppl., 303; Jenkins, *J. Am. Pharm. Assoc.* **27**, 484 (1938).

Dihydrate, crystals or cryst powder, having a slight odor. Stable in air. Sol in about 2.5 parts water forming a neutral soln (pH 6-7); very slightly sol in alc.

1687. Calcium Molybdate(VI). $CaMoO_4$; mol wt 200.03. Ca 20.04%, Mo 47.98%, O 32.00%. Prepn from sodium molybdate and $CaSO_4$: Carosella, **U.S.** pat. **2,460,974** (1949 to U.S. Vanadium); by heating a stoichiometric mixture of CaO or $CaCO_3$ and molybdic acid: Kroger, *Nature* **159**, 674 (1947).

Tetragonal crystals. d. 4.35. Insol in water, alcohol; sol in concd mineral acids.

USE: In phosphors and luminescent materials.

1688. Calcium Nitrate. CaN_2O_6; mol wt 164.10. Ca 24.42%, N 17.07%, O 58.50%. $Ca(NO_3)_2$. Prepn: *Gmelin's Calcium* (8th ed.) **28B**, 59-69, 341-382 (1956).

Deliquesc granules, mp about 560°. Very sol in water, heat being evolved; freely sol in methanol, ethanol, acetone; almost insol in concd HNO_3. pH of 5% aq soln 6.0. *Keep well closed.*

Note: $Ca(NO_3)_2$ crystallizes also with $4H_2O$ (30.5%), melting at 45°. Technical flake usually contains 28.6% H_2O.

USE: In explosives, fertilizers, matches, pyrotechnics; manuf of incandescent mantles, radio tubes, HNO_3; corrosion inhibitor in diesel fuels.

1689. Calcium Nitrite. CaN_2O_4; mol wt 132.10. Ca 30.34%, N 21.21%, O 48.45%. $Ca(NO_2)_2$. Prepd by reaction of nitric oxide with a mixture of calcium ferrate(III) and calcium nitrate: Ray, Ogg, Jr., *J. Am. Chem. Soc.* **79**, 265 (1957).

White or yellowish, deliquesc, hexagonal crystals. d 2.23. Freely sol in water; slightly sol in alc. *Keep well closed.*

USE: Corrosion inhibitor in lubricants, concrete.

1690. Calcium Oleate. ***9-Octadecenoic acid calcium salt; oleic acid calcium salt.*** $C_{36}H_{66}CaO_4$; mol wt 602.97. C 71.71%, H 11.03%, Ca 6.65%, O 10.61%. $Ca(C_{18}H_{33}O_2)_2$. Prepn: Harrison, *Biochem. J.* **18**, 1222 (1924); Pink, *J. Chem. Soc.* **1939**, 619.

Pale-yellow transparent solid. Dec above 140°. Slowly absorbs moisture from the air to form the monohydrate. Practically insol in water, alcohol, ether, acetone, petr ether; sol in chloroform, benzene.

USE: Thickening lubricating grease; waterproofing concrete; emulsifier for benzene, kerosene, etc.; in modeling waxes to vary hardness.

1691. Calcium Oxalate. ***Ethanedioic acid calcium salt.*** C_2CaO_4; mol wt 128.10. C 18.75%, Ca 31.29%, O 49.96%. CaC_2O_4. Prepn from calcium formate: Bredt, **U.S.** pat. **1,622,991** (1927); from calcium cyanamide: Barsky, Buchanan, *J. Am. Chem. Soc.* **53**, 1270 (1931).

Monohydrate, cubic crystals. Loses all of its water at 200°. When ignited is converted into $CaCO_3$ or CaO without appreciable charring. d 2.2. Practically insol in water or acetic acid; sol in dil HCl or HNO_3.

USE: In ceramic glazes; as carrier for separation of rare earth metals; analysis for calcium: Ingols, Murray, *Anal. Chem.* **21**, 525 (1949).

1692. Calcium Oxide. Lime; burnt lime; calx; quicklime. CaO; mol wt 56.08. Ca 71.47%, O 28.53%. Properly stored lime of commerce contains 90-95% free CaO. Commercial production from limestone: W. L. Faith *et al.*, *Industrial Chemicals* (John Wiley, New York, 3rd ed., 1965) pp 482-487. Lab prepn by ignition of $CaCO_3$: Ehrlich in *Handbook of Preparative Inorganic Chemistry* **vol. 1**, G. Brauer, Ed. (Academic Press, New York, 2nd ed., 1963) p 931. *Review:* R. S. Boynton in Kirk-Othmer *Encyclopedia of Chemical Technology* **vol. 14** (Wiley-Interscience, New York, 3rd ed., 1981) pp 343-382.

Crystals, white or grayish-white lumps, or granular powder; commercial material sometimes has a yellowish or brownish tint, due to iron. mp 2572°; bp 2850°; d 3.32-3.35. Readily absorbs CO_2 and H_2O from air, becoming air-slaked. Sol in water forming $Ca(OH)_2$ and generating a large quantity of heat; sol in acids, glycerol, sugar soln; practically insol in alc. *Keep tightly closed and dry.*

USE: In bricks, plaster, mortar, stucco and other building and construction materials; manuf of steel, aluminum, magnesium, and flotation of non-ferrous ores; manuf of glass, paper, Na_2CO_3 (Solvay process), Ca salts and many other industrial chemicals; dehairing hides; clarification of cane and beet sugar juices; in fungicides, insecticides, drilling fluids, lubricants; water and sewage treatment; in laboratory to absorb CO_2 (the combination with NaOH is known as soda-lime, *q.v.*). *Caution:* A strong caustic. May cause severe irritation of skin, mucous membranes.

1693. Calcium Palmitate. ***Hexadecanoic acid calcium salt; palmitic acid calcium salt.*** $C_{32}H_{62}CaO_4$; mol wt 550.90. C 69.76%, H 11.34%, Ca 7.28%, O 11.62%. $Ca(C_{16}H_{31}O_2)_2$. Prepn: Harrison, *Biochem. J.* **18**, 1222 (1924).

Powder or rhombic crystals. Dec above 155°. Practically insol in water, alcohol, ether, acetone, petr ether; slightly sol in chloroform, benzene, acetic acid.

USE: Thickening lubricating oils; waterproofing fabrics and lubricating greases; as corrosion inhibitor in halohydrocarbons.

1694. Calcium Pantothenate. ***N-(2,4-Dihydroxy-3,3-dimethyl-1-oxobutyl)-β-alanine calcium salt; pantothenic acid calcium salt;*** calcium D(+)-*N*-(2,4-dihydroxy-3,3-dimethylbutyryl)-*β*-alaninate; Calpanate; Galamila; Pantholin. $C_{18}H_{32}CaN_2O_{10}$; mol wt 476.53. C 45.37%, H 6.77%, Ca 8.41%, N 5.88%, O 33.57%. $[HOCH_2C(CH_3)_2CHOHCONHCH_2CH_2COO]_2Ca$. Prepn: Wehrmeister, **U.S.** pat. **2,780,645** (1957 to Commercial Solvents); Kagan, **U.S.** pat. **2,845,456** (1958 to Upjohn). Purification: Kapp, Griffith, **U.S.** pat. **2,935,528** (1960 to Nopco). Monograph: Greulich, Meiner, *Pharmazie* **12**, 643 (1957). *See also* Pantothenic Acid for ref relating to prepn. Only the *d*-isomer described here has vitamin activity.

Minute needles from CH_3OH. Sweetish taste with slightly bitter aftertaste. Dec 195-196°. Moderately hygroscopic. Reasonably stable to air and light. $[\alpha]_D^{25}$ +28.2° (c = 5). One gram dissolves in 2.8 ml H_2O. Sol in glycerol; slightly sol in alcohol, acetone. pH of aq soln (1 in 20): 7.2-8.0; pH in CO_2-free water: 8.7. Solns are most stable at pH 5-7. Rate of hydrolysis is a function of pH and is catalyzed by the presence of electrolytes. Solns are not stable to autoclaving, and sterilization by filtration is necessary. Stability data: Frost, McIntire, *J. Am. Chem. Soc.* **66**, 425 (1944).

THERAP CAT: Enzyme co-factor vitamin.

THERAP CAT (VET): As a dietary supplement (pantothenic acid source).

1695. Calcium Permanganate. $CaMn_2O_8$; mol wt 277.94. Ca 14.42%, Mn 39.53%, O 46.05%. $Ca(MnO_4)_2$. Prepn from $KMnO_4$ and $CaCl_2$: **Brit.** pat. **624,885** (1949 to Boots Pure Drug Co. and T. Hagyard); from $Al(MnO_4)_3$ and $Ca(OH)_2$: Jaskowiak, **U.S.** pat. **2,504,130** (1950 to Carus Chemical).

Violet or dark-purple, deliquesc crystals. Freely sol in water; dec in alcohol. *Keep tightly closed.*

USE: Antiseptic, disinfectant, deodorizer; with CaF_2 as binder for welding electrode coatings and fluxes.

1696. Calcium Peroxide. Calcium dioxide. CaO_2; mol wt 72.08. Ca 55.60%, O 44.40%. The commercial product usually contains about 60% CaO_2, water, and some $Ca(OH)_2$ and $CaCO_3$. Prepn: Young, **U.S.** pat. **2,533,660** (1950 to du Pont): Ehrlich in *Handbook of Preparative Inorganic Chemistry* **vol. 1**, G. Brauer, Ed. (Academic Press, New York, 2nd ed., 1963) p 936.

White or yellowish, odorless, almost tasteless powder. Dec in moist air. Slightly sol in water; sol in acids with formation of H_2O_2. *Keep well closed.*

USE: Stabilizer for rubber.

THERAP CAT: Antiseptic.

1697. Calcium Phenolsulfonate. ***p-Hydroxybenzenesulfonic acid calcium salt;*** calcium sulfocarbolate; calcium sulfophenolate. $C_{12}H_{10}CaO_8S_2$; mol wt 386.40. C 37.30%, H

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Alexander. U.S. pat. **2,702,740** (1955 to Metal Hydrides). *Reviews:* Halls, *Ind. Chem.* **22**, 680 (1946); Kilb, *USAEC* APEX-485, 57 pp (1959).

Orthorhombic crystals or powder; the commercial product is gray. d 1.7. mp 1.86. Decomposes with water, lower alcohols and carboxylic acids to form hydrogen; moderately powerful condensing agent with ketones and acid esters; more powerful reducing agent toward metal oxides than lithium or sodium hydrides.

USE: To prepare rare metals by reduction of their oxides; as a drying agent for liquids and gases; to generate hydrogen: 1 g of calcium hydride in water liberates 1 liter of hydrogen at STP; in organic syntheses.

1676. Calcium Hydroxide. Calcium hydrate; slaked lime. CaH_2O_2; mol wt 74.10. Ca 54.09%, H 2.72%, O 43.19%. $Ca(OH)_2$. Contains at least 95% $Ca(OH)_2$. Commercial prepn by hydration of lime. W. L. Faith *et al., Industrial Chemicals* (John Wiley, New York, 3rd ed., 1965) pp 483-484. Laboratory prepn by treating an aq soln of a calcium salt with alkali: Ehrlich in *Handbook of Preparative Inorganic Chemistry* vol. **1**, G. Brauer (Academic Press, New York, 2nd ed., 1963) p 934.

Crystals or soft, odorless, granules or powder. Slightly bitter, alkaline taste. Readily absorbs CO_2 from air forming $CaCO_3$. Loses water when ignited; forms CaO. d 2.08-2.34. Slightly sol in water; sol in glycerol, sugar or NH_4Cl solns; sol in acids with evolution of much heat. pH of aq soln satd at 25°: 12.4. *Keep well closed.* LD_{50} orally in rats: 7.34 g/kg, Smyth *et al., Am. Ind. Hyg. Assoc. J.* **30**, 470 (1969).

USE: In mortar, plaster, cement and other building and paving materials; in lubricants, drilling fluids, pesticides, fireproofing coatings, water paints; as egg preservative; manuf of paper pulp; in SBR rubber vulcanization; in water treatment; dehairing hides.

THERAP CAT: Astringent.

1677. Calcium Hypochlorite. Losantin. $CaCl_2O_2$; mol wt 142.99. Ca 28.03%, Cl 49.59%, O 22.38%. $Ca(OCl)_2$. Pure product has not been prepd. Commercial product usually contain 50% or more $Ca(OCl)_2$. Preparation of solid product contg 90-94% $Ca(OCl)_2$: Cady, *Inorg. Syn.* **5**, 161 (1957). Impurities include: $Ca(ClO_4)_2$, $CaCl_2$, $CaCO_3$, $Ca(OH)_2$ and water.

USE: Algicide, bactericide, deodorant, disinfectant, fungicide; in sugar refining; oxidizing agent; bleaching agent. Ingredient of ***Camporit*** which also contains NaCl. Also ingredient of ***HTH*** and ***Perchloron***.

1678. Calcium Hypophosphite. $CaH_4O_4P_2$; mol wt 170.07. Ca 23.57%, H 2.37%, O 37.63%, P 36.43%. $Ca(H_2PO_2)_2$. Prepn: *Gmelin's, Calcium* (8th ed.) **28B**, 1119-1121 (1958).

Monoclinic, prismatic crystals or granular powder. When heated above 300° it evolves spontaneously-inflammable phosphine. Sol in water; slightly sol in glycerol. Practically insol in alcohol. The aq soln is slightly acid. *Incompat.* KI, oxidizers.

USE: As corrosion inhibitor; in nickel plating. Pharmaceutic aid (retards oxidation of ferrous salts).

THERAP CAT: Calcium source.

THERAP CAT (VET): Has been used as a dietary supplement and also as a "nerve tonic".

1679. Calcium Iodate. Lautarite. CaI_2O_6; mol wt 389.90. Ca 10.28%, I 65.10%, O 24.62%. $Ca(IO_3)_2$. Prepd by passing chlorine into a hot soln of lime in which iodine has been dissolved: Bahl, Singh, *J. Indian Chem. Soc.* **17**, 397 (1940).

Nonhygroscopic, monoclinic-prismatic crystals. d_4^{15} 4.519. Stable up to 540°. Sensitive to reducing agents. Soly in water (g/100 ml): 0.10 (0°); 0.95 (100°). More sol in aq solns of iodides and in amino acid solns. Sol in nitric acid. Insol in alcohol.

Monohydrate, cubic crystals. Slightly sol in water.

Hexahydrate, orthorhombic crystals. Slightly sol in water.

USE: Nutritional source of iodine in foods and feedstuffs. More stable in table salts than iodides: *Food Field Reporter,* Aug. 8, 1956; Daum, *C.A.* **51**, 5324 (1957); to improve properties of yeast-leavened bakery products.

THERAP CAT: Antiseptic.

1680. Calcium Iodide. CaI_2; mol wt 293.90. Ca 13.64%, I 86.36%. Prepn: Farr, U.S. pat. **2,415,346** (1947 to Mallinckrodt); Chaigneau, *Bull. Soc. Chim. France* **1957**, 886; *Gmelin's, Calcium* (8th ed.) **28B**, 102, 610-622 (1958). The commercial product usually contains 16-20% water.

Very hygroscopic hexagonal lamella. Becomes yellow and completely insol on exposure to air due to liberation of I_2 and absorption of CO_2. mp 740°; bp 1100°. Very sol in water, methanol, ethanol, acetone; practically insol in ether, dioxane. The aq soln is neutral or slightly alkaline. *Keep tightly closed and protected from light.*

Hexahydrate, hexagonal, thick needles, or plates, or lumps, or powder. Very hygroscopic; becomes yellow in air, mp about 42°. Freely sol in water, alcohol. *Keep tightly closed and protected from light.*

THERAP CAT: Expectorant.

1681. Calcium Iodobehenate. *Iododocosanoic acid calcium salt;* Calioben; Saiodin; Sajodin. $C_{44}H_{84}CaI_2O_4$; mol wt 971.03. C 54.42%, H 8.72%, Ca 4.13%, I 26.14%, O 6.59%. $Ca(C_{21}H_{42}ICO_2)_2$. Prepn: *Beilstein,* vol. **2**, 392.

White or yellowish powder; odorless or with slight fat-like odor. Practically insol in water, alcohol, ether; freely sol in chloroform. *Protect from light.*

THERAP CAT: Internally for its iodine action.

THERAP CAT (VET): Has been used internally as a source of iodine.

1682. Calcium Iodostearate. *2-Iodooctadecanoic acid calcium salt;* stearodine. $C_{36}H_{68}CaI_2O_4$; mol wt 858.82. C 50.34%, H 7.98%, Ca 4.67%, I 29.56%, O 7.45%. $Ca(C_{17}H_{34}ICO_2)_2$. Prepn: *Beilstein,* vol. **2**, 1st suppl., 177.

Cream-colored, almost odorless powder. Practically insol in water or alcohol; sol in benzene, chloroform, ether.

THERAP CAT: Iodine source.

THERAP CAT (VET): Has been used internally as a source of iodine.

1683. Calcium Lactate. *2-Hydroxypropanoic acid calcium salt.* $C_6H_{10}CaO_6$; mol wt 218.22. C 33.02%, H 4.62%, Ca 18.37%, O 43.99%. $Ca[CH_3CH(OH)COO]_2$. Commercial prepn usually contains about 25% water, and on the anhydr basis it is at least 98% pure. Prepd commercially by neutralization of lactic acid, from fermentation of dextrose, molasses, starch, sugar or whey, with $CaCO_3$: Inskeep *et al., Ind. Eng. Chem.* **44**, 1955 (1952).

Pentahydrate, almost odorless, slightly efflorescent granules or powder. Becomes anhydr at 120°. pH: 6-7. Slowly sol in cold water, quickly sol in hot water; almost insol in alcohol.

USE: As a preservative in foods and beverages; in dentifrices.

THERAP CAT: Replenisher (calcium).

THERAP CAT (VET): May be used for hypocalcemic states.

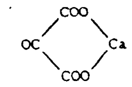
1684. Calcium Levulinate. *4-Oxopentanoic acid calcium salt; levulinic acid calcium salt.* $C_{10}H_{14}CaO_6$; mol wt 270.30. C 44.43%, H 5.22%, Ca 14.83%, O 35.52%. $(CH_3COCH_2CH_2COO)_2Ca$. Prepn: Cox, Dodds, U.S. pat. **2,033,909** (1936 to Niacet Chemicals).

Dihydrate, crystals or granular powder. mp 125°. Loses 1 H_2O on drying *in vacuo* at room temp and all H_2O at 50°. Very sol in water; the aq soln is practically neutral.

THERAP CAT: Replenisher (calcium).

THERAP CAT (VET): May be used in hypocalcemic states.

1685. Calcium Mesoxalate. *Mesoxalic acid calcium salt;* calcium ketomalonate; calcium oxomalonate; ketomalonic acid calcium salt; oxomalonic acid calcium salt; Mesoxan. C_3CaO_5; mol wt 156.11. C 23.08%, Ca 25.67%, O 51.25%. Prepn: Scheiber, Hopfer, *Ber.* **53**, 908 (1920); Kobayashi, **Japan.** pat. **4157**('52), *C.A.* **48**, 5212a (1954); Yanagisawa, **Japan.** pat. **7463**('60), *C.A.* **55**, 5880a (1961).



Crystalline powder, dec 210-220°. Sparingly sol in glacial

AAPFCO Official Publication No.53 2000

K-11. Kelp - (seaweed) is the dried marine algae of the botanical divisions of Rhodophyta (red algae), Phaeophyta (brown algae), and Chlorophyta (green algae). (Official 1992)

K-12. Potassium Thiosulfate (fertilizer grade) is a product composed principally of $K_2S_2O_3$. It is most commonly available in aqueous solution. (Official 1999)

K-13. Potassium Hydroxide (KOH, caustic potash) is a solid, strong base containing 66% soluble potash (K_2O). (Official 1999)

[K-14 Potassium Phosphite is a product obtained when phosphorous acid is neutralized with potassium hydroxide (aqueous) and consists primarily of dipotassium phosphite (K_2HPO_3) in a stable aqueous solution. The phosphorus atom is in the oxidation state of III. The guaranteed percentage of elemental phosphorus shall be stated as part of the brand name, for example, Brand X 20% Phosphorus(P). It does not contain any significant amount of available phosphate.] (Tentative 1999)

CALCIUM (Ca) and MAGNESIUM (Mg) PRODUCTS

C-1. Agricultural Liming Materials ~~means a~~ [are] product[s] whose calcium and magnesium compounds are capable of neutralizing soil acidity [and which are used for that purpose]. (Tentative 1999)

C-2. High Calcic Liming Materials are liming materials containing at least twenty-five percent (25%) calcium. Further, at least ninety- one percent (91%) of the total calcium and magnesium is calcium. (Official 1976)

C-3. High Magnesic Liming Materials are those containing at least six percent (6%) magnesium. (Official 1976)

C-4. Dolomite is a material composed chiefly of carbonates of magnesium and calcium in substantially equimolar (1-1.19) proportions. (Official 1950)

C-5. Ground Limestone (course-ground limestone) is calcic or dolomitic limestone ground sufficiently fine for effective use as a liming material. (Official 1950)

C-6. Pulverized Limestone (fine-ground limestone) is the product obtained by grinding either calcitic or dolomitic limestone so that all materials will pass U.S. Standard No. 20 sieve (850 um opening) and at least seventy-five percent (75%) will pass a U.S. Standard No. 100 sieve (150 um opening). (Official 1989)

C-7. Air-slaked Lime is a product composed of varying proportions of the oxide, hydroxide, and carbonate of calcium, or of calcium and magnesium, and derived from exposure of quicklime. (Official 1950)

C-8. Hydrated Lime is a dry ~~product consisting chiefly of calcium and magnesium hydroxides~~ [material, made from burnt lime, which consists of calcium hydroxide or a combination of calcium hydroxide with magnisium oxide and /or magnesium hydroxide]. (Tentative 1999)

C-9. Quick Lime, ~~Burned~~[Burnt] Lime, Caustic Lime, Lump Lime, or Unslaked Lime are calcined materials comprised chiefly of calcium oxide in natural association with lesser amounts of magnesium, and which are capable of slaking with water. (Tentative 1999)

C-10. Ground Shells is the product obtained by grinding the shells of mollusks so that not less than fifty percent (50%) shall pass a U.S. Standard No. 100 sieve. The product shall also carry the name of the mollusk from which said product is made. (Official 1950)

C-11. Marl is a granular or loosely consolidated earthy material comprised largely of shell fragments and calcium carbonate precipitated in ponds. (Official 1958)

C-12. Ground Shell Marl is the product obtained by grinding natural deposits of shell marl so that at least seventy-five percent (75%) shall pass a U.S. Standard No. 100 sieve (150 um opening). (Official 1989)

C-13. Waste Lime (by-product lime) is any industrial waste or by-product containing calcium or calcium and magnesium in forms that will neutralize acids [soil acidity] It may be designated by prefixing the name of the industry or process by which it is produced, i.e., gas-house lime, tanners' lime, acetylene lime-waste, lime-kiln ashes, calcium silicate, etc. (Tentative 1999)

C-14. Agricultural Slag is a fused silicate whose calcium and magnesium content is capable of neutralizing soil acidity and which is sufficiently fine to react readily in soil. (Official 1958)

C-15. Gypsum, Landplaster or Crude calcium sulfate is a product consisting chiefly of calcium sulfate with combined water ($CaSO_4 \cdot 2H2O$) and is incapable of neutralizing soil acidity. It shall contain not less than seventy percent (70%) $CaSO_4 \cdot 2H_2O$. (Official 1981)

C-16. Magnesium Sulfate is a product consisting chiefly of that material with or without combined water: epsom salts ($MgSO_4 \cdot 7H_2O$), kieserite ($MgSO_4 \cdot H_2O$) and calcined kieserite ($MgSO_4$). (Official 1958)

C-17. Calcined Brucite is a magnesium product concentrated from brucite limestone. It consists chiefly of magnesium oxide with lesser amounts of calcium hydroxide, silicates and sesquioxides. (Official 1968)

C-18. Pelletized Limestone is pulverized limestone that has been granulated by the addition of a water soluble binding agent. (Official 1996)

C-19 Calcium Thiosulfate (fertilizer grade) is a product composed principally of CaS_2O_3. (Official 1999)

SULFUR (S) PRODUCTS

S-1. Sulfate of Ammonia. See N-7.

S-2. Ammonium Sulfate Nitrate. See N-8.

S-3. Sulfate of Potash-Magnesia. See K-8.

S-4. Double sulfate of potash and magnesium. See K-9.

S-5. Sulfate of Potash. See K-10.

S-6. Gypsum. See C-15.

S-7. Magnesium Sulfate. See C-16.

S-8. Manganese Sulfate. See M-1.

S-9. Ammonium Thiosulfate - See N-37. (Official 1990)

S-10. Potassium Thiosulfate See K-12. (Official 1999)

S-11. Calcium Thiosulfate See C-19. (Official 1999)

MANGANESE PRODUCTS (Mn)

[M-1. Manganese (II) Sulfate (manganous sulfate, manganese sulfate), and its hydrated forms, is a manganese(II) salt of sulfuric acid. Anhydrous manganese (II) sulfate has the formula of $MnSO_4$.](Tentative 1999)

Brady, N.C. 1974 Nature + Prop. of Soils

8th ed.

Without a doubt, earthworms have definitely increased both the size and stability of the soil aggregates, especially in virgin soils.

FACTORS AFFECTING EARTHWORM ACTIVITY. Earthworms prefer a moist habitat that is reasonably well aerated. For this reason, they are found mostly in medium-textured upland soils where the moisture capacity is high, rather than in droughty sands or poorly drained lowlands. They must have organic matter as a source of food. Consequently, they thrive where farm manure or plant residues have been added to the soil. A few species are reasonably tolerant to low soil pH, but most earthworms thrive best where the soil is not too acid. This may be because the nutrition of some species depends upon certain lime-secreting glands. These species require a high level of exchangeable calcium for optimum activity.

Soil temperature affects earthworm numbers and their distribution in the soil profile. For example, a temperature of about 50°F (10°C) appears optimum for *Lumbricus terrestris*, earthworm numbers declining above or below this temperature. This relationship, as well as soil moisture requirements, probably accounts for the maximum earthworm activity noted in spring and autumn in temperate regions.

Earthworm counts must take into consideration the ability of these organisms to burrow deeply into the profile, thereby avoiding unfavorable moisture and temperature conditions. Although species differ markedly in the depth of soil they normally penetrate, cold weather or dry upper soil conditions will drive them into a more favorable environment deeper in the profile. Penetration as deep as 3 to 6 feet is not uncommon in temperate regions. Unfortunately, in barren soils a sudden heavy frost in the fall may kill the organisms before they can move lower in the profile. Soil cover is important in maintaining a high earthworm population under such circumstances.

Because of their sensitivity to soil and other environmental factors, there is a wide variation in the numbers of earthworms in different soils. In very acid soils under conifers, an average of fewer than one organism per square meter is common. In contrast, more than 500 per square meter have been found on rich grassland soils. The numbers commonly found in arable soils is from 30 to 300 per square meter (see Table 5:4), equivalent to from 120,000 to 1,200,000 per acre–furrow slice. The biomass or wet weight for this number would range from perhaps 100 to 1,000 pounds per acre.

5:4. SOIL MICROANIMALS

Of the abundant microscopic animal life in soils, two groups are particularly important—nematodes and protozoa. A third—the rotifers—deserves mention. The three groups will be considered in order (see Table 5:1).

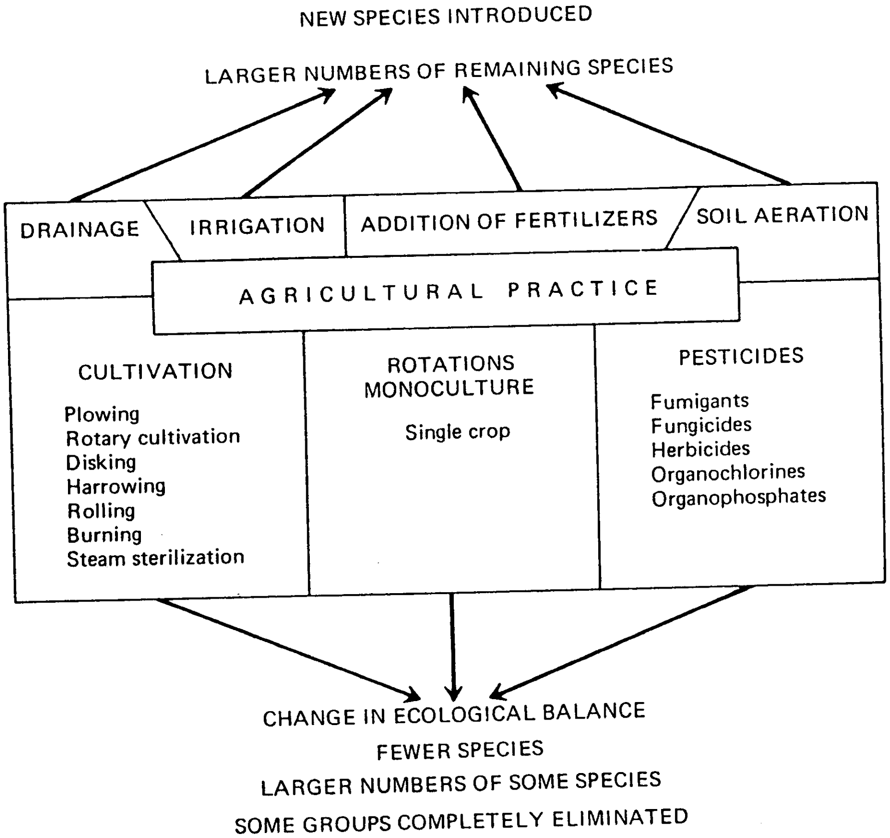


FIGURE 5:10. Ecological effects of agricultural practices on soil microarthropod population. The principles illustrated probably hold also for most other soil organisms. [*From Edwards and Lofty* (2).]

tend to reduce the species diversity and, especially with the soil fauna, the total organism population. At the same time, they can greatly increase or reduce the numbers of a given species, depending on the situation. Adding lime, fertilizers, and manures to an infertile soil will definitely increase the activities of certain bacteria and actinomycetes. Pesticides, on the other hand (especially the fumigants), can sharply reduce organism numbers, at least on a temporary basis. Likewise, the use of monoculture reduces species numbers but may actually increase the organism count of the remaining species.

Most changes in agricultural technology have ecological effects on soil organisms that can affect higher plants and animals, including man. For this reason, ecological side effects of modern technology must be carefully scrutinized. The effects of pesticides, both positive and negative, provide evidence of this fact.

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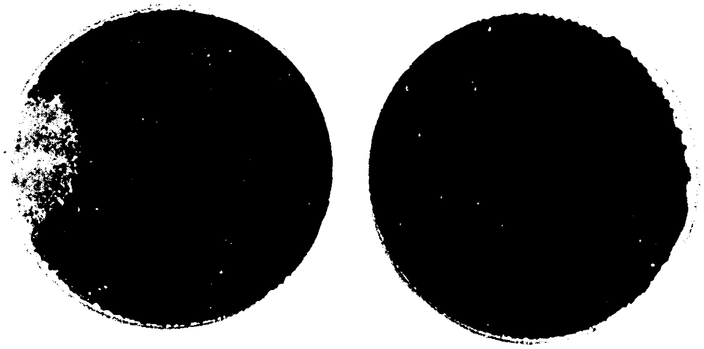

FIGURE 5:9. Organisms compete with each other in the soil. The growth of a fungus (fusarium) was rapid when this organism was grown alone in a soil (*left*), but when a certain bacteria (agrobacterium) was also introduced, the fungal growth did not appear. [*Photo courtesy M. A. Alexander, Cornell University.*]

such as penicillin, streptomycin, and aureomycin. Undoubtedly, many new and valuable substances of this type are yet to be discovered. Although the soil harbors numerous types of disease organisms, at the same time it supports others that are the source of life-saving drugs, the discovery of which marks an epochal advance in medical science.

5:13. EFFECTS OF AGRICULTURAL PRACTICE ON SOIL ORGANISMS

Changes in environment affect not only the number but the kinds of organisms in the soil. Placing either forested or grassland areas under cultivation brings about a drastic change in the soil environment. In the first place, the amount of plant residues (food for the organisms) is drastically reduced. Also, the species of higher plants are changed and generally less numerous. Monoculture or even rotations in the absence of weeds provides a much narrower range of original plant materials than is generally encountered in nature.

Tillage of the soil and applications of lime and fertilizer help to present a completely different environment to the soil inhabitants. Drainage or irrigation likewise can drastically affect soil moisture and aeration relations with their concomitant effects on soil organisms. Also, commercial agriculture transports organism species from one location to another, making possible their introduction in new areas.

It is obvious that agricultural practices have different effects on different organisms. There are a few generalizations that can be made, however. Figure 5:10, intended originally to show the ecological effects of agricultural practices on soil microarthropods, illustrates some principles relating to the total soil organism population. For example, agricultural practices generally

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Fert tech and use

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Lime-Fertilizer-Plant Interactions in Acid Soils[1]

Eugene J. Kamprath
North Carolina State University
Raleigh, North Carolina

Charles D. Foy
Agricultural Research Service, USDA
Plant Stress Laboratory
Beltsville, Maryland

Soils of the humid regions have developed under conditions in which rainfall exceeds evapotranspiration during most of the year. Under this condition there has been a gradual depletion of soil bases and the development of soil acidity. The soil clays often contain coatings of Fe and hydroxy Al. These materials significantly affect the retention and availability of fertilizer cations and anions in acid soils. The capacities of these soil materials to fix P, Mo, S, and B are influenced by liming.

Acid mineral soils at PH ≤ 5 often contain appreciable amounts of Al and Mn, which are detrimental to plant growth, in the soil solution. Optimum growth and efficient use of fertilizer nutrients in acid soils require the addition of lime to eliminate the toxic effects of Al, H, and Mn. This chapter describes some of the effects of soil acidity on plant growth and fertilizer nutrient availability and shows how these effects are modified by liming.

LIMING IN RELATION TO CATION EXCHANGE REACTIONS AND PLANT GROWTH

A. Cation Saturations and Soil Solution Contents of Acid Soils

Since 1950, certain concepts about acid soils have changed. Trivalent Al rather than exchangeable H^+ is now recognized as an important exchangeable cation in acid soils. Coleman and Thomas (1967) have given an excellent discussion of the basic chemistry of acid soils and the ion-exchange chemistry of Al.

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[1] Joint contribution from the Dep. of Soil Science, North Carolina State Univ., Raleigh, and the Plant Stress Laboratory, USDA-SEA-ARS, Beltsville, MD.

Fertilizer Technology and Use (3rd Edition).

Table 4-1. Exchangeable and percent saturation of Al at various pH levels in mineral soils.

Soil	pH	Exchangeable Al	Exchangeable Bases	Effective CEC	Al saturation
		meq/100 g			%
Paleudult†	4.5	0.91	0.20	1.11	82
	5.9	0.10	1.60	1.70	6
Paleudult‡	4.7	1.08	0.68	1.76	61
	5.7	0.09	2.14	2.25	4

† Kamprath, 1970. ‡ Richburg and Adams, 1970.

1. Mineral Soils

a. Cation Saturation

i. Exchangeable Aluminum and Basic Cations

Coleman and Thomas (1967) defined exchangeable cations in acid soils as those cations extracted with a neutral unbuffered salt. The sum of these cations was termed the *effective cation exchange capacity*. A neutral unbuffered salt solution will extract only cations that are held at active exchange sites at the particular pH of the soil. The exchangeable acidity extracted from soils with a neutral unbuffered salt is Al^{3+} (Lin & Coleman, 1960; Bhumbla & McLean, 1965).

Examples of the exchangeable Al^{3+} saturation of the effective cation exchange capacity (CEC) (sum of exchangeable Al^{3+} and bases) at different pH values is given in Table 4–1. Below pH 5 Al^{3+} generally accounted for over half of the exchangeable cations, while at pH 6 the effective CEC was essentially base-saturated. The highly leached soils of Brazil, primarily Ultisols and Oxisols, also have exchangeable Al^{3+} as the dominant cation below pH 5 (Pratt & Alvahydo, 1966).

Acid mineral soils at pH ≤ 5 have their active exchange sites occupied by Al^{3+} and at pH 6 these sites are countered by exchangeable bases. As will be discussed later, the relative cation saturations have an important effect on the cation composition of the soil solution and in turn on plant growth.

ii. Exchangeable Manganese

The exchangeable Mn^{2+} content of soils is related to soil pH. Highest levels of exchangeable Mn^{2+} are present when pH is ≤ 5 and decrease sharply when soils are limed to pH 6 (Foy, 1964; Jones & Fox, 1978).

b. Soil Solution Composition

i. Aluminum

The concentration of Al in the soil solution is related to pH of the soil, the Al saturation of effective cation exchange capacity, and the salt concentration of the system. The solubility of Al in displaced soil solution at various pH values is the same as the solubility of Al in water at the same pH values (Magistad, 1925; Pierre et al., 1932). At a pH of 5.5 the concentration of Al in the soil solution is quite low. However, as the pH drops from 5 to 4.5, the Al concentration increases markedly.

The Al concentration of the soil solution is related to the Al saturation of the effective CEC of the soil. The concentration of Al in the soil solution is quite low until the exchangeable Al^{3+} saturation exceeds 60% and then increases rapidly (Nye et al., 1961; Evans & Kamprath, 1970). When the Al saturation is $> 60\%$, the soil solution concentration of Al is > 1 mg/kg and may be as high as 5 or 6 mg/kg (Evans & Kamprath, 1970; Helyar & Anderson, 1974; Pearson et al., 1977).

As the salt concentration in the soil increases, the concentration of Al in the soil solution increases. This is due to the cation of the salt replacing some of the exchangeable Al^{3+}, which in solution undergoes hydrolysis, thereby lowering the pH and resulting in a greater solubility of Al (Black, 1968). The water-soluble Al content of a soil at pH 5.1 was doubled with heavy fertilization (MacLeod & Jackson, 1967).

ii. Manganese

Water-soluble Mn content of acid soils is closely related to the soil pH, being high below pH 5 but decreasing rapidly as pH increases to 6 (Fried & Peech, 1946; Berger & Gerloff, 1948; Morris, 1948). The addition of a soluble salt that causes a decrease in soil pH results in an increase in water-soluble Mn.

iii. Calcium

The predominant cation in the soil solution of most acid soils ranging from 0.75 to 19 meq/L is Ca, with most concentrations > 3 meq/L. Concentrations of soil solution Ca are increased considerably when acid soils are limed (Adams & Lund, 1966; Evans & Kamprath, 1970; Pearson et al., 1977).

2. Organic Soils

a. Cation Saturation—The exchangeable cation status of organic soils is difficult to describe, since different cations are complexed to various degrees by organic matter. Trivalent cations, such as Al^{3+}, are retained more strongly than are divalent cations, such as Ca^{2+} and Mg^{2+}. Extraction with a neutral unbuffered salt, however, can give an estimate of the readily exchangeable cations in equilibrium with the soil solution.

The negative charges of organic matter in acid soils are generally countered by Al. Less than 50% of the Al bound by organic soils was extractable with KCl. This indicates a large part of the Al is held very strongly by the organic matter (Hargrove & Thomas, 1981; Bloom et al., 1979).

The exchangeable acidity extracted from acid organic soils with a neutral unbuffered salt is primarily Al^{3+} with relatively little H^+ (Table 4–2).

Table 4-2. Content of exchangeable bases, H, and Al in an acid organic soil, 52% organic matter.†

Soil pH	Exchangeable		
	Bases	Al	H
	meq/100 g		
4.1	13.8	7.6	0.8
4.3	19.0	4.6	0.4
4.5	21.0	2.8	0.2
4.7	23.8	2.0	0.2

† E. J. Kamprath, 1967, unpublished data. Exchangeable cations extracted with a neutral unbuffered salt.

b. Soil Solution Composition—The soil solution of acid organic soils contains very little Al at pH ≥ 5 (Evans & Kamprath, 1970). Complexing of Al by organic matter reduces the amount of Al in soil solution. The Ca concentration of organic soils limed to pH 4.7 to 5.0 is generally relatively high and more than adequate for plant growth (Evans & Kamprath, 1970).

B. Plant Growth in Relation to Cation Saturation and Solution Concentration

Plant growth in acid soils as influenced by Al, Mn, and Ca has been discussed thoroughly in the monograph *Soil Acidity and Liming* (Adams, 1984b). Therefore, this discussion is limited to some of the general aspects of the problem.

1. Aluminum

a. Relative Tolerance of Plants—Plant species differ in their tolerance to Al. The relative tolerance to Al in decreasing order was corn (*Zea mays* L.), cotton (*Gossypium hirsutum* L.), and barley (*Hordeum vulgare* L.) (Foy & Brown, 1964). Soybeans [*Glycine max* (L.) Merr.] and cotton were considerably less tolerant to Al than corn when grown in solution culture (Rios & Pearson, 1964). Earlier work had indicated that lettuce (*Lactuca sativa* L.), beets (*Beta vulgaris* L.), timothy (*Phleum pratense* L.), and barley were very sensitive to Al; Radishes (*Raphonus sativus* L.), sorghum [*Sorghum bicolor* (L.) Moench], cabbage (*Brassica oleracea* L. var. *capitata*), oats (*Avena sativa* L.), and rye (*Secale cereale* L.) were medium sensitive; and corn was relatively tolerant (McLean & Gilbert, 1927; Ligon & Pierre, 1932). However, within a given species, there may be a wide range in tolerance to Al (Foy, 1974).

b. Aluminum Saturation and Solution Concentration—Growth of plants has been found to be related to the Al saturation of the effective CEC (Kamprath, 1970; Evans & Kamprath, 1970; Fox, 1979; Farina et al., 1980; Alley, 1981). When Al saturations were > 50 to 60%, growth of corn was drastically decreased on mineral soils (Kamprath, 1970; Fox, 1979; Alley, 1981). Yields of corn under field conditions were close to 90% of maximum when Al saturations were ≤ 30%. Root growth of corn was not decreased until the Al saturation was 60% (Brenes & Pearson, 1973) Growth of more sensitive crops such as cotton, soybeans, and alfalfa (*Medicago sativa* L.) was optimum when the Al saturation was close to zer (Kamprath, 1970; Alley, 1981). Maximum growth of six Stylosanthes spe cies was obtained at an Al saturation of < 5% (de Carvalho et al., 1980).

The addition of a high rate of KCl to an unlimed soil increased the con centration of Al in the soil solution and markedly reduced the growth o sweet corn (Ragland & Coleman, 1959) roots. Therefore, where high rate of fertilization are used, it is desirable that the CEC have a relatively lo Al saturation to avoid the detrimental effects of Al.

Root growth of cotton in acid subsoils was related to the activity of A in the soil solution. When the molar activity of Al^{3+} was $> 0.5 \times 10^{-5}$, co ton root decreased (Adams & Lund, 1966). As the concentration of Ca an other basic cations increased, Al toxicity was less severe. Foy et al. (1969 also reported that, at lower levels of Ca in the nutrient solution, differenc in Al tolerances between two varieties of soybeans became larger. Walla et al. (1971) have suggested that Ca acts as a detoxifier of other ions prese in excess.

The pH for optimum growth of plants is lower for organic soils than f mineral soils. Growth of soybeans and corn on organic soils was optimu in the pH range of 4.6 to 5.0 (Welch & Nelson, 1950; Evans & Kamprat 1970; Mengel & Kamprath, 1978). Aluminum is complexed by the orga matter and at pH 5 the soil solution Al is very low. The addition of hum acid to a water culture prevented the occurrence of Al toxicity in alfal (Brogan, 1964).

2. Manganese

There is a close correlation between the water-soluble Mn content soils and the Mn toxicity symptoms (Berger & Gerloff, 1948; Morris, 19 Adams & Wear, 1957; Parker et al., 1969). Liming to a pH of around generally decreased the water-soluble Mn to a low level and eliminated toxicity symptoms of cotton, soybeans, and Korean lespedeza (*Lespe stipulacea* Maxim.).

Manganese toxicity of alfalfa occurred on several acid soils when exchangeable Mn^{2+} content of the air-dried soils was 50 mg/kg Mn more. Alfalfa yields were generally highest when the exchangeable M content was reduced to ≤ 20 mg/kg by liming (Foy, 1964).

Toxicities are less likely to occur on soils with a high CEC beca more Mn^{2+} is held on exchange sites, and the concentration of Mn in soil solution is decreased (Adams, 1984a). Addition of peat to soils which alfalfa had shown Mn toxicity alleviated the problem (Foy, 19 Apparently the peat complexed the Mn, thereby reducing its solubi Manganese toxicity of plants grown in a nutrient solution was red when the Ca concentration of the solution was increased (William Vlamis, 1957).

B. Consumption Data

1. *Liming Materials*

Use of agricultural limestone in the USA was very low until 1935 [illegible] new federal soil conservation programs provided financial assistanc [illegible] farmers for applying lime, and annual lime use increased > 10-fold in [illegible] (Barber, 1967). Since then, it has continued to increase steadily from [illegible] 21 million metric tons in 1960 to more than 32 million metric tons in [illegible] (Table 12–4). This may be related to more educational programs, [illegible] application equipment, and a greater number of lime vendors. A [illegible] amount of liming materials now is applied by custom applicators with [illegible] handling equipment. Increased N use results in an increase in soil ac [illegible] which requires more frequent lime applications. Effects of lime app [illegible] tions are discussed in chapter 4 of this book. Use of gypsum and [illegible] containing materials for direct soil application has not increased appr [illegible] bly since 1970 (Table 12–4). Use of dolomitic lime for soils requirin [illegible] applications may account for variable consumption of Mg materials [illegible] 1960.

2. *Micronutrients*

The Crop Reporting Board of the Statistical Reporting Service [illegible] U.S. Department of Agriculture began publishing summaries of mic [illegible] trient use in 1968. Data in Table 12–5 were obtained from the know [illegible]

Table 12-4. Amounts of agricultural lime, gypsum, and Mg materials used [illegible] direct application to soils in the USA.

Year	Lime†	Gypsum‡	Mg materia[illegible]
	1000 metric tons		
1960	21 076	1 300	–
1965	26 439	1 410	4.6
1970	34 423	1 150	1.8
1975	32 262	1 630	3.6
1980	32 648	1 860	5.0

† Levenson et al. (1981).
‡ Statistical Reporting Service (1961, 1966, 1971, 1976, 1981).

Table 12-5. Amounts of micronutrients sold in the USA (Statistical Reporti[illegible] Service, 1968, 1972, 1975, 1978, 1981).

Year	Cu	Fe	Mn	Mo	Z[illegible]
	1000 metric tons†				
1967–1968	2.2	3.1	10.5	0.07	13.1
1971–1972	0.6	1.2	11.2	0.09	14.4
1974–1975	0.5	1.9	10.3	0.13	12.2
1977–1978	1.2	3.9	16.8	0.10	32.1
1980–1981	1.4	6.4	12.7	0.01	39.9

† Amounts expressed on elemental basis.

[illegible] cers of Cu, Fe, Mn, Mo, and Zn sources for use in both mixed and direct [illegible] plication in each region of the USA since 1967. Boron use data were not [illegible] luded since there were so few producers of fertilizer B. However, recent [illegible] ports have estimated 1982 use at 3037 metric tons of B (Lyday, 1982).

[illegible] Amounts of Cu and Fe used in the USA decreased from 1968 to 1972 [illegible] d increased thereafter (Table 12–5), but the amount of Cu sold in 1980 [illegible] was lower than in 1967. Decreased use of Cu was related to lower con[illegible] mption in Florida, where recommended rates were decreased. Toxicities [illegible] plants can result if Cu levels are too high, especially on acid, sandy soils. [illegible] mounts of Zn and Mn are the highest because these micronutrients are [illegible] commended for such large-area crops as corn, wheat (*Triticum aestivum* [illegible]), soybeans, and rice. Rapid increases in Zn usage since 1975 are related [illegible] ctual increases in consumption as well as to the inclusion of more pro[illegible] cers reporting Zn sources, including some industrial by-products.

[illegible] The figures in Table 12–5 are reported on an elemental basis; thus, the [illegible] ual amount of materials used is much higher. This method of reporting [illegible] necessary since the nutrient content of the micronutrient sources var[illegible] widely. The tonnage of micronutrient materials sold in this country is [illegible] ly about 1% of the tonnage of NPK materials.

C. Regulations

[illegible] Fertilizer regulations are governed by each state in the USA. In 1963, [illegible] eneral proposal was made that minimum percentages for the allowable [illegible] ls of micronutrients be established and guaranteed on fertilizer labels. [illegible] niform state fertilizer bill for general standardization was proposed by [illegible] AAPFCO for legislation by each state to simplify interstate shipping of [illegible] lizers. The suggested minimum percentages acceptable for registra[illegible] of each nutrient are shown in Table 12–6. Control officials emphasized [illegible] these were not to be considered as recommended levels; they are sim[illegible] levels that can be determined accurately in control laboratories. One

[illegible] ble 12-6. Suggested minimum percentages of secondary and micronutrients that [illegible] an be guaranteed on a fertilizer label and also allowable deficiencies in fertilizer grades (Assoc. of Am. Plant Food Control Officials, 1968).

[illegible]utrient	Minimum guarantee, %	Allowable deficiency†
Ca	1.00	0.2% + 5% of amount guaranteed
Mg	0.50	0.2% + 5% of amount guaranteed
S	1.00	0.2% + 5% of amount guaranteed
B	0.02	0.003% + 15% of amount guaranteed
Cu	0.05	0.005% + 10% of amount guaranteed
Fe	0.10	0.005% + 10% of amount guaranteed
Mn	0.05	0.005% + 10% of amount guaranteed
Mo	0.0005	0.0001% + 30% of amount guaranteed
Zn	0.05	0.005% + 10% of amount guaranteed

[illegible] entage of element below the guaranteed percentage on the fertilizer label that is [illegible] ed before the element is considered deficient in the fertilizer grade.

disadvantage of allowing such low levels of micronutrients to be guaranteed on fertilizer labels is that these amounts applied to soils at the usual NPK rates are too low to be of much benefit to crops if there are micronutrient deficiencies. Some states have set minimum guarantee levels more in line with their recommended levels of these elements.

This bill also states that such elements shall be deemed deficient in the fertilizer formulation if they are lower than the guarantee on the label by an amount exceeding the values shown in Table 12–6. For example, the allowable deficiency would be 0.205% Zn in a fertilizer grade containing 2.0% Zn. Guarantees and allowances vary by states. Increasing numbers of fertilizers are being offered with a guarantee for micronutrient content. Frequency of deficiencies appears to be in line with those found for the macronutrients.

Another suggestion was that the fertilizer laws require a warning or caution statement on the label for any product containing > 0.03% B or 0.001% Mo in water-soluble form. This is to prevent toxicity of B to the plant through overuse and as a safeguard against Mo toxicity to animals resulting from consumption of forage with a high Mo concentration. To date, 38 states have adopted portions of this bill in their fertilizer laws.

III. METHODS AND RATES OF APPLICATION

The use of secondary and micronutrient fertilizers is governed by principles affecting both the need for and application of these nutrients. Needs are determined by crop requirements and soil conditions, which include amounts of a given nutrient present and reactions that affect their availability to plants. Efficient and effective use of any fertilizer depend on the source, rate, and method of application. Also, the philosophy of whether the crop or the soil is being fertilized must be considered. Soil fertilization with certain nutrients also may result in substantial residual effects, and these need to be evaluated in long-term studies. The focus in this section is on rate and method of application, but sources and time of application also are included as applicable. Major emphasis is on research results published since 1971, and residual effects are discussed briefly.

A. Calcium

The rather large amount of exchangeable Ca^{2+} in the soil that normally dominates the exchange complex satisfies the Ca requirements of most crops. Under acid conditions the amount of exchangeable Ca^{2+} in soil decreases, whereas exchangeable Al^{3+} increases, and Al toxicity may eventually cause reduction in plant growth. Correction of this acid condition is accomplished by liming with either calcitic or dolomitic lime, which maintains an abundant supply of Ca in the soil.

An international symposium on Ca nutrition of economic crops was held in 1977 (Shear, 1979). The proceedings provide excellent information on the nature of the problem and approaches as to correction, especially on horticultural crops.

Calcium deficiencies have been reported in some crops even though soil acidity may not have been extreme. Such deficiencies are usually localized in fruits, storage organs, or shoot tips—plant parts that are naturally low in Ca. Some examples are poor kernel formation in peanuts (*Arachis hypogaea* L.), bitter pit in apples (*Malus sylvestris* Mill.), blossom end rot in tomatoes (*Lycopersicon esculentum* Mill.), tipburn in lettuce (*Lactuca sativa* L.), and black heart of celery *(Apium graveolens)*. Many other examples existing in fruits and vegetables have been listed by Shear (1975).

The field crop most likely to show Ca deficiency due to the need for a liberal supply of Ca for proper development of its subterranean fruit is peanuts. Walker (1975) reviewed the Ca requirement of peanuts and reported lime to be somewhat effective, but the more soluble $CaSO_4$ (gypsum, or "landplaster") was superior. Gypsum is usually applied at 600 to 800 kg/ha just before fruiting in a 45-cm band over the row. Only a few definitive studies have been conducted to establish the optimum rate of gypsum for peanuts. Yield responses likely are mediated by environmental conditions and are not guaranteed, even under low soil Ca levels. Furthermore, it has not been shown that the Ca rate should be increased with decreasing levels of soil Ca. Essentially full yield response has been obtained with gypsum rates as low as 200 kg/ha (Cox, 1972), but the recommended rates usually are higher for several reasons. The yield and grade may continue to increase with increasing rate of applied Ca; Walker et al. (1979) found this to be true even above 600 kg of gypsum/ha. Thus, it is economical to apply the higher rates because of the increased value of the crop. Adequate Ca also ensures good quality seed that germinate well (Cox et al., 1976), and high Ca rates may help reduce certain forms of pod rot disease (Hallock & Garren, 1968; Walker et al., 1979).

The term *gypsum* is used in a general sense to mean a material with a calcium sulfate base. Little pure $CaSO_4 \cdot 2H_2O$ is sold; most commercial sources range from 50 to 90% $CaSO_4$. Textures range from very fine to granular, and some by-product precipitated materials vary in particle size due to lumps forming in the damp material. Because fine materials react more quickly than coarser materials (Daughtry & Cox, 1974; Keisling & Walker, 1978), fine materials may have an advantage for peanuts if applied at the typical early flowering stage. Coarser materials are often applied by bulk spreading very early in the growing season, which is the only period when such equipment may be used without damaging plants. All materials seem to be effective (Hallock & Allison, 1980), but the broadcast rate must be about twice the banded rate due to the extra material that covers the area between the rows.

Although generally considered less effective than gypsum, limestone was a satisfactory source of Ca for 'Florunner' peanuts (Adams & Hartzog, 1980). The rate needs to be higher than that for gypsum (Adams & Hartzog, 1979), and lime must be incorporated at a very shallow depth to affect primarily the fruiting zone in the soil. Sullivan et al. (1974), however, found this treatment completely ineffective with cv. NC5.

Foliar applications of Ca are not effective with peanuts since there is little xylem flow to carry the nutrient to the developing fruit. A similar problem exists with head lettuce. Misaghi et al. (1981) found foliar sprays of either calcium chloride ($CaCl_2$) or calcium nitrate [$Ca(NO_3)_2$] ineffective in reducing tipburn incidence and severity. The deficiency occurs on the inner and middle leaves, which are not exposed after head formation. Soil applications of $Ca(NO_3)_2$ were not effective, but $CaCl_2$ at 224 kg/ha or greater increased tissue Ca and reduced tipburn in one of six trials.

Among the horticultural crops showing Ca deficiency, apples have been studied most extensively. Recently, Lidster et al. (1978a, 1978b) studied effects of prebloom and summer foliar applications of Ca as well as a postharvest dip of the fruit in reducing breakdown development in stored 'Spartan' apples. They found prebloom $CaCl_2$ sprays to be ineffective, but summer sprays (0.6% $CaCl_2$) applied four times at 2-week intervals beginning in mid-July increased fruit Ca levels and decreased breakdown development significantly. A postharvest dip in 4% $CaCl_2$ was even more effective, but the most effective method was to combine summer sprays with the postharvest dip.

Application of lime and minimizing the K supply have been used to reduce Ca deficiency, termed *metsubure,* in taro [*Colocasia esculenta* (L.) Schott] corn (Tanabe & Ikeda, 1980, 1981). Both treatments affected the K/Ca ratio in the corms. There was no effect of N source as sometimes occurs with other crops, but varietal differences were noted. There appears to be great potential to develop varieties for tolerance to low Ca conditions for this crop as well as for many others.

B. Magnesium

Availability and plant uptake of Mg, like Ca, decreases under acid soil conditions due to a pH effect and also due to the direct loss of Mg from the root zone. Increasing the pH of a soil, even with a calcitic source of lime, often increases the uptake of Mg (Christenson et al., 1973). However, the primary method to ensure an adequate level of Mg in acid soils is by applying dolomitic lime. This has been the dominant source of Mg, even in the South Atlantic states, where Mg deficiencies should be most severe. The most common fertilizer sources of Mg are MgO and the sulfate form, usually applied as potassium sulfate–magnesium sulfate ($K_2SO_4 \cdot MgSO_4$).

The status of Mg research in the southeastern USA as well as factors affecting the availability of Mg to plants and animals were discussed in a symposium in 1972 (Jones et al., 1972). Grass tetany, a Mg deficiency occurring during lactation in ruminant animals, is the most important problem associated with Mg nutrition. Some low Mg levels in plants also were noted, but most of these were predictable by soil test data. Research results indicated only a small number of yield responses to Mg fertilization.

Soil test interpretations may have changed somewhat since that symposium was held in 1972. At that time, only one state based Mg availability on the cation saturation ratio in soil. This method is becoming more popular, but little substantiating field research has been published. In greenhouse work, McLean and Carbonell (1972) found that 6 to 10% Mg saturation was an adequate level for most Ohio soils, whereas < 5% Mg saturation is considered deficient and < 10% is low in North Carolina.

General recommendations for Mg based on soil tests are to use dolomite if lime is needed or Mg at 20 to 40 kg/ha if it must be applied in NPK fertilizers. There have been no recent studies, however, to verify these recommendations. Gallaher et al. (1975) in a 3-yr Mg rate study with grain sorghum [*Sorghum bicolor* (L.) Moench], found a positive yield response the first year, a trend in the second, and no response in the 3rd yr. The maximum Mg rate (68 kg/ha as $MgSO_4$) was required the 1st yr and only 34 kg/ha the second. Klein et al. (1981) reported that 44 kg/ha of $MgSO_4$ was the optimum rate for potatoes (*Solanum tuberosum* L.). This rate had little effect on yield but improved quality by reducing discoloration, which was associated with lower amounts of phenols and more lipids and phospholipids in the tubers. Jones and Jones (1978) compared $MgSO_4$ with dolomite at 20 kg of Mg/ha for tomato production. Yields were increased by both sources in one of three crops, but the sulfate form was more effective than dolomite in increasing leaf Mg in all crops.

Application of $MgSO_4$ does not always increase tissue Mg concentration appreciably. In three Mg rate studies in Kansas, corn leaf Mg levels at silking ranged from 0.10 to 0.12% and showed little response up to 270 kg/ha of Mg as $MgSO_4$ (Whitney, 1973). Lack of a response seemed to be associated with very high Ca activities in these soils.

C. Boron

Sodium tetraborate is the main source of fertilizer B. Levels of hydration among the materials available result in B concentrations ranging from 11 to 20%. The most concentrated form is especially adapted for foliar sprays. Boron may be applied to either the soil or the foliage to correct a deficiency; Gupta and Cutcliffe (1978) found both methods to be effective in controlling brown heart in rutabaga (*Brassica napobrassica* L.). Several foliar applications at a low rate were more effective than a single application at a higher rate; this has been shown with other crops and is apparently due to the immobility of B in leaf tissue (Anderson & Ohki, 1972).

The rate of B required to correct a deficiency in annual crops is low. Murphy and Lancaster (1971) obtained maximum cotton yields with either 0.5 kg of B/ha applied to the foliage (fives times at 0.1 kg/ha each) or > 0.3 kg/ha applied to soil. Hill and Morrill (1974) found a similar rate sufficient to maintain the quality of peanuts; B could be applied any time up to 60 d after planting and still be effective for that crop. Rates > 1.0 kg/ha may reate B toxicity. Blamey and Chapman (1979) noted yield reductions even before observing B toxicity symptoms in peanuts when high rates were applied to a sandy loam. Rates of 2 to 3 kg/ha are typically applied to alfalfa (*Medicago sativa* L.) when grown on finer-textured soils.

D. Chlorine

Although Cl is readily leached from surface soils in regions of high ainfall, its supply is usually replenished by applications of potassium chlode (KCl), the predominant K source. In regions of low rainfall, Cl may

A dietary Ca/P ratio between 1:1 and 2:1 is assumed to be ideal for growth and bone formation, since this is approximately the ratio of the two minerals in bone (Underwood, 1981). The Agricultural Research Council (1980) agreed that this is a generally safe range. Ruminants can tolerate a wide range of Ca:P ratios, particularly when their vitamin D status is high (Underwood, 1981). Ratios between Ca and P as high as 2:1 have been shown to be beneficial in reducing urinary calculi. When calculi problems are encountered, higher levels of Ca may be advisable. Ratios between Ca and P of 7:1 in the diet have been reported to be satisfactory for cattle, provided P is adequate (NRC, 1976).

Available moisture and stage of growth may markedly affect concentrations of P in forages, while having little effect on Ca concentrations. Spring rain promotes new growth and relatively high P concentrations. As plants mature and P concentrations decrease, the P available to animals would decrease (Beeson & Matrone, 1976).

Calcium concentrations in pasture plants can be increased by increasing the proportion of legumes and herbs in the forage. High rates of K fertilizer, or high K levels in soil, can reduce Ca concentrations, particularly on sandy soils (Grunes et al., 1970; Comm. Miner. Nutr., 1973).

Poultry and pigs *(Sus scofra domesticus)* appear to be less tolerant of high dietary Ca/P ratios. The optimum ratio for growing chicks and pigs lies between 1:1 and 2:1. Ratios below this are well tolerated, and ratios greater than 3:1 are poorly tolerated. For laying hens, the permissible ratio is considerably higher due to their greater requirements for Ca than for P. The P requirements of poultry and pigs, but not of ruminants with a functioning rumen, increase as the proportion of dietary P occurring as phytate increases (Underwood, 1981).

The National Research Council (1980) indicated that humans appear to be able to tolerate ratios of Ca/P between 1:2 and 2:1. They stated that some have concluded that the Ca/P ratio ideally should remain at or above 1. In setting their recommended allowances for both Ca and P, a Ca/P ratio of unity has been maintained. They also indicated that for adult humans, wide variation of the Ca/P ratio in the diet is tolerated, provided the amount of vitamin D is adequate (NRC, 1980). A recent survey (McCarron et al., 1982) indicates that low Ca intake may be related to increased hypertension in people in the USA.

3. *Interactions of Phosphorus and Other Elements*

In a field experiment in which available Zn in the soil was not high, P fertilization depressed concentrations of Zn in table beet roots, petioles, and blades; in cabbage heads *(Brassica oleracea* var. *capitata)*; in snap bean pods (*Phaseolus vulgaris* L.) and immature seeds; and in immature pea seeds (*Pisum sativum* L.). However, when Zn fertilizer was added, P fertilization increased the Zn concentrations (Peck et al., 1980). In solution culture, low Zn levels greatly increased P concentrations in okra [*Abelmoschus esculentus* (L.) Moench] (Loneragan et al., 1982). It is known whether this also occurs in the field.

High levels of P sometimes decrease Fe concentrations in plan (Brown, 1961). In their review, Murphy et al. (1981) indicated that hig levels of P frequently depress uptake of Zn, Fe, and Cu by plants.

In pigs, phytate has been shown to increase levels of Zn required i feed. For monogastric animals, high levels of dietary phosphate reduce F absorption, presumably by the formation of insoluble ferric phosphat (Underwood, 1977, 1981). There have been some reports that high level of dietary phytate reduce Fe absorption in monogastric animals (Underwood, 1981). However, Welch and Van Campen (1975) found that Fe absorption by rats was not related to phytic acid levels in soybean seeds.

High levels of phosphate have also been shown to reduce Fe absorp tion in man. Severe Zn deficiency in Middle East countries has occurred i young males eating diets consisting predominantly of unrefined cereal high in phytate (Underwood, 1977).

C. Calcium, Magnesium, and Potassium

Uncomplicated deficiencies of Ca, Mg, and K are apparently rare i both animals and humans. These nutritional disorders are usually due to a imbalance among these elements, to imbalance of one or more of these with other elements, or to interferences with the utilization of dietary Ca o Mg.

A conditioned Ca deficiency called *milk fever* is fairly common i heavily producing, heavily fed milk cows soon after the birth of the calve (Underwood, 1981). Milk fever apparently results from deranged Ca metabolism within the animal body. This disease has not responded to increase in dietary levels of Ca. A deficiency of vitamin D may lead to poo absorption of dietary Ca and Mg.

The range of Ca concentrations in plants is predominately a characteristic of the plant species, and is less dependent on the level of available C in the soil. Most legumes contain more Ca than do grasses. Cereal grain are generally low in Ca, and Ca supplements are frequently provided t grain-fed animals to provide desired Ca/P ratios.

Milk is a major source of Ca in many human diets. The Ca concentration in milk is nearly constant and is not altered by changes in the level o Ca in the cow's ration.

As far as direct nutritional effect of K fertilizers is concerned, Wilde (1968) has stated: "If you can induce the plant to grow, it will always contain enough K for animal nutrition. Man and animals suffer K deficiencie only when ill for reasons other than improper food composition.

A conditioned deficiency of Mg, known as *grass tetany* or *grass staggers,* is a major problem to cattle producers under some circumstances. This problem has been reviewed by Grunes et al. (1970), Grunes (1973), Mayland and Grunes (1979), and other articles in the publications by Rendig and Grunes (1979) and Littledike et al. (1981). The level of Mg in forages has been related to soil parent material in several regions of the USA

(Kubota et al., 1980). Grass tetany affects, and is frequently fatal to, lactating cows that graze on certain grass or small grain forages during the cool seasons of the year. Similar animals that graze on legumes at these same times rarely show evidence of this disease, and there are very few instances of the disease during the warm, summer months. The level of Mg, and often the level of Ca, in the blood of the animals is very low at the time the disease strikes, and affected animals will recover if they are given timely intravenous injections of the proper forms of Mg and Ca.

A wide K/(Mg + Ca) or K/Mg ratio within the forage grass has been associated with this problem. High levels of available K in the soil tend to depress concentrations of Mg in grasses, and increased incidence of grass tetany has been observed following heavy applications of K in fertilizers or manure. However, as pointed out by Grunes et al. (1970), the etiology of the problem is complex and serious outbreaks of grass tetany have occurred on pastures that have not been fertilized with K. High levels of N in the soil also increase the incidence of grass tetany.

On acid, coarse-textured soils, the use of Mg fertilizers or dolomitic limestone has been effective in increasing the Mg concentration in the grass and in decreasing the incidence of grass tetany. This practice has been less successful on finer-textured soils or soils of higher pH. Incorporation of the dolomitic lime into the soil increases its effectiveness.

Whenever liberal application of K and/or N fertilizers are applied for the grass species that grow well in the cool seasons and whenever these grasses are grazed by lactating cows or ewes, special attention should be given to maintenance of a high level of daily Mg intake by the animals. On some soils, Mg fertilization of the soil will be effective for this purpose, but on other soils, dusting of pastures with magnesium oxide (MgO) or the use of a mineral supplement high in Mg may be necessary.

Adding magnesium sulfate ($MgSO_4$) to drinking water is helpful but some diarrhea may occur. Magnesium acetate [$Mg(C_2H_3O_2)_2$] may be used instead of $MgSO_4$. To be effective, the drinking trough must be the only source of water.

On wheat pasture, fertilization with N has increased frothy bloat of younger cattle (Stewart et al., 1981). Bloat-producing pastures were shown to be low in dry matter and soluble carbohydrates and high in crude protein, soluble N, soluble protein N, and soluble nonprotein N. Interestingly, these indices occur in the same relative standings in forages that tend to produce grass tetany. Bloat-producing pastures were lower in total fiber, but this constituent has not been related to grass tetany.

Magnesium deficiencies of humans and monogastric animals have been observed, but there are no recorded cases where these deficiencies have been traced to a deficiency of available Mg in the soil. However, as indicated by Grunes et al. (1970), severe Mg deficiency has occurred in children in developing countries eating Mg-poor foods such as cornstarch, yam (*Dioscorea* sp.), and cassava (*Manihot esculenta* Crantz). Recently, there has been a good deal of interest in Mg in relation to human nutrition (Cantin & Seelig, 1980; NRC, 1980; Seelig, 1980; Wacker, 1980). The use

of stable isotopes of Mg (Schwartz et al., 1980) should markedly increas
Mg research and understanding in humans.

D. Sulfur

Sulfur moves from the soil into the plant as the sulfate ion (SO_4^{2-}
Within the plant the S is reduced to sulfide (S^{2-}) and incorporated into th
essential amino acid cysteine. Some of the cysteine is converted t
methionine, another essential S amino acid, and from methionine int
other organic S compounds in the plant. Most of the cysteine an
methionine formed is combined into the polypeptide chains of protein ac
cording to the genetics of the plant and so cysteine and methionine do nc
accumulate in the free or uncombined form in normal plants. Cysteine
methionine, and some of the other organic S compounds are essential to a
living cells, both plant and animal. The metabolism of S in plants has bee
reviewed by Thompson et al. (1970).

When SO_4^{2-} is taken up by the plant in amounts greater than neede
for protein synthesis, SO_4^{2-} will accumulate in the plant. The presence o
SO_4^{2-} in the tops of plants may be a useful indicator of an adequate suppl
of available S in the soil, unless some factor other than S supply is limitin
the rate of protein synthesis (Ensminger & Freney, 1966).

When a monogastric animal eats a plant food, the protein is hydro
lyzed to release the essential S amino acids and these are then absorbe
from the GI tract and incorporated into animal proteins. Monogastric ani
mals cannot reduce SO_4^{2-} and so they must obtain the essential S amin
acids from their diet. Monogastric animals can convert methionine to cys
teine and their requirement for both of these can be met by an adequat
level of methionine in the diet. Monogastric animals also require two S
containing vitamins. Very small amounts of dietary SO_4^{2-} can be utilized b
animals in the formation of SO_4^{2-}esters such as the chrondroitin sulfate o
connective tissue. However, most of the SO_4^{2-} ingested by monogastric ani
mals is excreted in the urine within a few days of ingestio
(Dziewiatkowski, 1970). Excess dietary SO_4^{2-} is not detrimental to the ani
mal, except as it may accentuate a Mo–Cu interaction that will be discusse
in the sections on trace element fertilizers.

The effect of S fertilizers added to a S-deficient soil on the nutrition o
monogastric animals, including people, is to provide higher yields an
higher production per hectare of the essential S amino acids and protein.

The nutritional value of each unit of protein is determined by the ge
netic control over the ratios of S amino acids to other amino acids in th
plant protein. Plant proteins, and particularly the proteins in the seeds o
some of the legumes such as soybeans, are usually low in S amino acids i
relation to the requirements of monogastric animals. Supplementation o
diets of pigs and chickens, fed largely corn plus soybean protein, wit
methionine or high methionine proteins such as fish meal is a commo
practice. The S (or more accurately S amino acid) requirements of human
have been reviewed by Swendseid and Wang (1970). Deficiency of S amin

Goselin 1984

Gosselin R.E 1984

48 Sulfamic Acid 48

midosulfonic acid

oxicity Rating: 3. Recommended for flame-proof- g fabrics and wood and also sold as a swimming ol additive. Toxicity rating of 3 in rats (minimal hal dose less than 1.6 gm./kg.). Solutions proce irritation on subcutaneous injection in rats, the conjunctiva of rabbits and on cutaneous application to humans. Circulation and respiration were not greatly influenced after i.v. injection of 100 mg./kg. in rats. Because sulfamic acid is a strong acid, concentrated solutions may produce corrosive effects like mineral acids.

ee also: Acid, *Reference Congener in Section III.*
ef.: Ambrose, 1943.

49 Thioglycolic Acid 49

ercaptoacetic acid

stronger acid than acetic acid. Concentrated lutions on the skin produce chemical burns and istering. An assertion that the acid releases significant amounts of hydrogen sulfide needs additional study.

See also: Acid, *Reference Congener in Section III.*
Ref.: Merck and Co., 1976.

50 Trichloroacetic Acid 50

CA

corrosive organic acid which rapidly penetrates nd "fixes" tissues. Systemic effects are presumbly secondary to gastrointestinal damage and to acidosis, not due to the trichloroacetate ion except after large doses; see also Sodium Trichloroacetate in the index.

See also: Acid, *Reference Congener in Section III.*
Ref.: Woodward et al., 1941.

Caustic alkalis

51 Lye 51

Caustic potash, Caustic soda

Any strong alkali, usually sodium or potassium hydroxide or carbonate. A corrosive poison.

See also: Lye, *Reference Congener in Section III.*

52 Sodium Carbonate 52

Solvay soda, Soda ash

The technical decahydrate is known as sal soda or ashing soda. As with other alkaline corrosives the azard is related more to concentration than to dose. Concentrated solutions tend to produce local necrosis of mucous membranes.

See also: Lye, *Reference Congener in Section III.*

53 Sodium Sesquicarbonate 53

Double salt of sodium carbonate and sodium bicarbonate. Presumably less corrosive than sodium carbonate but more alkaline than sodium bicarbonate.

See also: Lye, *Reference Congener in Section III.*

54 Calcium Oxide 54

Quicklime, Burnt lime, Unslaked lime

Unslaked lime (quicklime) is calcium oxide (CaO); it reacts with water with the evolution of heat, to form calcium hydroxide ($Ca(OH)_2$). This reaction on the skin or in the mouth produces both a thermal and a caustic burn. Quicklime tends to form clumps in the conjunctival sac, which are dangerous and difficult to wash out.

See also: Lye, *Reference Congener in Section III.*
Ref.: National Safety Council, Date Unknown d.

Gosselin R.E., R P Smith, H.C Hodge, J.E Braddock
Clinical Toxicology of Commercial Products 5th Ed. 1984
Williams + Wilkins, Baltimore

55

55 Lime (Slaked)

Calcium hydroxide

Slaked lime (calcium hydroxide) is a simple alkali; because of low solubility and apparently slow penetration into tissues, its aqueous solutions are not corrosive. Lime water, which is a saturated aqueous solution of $Ca(OH)_2$ (0.15%), has a pH of about 12.4, but unlike sodium or potassium hydroxide solutions of this pH, it usually produces only superficial opacities of the cornea, apparently because it penetrates corneal epithelium so slowly. In contrast, an aqueous suspension of lime or dried powdered lime contains particles that readily adhere to the conjunctiva; they often induce ulcerations of the corneal epithelium and stromal opacities but rarely penetrate to the iris or lens. It is difficult but essential to wash out the conjunctival sac completely. A .01-.05 M near neutral solution of sodium edetate (EDTA) is said to be useful to loosen adherent particles. See also Calcium Salts in the index.

See also: Lye, *Reference Congener in Section III.*
Ref.: Grant, 1974; Griffith et al., 1980; National Safety Council, Date Unknown d.

56

56 Portland Cement

When any limestone that contains clay is calcined in a kiln, the resulting calcium oxide (see above) is impure because the product also contains calcium silicates, aluminates, sulfates, aluminoferrites, oxides of magnesium and manganese, and often small amounts of nickel, cobalt and chromium oxides. This mixture is sometimes called lean lime or hydraulic lime because it slakes with only a feeble heat of hydration and because it is able to "set" under water. As originally prepared in the Kent district of England, it has become generally known as Portland cement. Mixed with water, sand or pebbles, it sets in a hard mass known as concrete; cement represents only about 15% (by weight) of hardened concrete. Unhydrated Portland cement is a respirable dust, but it is not silicotogenic. Yugoslavian cement workers, however, were found to have small but significant reductions in the 1-second forced expiratory volume without any change in vital capacity (Kalacic, 1973). The principal health hazard of cement arises when water is added, and the calcium oxide is hydrated to form alkaline calcium hydroxide (slaked lime). Although many persons appear to tolerate brief skin contact with wet cement, others develop extensive skin burns with dermal necrosis requiring skin grafting. Especially among chronically exposed workers, cement dermatitis assumes many forms: skin dryness, fissures, dystrophy of nails, eczematous rashes, [illegible] The causes of cement dermatitis have been widely debated. Most American authorities regard the alkalinity of wet cement (pH about 12), its abrasiveness and perhaps its hygroscopicity as the three qualities that make it hazardous to skin and mucous membranes. Several European dermatologists, however, have reported skin hypersensitivity to hexavalent chromium (see Chromium Trioxide in the Index) among cement workers. Because some European cements (e.g., from Switzerland) contain considerable amounts of chromates, chromium allergy has been regarded as a contributory cause of cement dermatitis (Calnan, 1960, 1973). A study in 1974 found no evidence that allergy to chromium, nickel or cobalt were importantly related to dermatitis in the American cement industry (Perone *et al.*, 1974). Because the older European evidence has not been adequately explained, the issue is not satisfactorily resolved. Acute dermal reactions to wet cement are usually treated like lye burns. Obviously gloves, impervious [illegible] and other protective gear should be worn [illegible] pouring cement.

See also: Lye, *Reference Congener in Section III.*
Ref.: Calnan, 1960; Calnan, 1973; Greening and Tonry, 1978; Kalacic, 1973; Perone et al., 1974; [illegible] Williams, 1963.

57

57 Sodium Metasilicate

Formula Na_2SiO_3. Usually prepared as a glass by the thermal fusion of sand and soda ash. More soluble and more caustic than sodium silicate. Present as a major ingredient in some modern phosphate-free and low-phosphate household laundry detergents and dishwasher products. The most alkaline and corrosive substance in such [illegible] 0.5 percent solution in water has a pH of [illegible] with a relatively high buffer capacity. [illegible] on skin, in eyes and on all mucous membranes.

See also: Lye, *Reference Congener in Section III.*
Ref.: Schneider, 1970.

58

58 Sodium Silicate

Sodium orthosilicate

Toxicity Rating: 3(?). Generally a mixture of molecular species of variable composition. In commerce mole ratios of SiO_2 to Na_2O vary from 1.5 to 3.3. The mixture used as a builder in some laundry detergents usually has a mole ratio of [illegible] The higher the ratio (e.g., [illegible] the lower the solubility and alkalinity. [illegible] less caustic than sodium metasilicate, which [illegible]

Hardy 2001

Calcium hydroxide

Synonyms

- Calcium dihydroxide
- Calcium hydrate
- Hydrated lime
- Slaked lime

Formula	$Ca(OH)_2$
Formula mass	74.1

Physical properties.

Melting pt. (°C)	580 (decomposes)	**Solubility in water**	0.18 g /100 ml
Boiling pt. (°C)		**Flash point (°C)**	
Specific gravity	2.24	**Autoignition temp. (°C)**	
V.P. (mm Hg)		**Upper explosive limit (%)**	
Vapor density	2.5	**Lower explosive limit (%)**	

Registry numbers.

CAS	1305-62-0
EINECS	215-137-3
RTECS	EW2800000
RCRA	
UN	1759
UN Guide	154
UN Hazard Class	8

NFPA ratings (0-4)

Health	3
Flammability	0
Reactivity	0

Exposure limits

TLV: 5 ppm; mg/m^3 (ACGIH 1996).
OSHA PEL: TWA 15 mg/m^3 (total) 5 mg/m^3 (resp)
NIOSH REL: TWA 5 mg/m^3

CAS Number 1305-62-0 is listed on the TSCA inventory.

Description.

White, odorless powder.

Hazards.

Decomposes on heating producing calcium oxide. The solution in water is a medium strong base. Reacts violently with acids. Attacks many metals in presence of water forming flammable/explosive gas (H2).

Hardy 2001

Calcium oxide

Synonyms

- Quicklime
- Lime
- Burnt lime

Formula	CaO
Formula mass	56.1

Physical properties.

Melting pt. (°C)	2572	**Solubility in water**	Reacts
Boiling pt. (°C)	2850	**Flash point (°C)**	
Specific gravity	3.3	**Autoignition temp. (°C)**	
V.P. (mm Hg)		**Upper explosive limit (%)**	
Vapor density	1.9	**Lower explosive limit (%)**	

Registry numbers.

CAS	1305-78-8
EINECS	215-138-9
RTECS	EW3100000
RCRA	
UN	1910
UN Guide	157
UN Hazard Class	8

NFPA ratings (0-4)

Health	3
Flammability	0
Reactivity	1

Exposure limits

TLV: 2 ppm; mg/m^3 (ACGIH 1996).
MAK: 5 ppm; mg/m^3; (1996).
OSHA PEL: TWA 5 mg/m^3
NIOSH REL: TWA 2 mg/m^3
NIOSH IDLH: 25 mg/m^3

CAS Number 1305-78-8 is listed on the TSCA inventory.

Description.

White or gray, odorless lumps or granular powder.

Hazards.

The solution in water is a medium strong base. Reacts with water generating sufficient heat to ignite combustible materials. Reacts violently with acids, halogens, metals.

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KARL S. VORRES
Argonne National Laboratory

LIGNOSULFONIC ACIDS. See LIGNIN.

LIME AND LIMESTONE

The elements calcium and magnesium, which are distributed very widely in the earth's crust, most commonly occur in carbonate forms of rock, generally classified as limestone [*1317-65-3*]. Although vast strata of this ubiquitous rock are buried so deeply as to be inaccessible, great tonnages of this stone are extracted for commercial use. Annual world production was estimated at 2×10^9 metric tons in 1990. Limestone, literally one of the most basic raw materials of industry and construction, occurs in varying degrees in nearly every country (1).

Limestone may be classified as to origin, chemical composition, texture of stone, and geological formation. Chemically it is composed primarily of calcium carbonate [*471-34-1*], $CaCO_3$, and secondarily of magnesium carbonate [*546-93-0*], $MgCO_3$, with varying percentages of impurities (see also CALCIUM

COMPOUNDS, CALCIUM CARBONATE). Although these carbonates occur in many other rocks, ores, and soils, in its broadest definition limestone is distinguished by a content of more than 50% total carbonate. More restrictive interpretations demand at least 75% or even 90%, depending on point of view. In a cursory manner, limestone can be distinguished from most other rock by applying a dilute hydrochloric acid solution to it. If the stone effervesces, it is a basic carbonate rock with a definite alkaline reaction. Limestone's most important chemical characteristic is that when subjected to high temperature it decomposes chemically into lime, calcium oxide [*1305-78-8*], CaO, with decarbonation occurring through the expulsion of carbon dioxide gas. This primary product, know as quicklime, can then be hydrated, or slaked, into hydrated lime, calcium hydroxide [*1305-62-0*], $Ca(OH)_2$, ie, the water is chemically combined with the calcium oxide in an equimolecular ratio.

Limestone was fashioned into many useful tools and implements in prehistoric time. The use of lime as a cementing and plastering material is probably almost as old as the history of fire. Lime is one of the oldest chemicals known, and the process of lime burning is one of the oldest chemical industries. Primitive kilns discovered by archeologists are believed to have been used during the Stone Age for burning lime. Lime plaster, still in good condition, has been found in Egyptian pyramids built over 4500 years ago. The pyramids themselves were built largely of nummulitic limestone and mortar. Lime plaster and mortar were used by the early Greeks, Romans, Etruscans, Arabians, and Moors. Lime is mentioned several times in the Old and New Testaments of the Bible. Vitruvius, a Roman architect under Augustus, wrote the first detailed lime specifications. Many public works were built by the Romans using hydraulic lime and limestone aggregate. Both were extensively used in building the road base and pavement of the Appian Way.

In North America, quicklime was produced locally as early as 1635 in Rhode Island. It was not until 1733, when lime was shipped by boatload from Rockland, Maine, to Boston, that lime manufacture was established as a significant industry in commerce. The commercial hydration of lime is a relatively recent development initiated in 1904. Technical progress has allowed the industry to advance rapidly during the latter part of the twentieth century.

Definitions. In addition to showing varying degrees of chemical purity, limestone assumes a number of widely divergent physical forms, including marble, travertine, chalk, calcareous marl, coral, shell, oolites, stalagmites, and stalactites. All these materials are essentially carbonate rocks of the same approximate chemical composition as conventional limestone (2–4).

Limestone is generally classified into the following types: (*1*) high calcium, in which the carbonate content is essentially calcium carbonate having no more and usually less than 5% magnesium carbonate; (*2*) magnesian, which contains both calcium and magnesium carbonates, and has a magnesium carbonate content of 5–20%; and (*3*) dolomitic, which contains > 20% but not more than 45.6% $MgCO_3$, the exact amount contained in a true, pure, equimolecular dolomite. The balance is $CaCO_3$. Similarly, limes calcined from these stone types are identified as high calcium, magnesian, and dolomitic limes. The magnesian lime and limestone are more prevalent in Europe and other countries than in the United States.

The carbonate minerals that comprise limestone are calcite [*13397-26-7*] (calcium carbonate), which is easily the most abundant mineral type; aragonite [*14791-73-2*] (calcium carbonate); dolomite [*17069-72-6*] (double carbonate of calcium and magnesium); and magnesite [*13717-31-5*] (magnesium carbonate). Individual limstone types are further described by many common names (1). Some of this nomenclature is repetitious and overlapping. The following terms are in common use in Europe and the United States.

Argillaceous limestone is an impure type containing considerable clay or shale, and as a result has a relatively high silica and alumina content.

Calcitic limestone is generally used by agronomists to denote a high calcium stone. This term can be misleading, however, because its use could suggest pure calcite, which calcitic limestone usually is not.

Carbonaceous limestone contains various types of organic material, such as peat, natural asphalt, and even oil shale (qv), as impurities. Such stone is often black and may exude a fetid odor.

Cementstone is an impure (usually argillaceous) limestone, possessing the ideal balance of silica, alumina, and calcium carbonate for Portland cement (qv) manufacture. When calcined it produces a hydraulic cementing material.

Chalk is a soft, fine-grained, fossiliferous form of calcium carbonate that varies widely in color, hardness, and purity. Its grain size is so minute that it appears amorphous, but actually it is cryptocrystalline with a very high surface area.

Chemical-grade limestone is a pure type of high calcium or dolomitic limestone used by the chemical-process industry or where exacting chemical requirements are necessary. It contains a minimum of 95% total carbonate. In a few areas of the United States this minimum may be extended to 97 or 98%.

Compact limestone is a general term depicting a dense, fine-grained, homogeneous, usually hard type of stone.

Dolomitic limestone contains considerable $MgCO_3$. A true dolomitic stone contains a ratio of 40–44% $MgCO_3$ to 54–58% $CaCO_3$. However, the term is more loosely used to denote any carbonate rock that contains more than 20% $MgCO_3$. It varies in color, hardness, and purity.

Ferruginous limestone contains considerable iron as an impurity and is yellow or red in color.

Fluxstone is a pure form of limestone used as flux or purifier in metallurgical furnaces. It can be high calcium, magnesian, or dolomitic, providing it contains at least 95% carbonate.

Fossiliferous limestone is a general term for any carbonate stone in which the fossil structure is visually evident.

High calcium limestone is a general term for stone that contains largely $CaCO_3$ and not much (2–5% max) $MgCO_3$. It occurs in varying degrees of purity.

Hydraulic limestone is an impure argillaceous carbonate somewhat akin to cementstone, except that it may contain more $MgCO_3$, and usually it produces cement-like materials of lower hydraulicity.

Iceland spar is the purest limestone, virtually pure calcite of about 99.9% $CaCO_3$. It is also known as optical calcite; its occurrence is rare.

Magnesian limestone is intermediate between high calcium and dolomitic, and contains 5–20% $MgCO_3$. It occurs in varying purity.

Marble is a metamorphic, highly crystalline rock that may be high calcium or dolomitic limestone of varying purity. It occurs in virtually every color in diverse mottled effects and is the most beautiful form of limestone. It is usually very hard and can be cut and polished to a very smooth surface.

Marl, an impure, soft, earthy, carbonate rock, contains varying amounts of clay and sand intermixed in a loosely knit crystalline structure.

Oolitic limestone is composed of small rounded grains of $CaCO_3$, precipitated in concentric laminates around a nucleus of $CaCO_3$ or silica. It is frequently very pure but may be impure.

Oyster shell, another of the many forms of fossiliferous limestones, is a relatively pure source of $CaCO_3$.

Phosphatic limestone is usually a high calcium type that contains appreciable percentages (up to 5%) phosphorus. It originates from invertebrate marine organisms.

Stalactites and *stalagmites* are conical, icicle-like shapes of pure $CaCO_3$ that form on roofs and floors, respectively, of caverns. These are precipitated from cold groundwater that drips from limestone crevices.

Travertine is a calcium carbonate formed by chemical precipitation from natural hot-water mineral springs. In appearance and use it is closely akin to marble.

Whiting at one time connoted only a very fine form of chalk of micrometer sizes but the term is now used more broadly to include all finely divided, meticulously milled carbonates derived from high calcium or dolomitic limestone, marble, shell, or chemically precipitated calcium carbonate. Unlike all of the above natural forms of limestone, it is strictly a manufactured product.

The term lime also has a broad connotation and frequently is used in referring to limestone. According to precise definition, lime can only be a burned form: quicklime, hydrated lime, or hydraulic lime. These products are oxides or hydroxides of calcium and magnesium, except hydraulic types in which the CaO and MgO are chemically combined with impurities. The oxide is converted to a hydroxide by slaking, an exothermic reaction in which the water combines chemically with the lime. These reversible reactions for both high calcium and dolomitic types are

Quicklime

$$\underset{\substack{\text{high calcium}\\ \text{limestone}}}{CaCO_3} + \text{heat} \rightleftharpoons \underset{\substack{\text{high calcium}\\ \text{quicklime}}}{CaO} + CO_2$$

$$\underset{\text{dolomitic limestone}}{CaCO_3{\cdot}MgCO_3} + \text{heat} \rightleftharpoons \underset{\text{dolomitic quicklime}}{CaO{\cdot}MgO} + 2\,CO_2$$

Hydrated lime

$$\underset{\substack{\text{high calcium}\\ \text{quicklime}}}{CaO} + H_2O \rightleftharpoons \underset{\substack{\text{high calcium}\\ \text{hydrate}}}{Ca(OH)_2} + \text{heat}$$

$$\underset{\text{dolomitic quicklime}}{CaO{\cdot}MgO} + H_2O \rightleftharpoons \underset{\text{dolomitic hydrate}}{Ca(OH)_2{\cdot}MgO} + \text{heat}$$

$$\underset{\text{dolomitic quicklime}}{CaO{\cdot}MgO} + 2\,H_2O \rightleftharpoons \underset{\text{dolomitic hydrate}}{Ca(OH)_2{\cdot}Mg(OH)_2} + \text{heat}$$

In most types of dolomitic quicklimes, when hydrated under atmospheric conditions, all the CaO component readily hydrates, but very little of the MgO slakes. The result is a dolomitic monohydrate or a combination of hydroxide and oxide. However, when dolomitic quicklime is hydrated under pressure or is subject to long retention periods, most of the MgO hydrates to form a so-called highly hydrated dolomitic lime. In the relatively pure commercial limes, the available lime contents of quicklime are 88–94%, and the total oxide content (CaO + MgO) is 92–98% in North America. The average purity of the limes in Europe, South America, and elsewhere, except for Japan, is generally not as high as in the United States and Canada, because the countries outside of North America possess fewer high grade limestone deposits. For reasons of necessity and economy, some submarginal (in quality) limestone deposits are exploited.

The common nomenclature for specific types and forms of lime, some of which is repetitious and overlapping, is as follows (1).

Air-slaked lime contains various proportions of the oxides, hydroxides, and carbonates of calcium and magnesium which result from excessive exposure of quicklime to air that vitiates its quality. It is partially or largely decomposed quicklime that has become hydrated and carbonated.

Autoclaved lime is a special form of highly hydrated dolomitic lime, used largely for structural purposes, that has been hydrated under pressure in an autoclave.

Available lime, the total free lime (ie, CaO) content in a quicklime or hydrate, is the active constituent of a lime. It provides a means of evaluating the concentration of lime.

Building lime may be quick or hydrated lime, but usually connotes the latter, where the physical characteristics make it suitable for ordinary or special structural purposes (see BUILDING MATERIALS, SURVEY).

Carbide lime is a waste lime hydrate by-product from the generation of acetylene from calcium carbide and may occur as a wet sludge or dry powder of widely varying purity and particle size. It is gray and has the pungent odor associated with acetylene (see HYDROCARBONS, ACETYLENE).

Chemical lime is a quick or hydrated lime used for one or more chemical or industrial applications. Usually chemical lime has a relatively high chemical purity.

Dead-burned dolomite is a specially sintered or double-burned form of dolomitic quicklime which is further stabilized by the addition of iron oxides. Historically, it was used as a refractory for lining steel furnaces, particularly open hearths, but as of this writing is used primarily in making dolomite refractory brick (see REFRACTORIES).

Fat lime is a pure lime (quick or hydrated), as distinct from an impure or hydraulic lime; it is also used to denote a lime hydrate that yields a plastic putty for structural purposes.

Finishing lime is a refined hydrated lime, milled to make it suitable for plastering, particularly the finish coat. Putty derived from this hydrate possesses unusually high plasticity.

Fluxing lime is lump or pebble quicklime used as flux in steel (qv) manufacture; the term may also be applied more broadly to include fluxing of nonferrous metals and glass (qv). It is a type of chemical lime.

Ground burnt lime refers to ground quicklime used for agricultural liming.

Hard-burned lime is a quicklime that is calcined at high temperature and is generally characterized by relatively high density and moderate-to-low chemical reactivity.

Hydraulic hydrated lime is a chemically impure form of lime with hydraulic properties of varying extent. It contains appreciable amounts of silica, alumina, and usually some iron, chemically combined with much of the lime. Hydraulic hydrated lime is employed solely for structural purposes.

Lime putty is a form of lime hydrate in a wet, plastic paste form, containing free water.

Lime slurry is a form of lime hydrate in aqueous suspension that contains considerable free water.

Lump lime is a physical shape of quicklime, derived from vertical kilns.

Mason's lime is a hydrated lime used in mortar for masonry purposes.

Milk-of-lime is a dilute lime hydrate in aqueous suspension which has the consistency of milk.

Pebble lime is a physical shape of quicklime.

Refractory lime is synonymous with dead-burned dolomite, an unreactive dolomitic quicklime, stabilized with iron oxides, that is used primarily for lining refractories of steel furnaces, particularly open hearths.

Slaked lime is a hydrated form of lime, available as a dry powder, putty, or aqueous suspension.

Soft-burned lime is a quicklime that is calcined at a relatively low temperature. It is characterized by high porosity and chemical reactivity.

Type S hydrated lime, also called special hydrated lime, is an ASTM designation that distinguishes a structural hydrate from a normal hydrated lime, designated type N. Type S lime meets specified plasticity and gradation requirements. It may be dolomitic or high calcium and is more precisely milled than type N hydrates. Type SA hydrated lime is a Type S hydrate to which a small amount of air entraining agent has been added, having up to 14% air content; it is used in mortar.

Unslaked lime is any form of quicklime.

Geology

Limestone, as a constituent of the earth's crust, is a rock of sedimentary origin (4) from material precipitated by chemical and organic action on drainage waters. Calcium, a common element, is estimated to comprise 3–4% of the earth's crust, and the calcium constituent of limestone must have come originally from igneous rocks. By the action of various eroding and corroding forces, including the solution of carbonic and other mineral acids, the rocks are disintegrated and the calcium is dissolved and removed in the drainage waters emptying

into the sea. The amount of material removed in this manner is astonishing. It is estimated that the Thames River in England annually carries more than 550,000 metric tons of dissolved material, of which approximately two-thirds is calcium carbonate. This represents the removal of about 62 t/km^2 of limestone from the drainage area involved.

Upon reaching the ocean, some of the dissolved calcium carbonate may be reprecipitated because of its lower solubility in seawater. Surface evaporation and temperature changes may reduce the carbon dioxide content of the water, causing precipitation of calcium carbonate from saturated conditions. The calcium carbonate sedimented in this manner may give rise to limestone of purely chemical (sometimes termed physical) origin. Also of chemical origin, by a similar evaporation–deposition process around springs and streams, are limestones known as travertine and calcareous tufa and stalactities and stalagmites in caves. By far the largest part of the limestone in existence as of the twentieth and twenty-first centuries is of organic origin formed through skeleton-building processes of marine life. The lime remaining in solution following chemical precipitation is utilized by many different varieties of sea life, such as corals, foraminifera, mollusks, arthropods, and echinoderms, to form shells and skeletons, which ultimately accumulate on the sea bottom. The skeletal structures are almost pure calcium carbonate and are frequently found intact in such limestones as chalk and marl.

The calcareous sediment produced in either manner may become contaminated during deposition with argillaceous, siliceous, or ferruginous silts, which affect the chemical composition and nature of the resulting limestone. The size and shape of the calcareous particles, together with conditions of pressure, temperature, and solvent action to which a deposition is subsequently exposed, are factors that influence the physical characteristics of the stone. The degree of consolidation of the calcareous sediment ranges from little change, as exhibited by the soft marls and chalks in which the skeletal particles are loosely cemented, to the metamorphosed, dense, crystalline rock, marble, which shows no indication of its origin. Between these two extremes many types and kinds of limestone are known. Examples of limestone in the process of formation are the globigerina ooze, which covers vast areas of bottom at ocean depths of 1800–5500 m, and coral reefs in tropical seas.

The origin of magnesian and dolomitic limestone is uncertain; it is generally believed, and considerable evidence supports the theory, that it is formed by direct chemical replacement of the calcium in the limestone by magnesium from waters high in magnesium salts. Several small deposits of dolomite appear to have originated through the coprecipitation of both carbonates.

Geographical Occurrence. Limestone, present in the majority of geological formations, is widely distributed throughout the world in deposits of varying sizes and degrees of purity. Significant deposits in the U.K. are chiefly confined to the Devonian, lower Carboniferous, Jurassic, and Cretaceous systems. In the United States, the geological distribution is broader. Quantities of stone occur in the older Cambrian, Ordovician, and Silurian systems, as well as in the previously mentioned groups. Although some outcrops are known in the pre-Cambrian system, limestones as a whole are not as prevalent as in the older Paleozoic rocks.

The deposits of limestone in the United States, if no limitation as to quality is placed, are widespread, occurring in nearly every state, usually in tremendous amounts. It is estimated that 15–20% of the areas of the United States is underlain by limestone. Even though the deposits are extensive, they are frequently so overburdened that quarrying or mining is not economical. Only a small proportion of the total limestone is of a grade suitable to meet the high requirements demanded for either industrial lime or stone for metallurgical and chemical processes. The lower grade stones are generally suitable for agricultural and construction uses where the chemical composition is not a limiting factor.

Detailed information concerning the location and analysis of limestone deposits in the United States can be obtained from the various state geological surveys, the U.S. Bureau of Mines, and the U.S. Geological Survey. Descriptive summaries of the limestone deposits in the various states have been published (5,6).

Impurities. The chemical composition and properties of lime and limestone depend on the nature of the impurities and the degree of contamination of the original stone. The contaminating materials either were deposited simultaneously with the $CaCO_3$ or entered during some later stage (6).

Alumina in combination with silica is present in limestone chiefly as clay, though other aluminum silicates in the form of feldspar and mica may be found. When present in appreciable quantities, clay converts a high calcium limestone into a marl or argillaceous stone, which when calcined yields limes with hydraulic properties. Limestones containing 5–10% clayey matter yield feebly hydraulic limes; those containing 15–30% produce highly hydraulic limes.

Siliceous matter other than clay may occur in the free state as sand, quartz fragments, and chert, and in the combined state as feldspar, mica, talc (qv), and serpentine. Metallurgical and chemical limestones should contain less than 1% alumina and 2% silica.

Iron compounds (qv) in limestone are seldom injurious to a lime product unless a very pure lime is required. Normally, the iron compounds are in the form of limonite [*1317-63-1*] (ferric hydroxide) and pyrite [*1309-36-0*], FeS_2. Occasionally, hematite, magnetite, marcasite, and other forms of iron are found in limestone.

Sodium and potassium compounds are rarely present to any extent in limestone and are not objectionable unless a pure lime is required. When present in small proportions, these impurities are usually volatilized during burning. Carbonaceous matter is sometimes present in limestone. It is of little importance to the resulting lime because it burns and is lost during calcination. Sulfur and phosphorus compounds (generally sulfates and phosphates) are objectionable impurities in chemical lime and limestone. In metallurgical processes requiring relatively pure fluxing lime and limestone, these acidic components should not be present in quantities greater than 0.03% sulfur and 0.02% phosphorus.

Many lime plants are able to reduce the impurities in their lime product by careful screening and selecting of stone for burning. Because 9 kg of limestone produce only 5 kg of quicklime, the percentage of impurities in a quicklime is nearly double that in the original stone. Analyses of typical samples of high calcium, magnesian, and dolomitic limestones found in the United States are listed in Table 1.

Table 1. Composition of U.S. Limestones,[a] wt %

	Limestone[b]							
Component	1	2	3	4	5	6	7	8
CaO	54.54	38.90	41.84	31.20	29.45	45.65	55.28	52.48
MgO	0.59	2.72	1.94	20.45	21.12	7.07	0.46	0.59
CO_2	42.90	33.10	32.94	47.87	46.15	43.60	43.73	41.85
SiO_2	0.70	19.82	13.44	0.11	0.14	2.55	0.42	2.38
Al_2O_3	0.68	5.40	4.55	0.30	0.04	0.23	0.13	1.57
Fe_2O_3[c]	0.08	1.60	0.56	0.19	0.10	0.20	0.05	0.56
SO_3[d]	0.31		0.33			0.33	0.01	
P_2O_5			0.22		0.05	0.04		
Na_2O	0.16		0.31	0.06	0.01	0.01		
K_2O			0.72		0.01	0.03		
H_2O			1.55		0.16	0.23		
other			0.29		0.01	0.06	0.08	0.20

[a] Ref. 1.

[b] 1 = Indiana high calcium stone; 2 = Lehigh Valley, Pa., cement rock; 3 = Pennsylvania cement rock; 4 = Illinois Niagaran dolomitic stone; 5 = Northwestern Ohio Niagaran dolomitic stone; 6 = New York magnesian stone; 7 = Virginia high calcium stone; and 8 = Kansas Cretaceous high calcium stone (chalk).

[c] Includes some Fe as FeO.

[d] Includes some elemental S.

Properties of Limes and Limestones

The chemical and physical properties of limestone vary tremendously, owing to the nature and quantity of impurities present and the texture, ie, crystallinity and density. These same factors also exert a marked effect on the properties of the limes derived from the diverse stone types. In addition, calcination and hydration practices can profoundly influence the properties of lime.

Color. The purest forms of calcite and magnesite are white, often with an opaque cast, but most conventional limestone, even relatively pure types, are gray or tan. The presence of carbonaceous impurities can render the grays dark, even approaching black. The presence of iron gives the tan, brown, pink, and buff colors of some limestones. Impurities, such as pyrite, marcasite, and siderite may alter the surface color through weathering. Marble and travertine have many brilliant colors of diverse mottled, variegated effects ranging to milky white.

Quicklime is usually white of varying intensity, depending on chemical purity; some species possess a slight ash-gray, buff, or yellowish cast. Invariably quicklime is lighter in color than the limestone from which it is derived. Hydrated limes, except for hydraulic and impure hydrates, are extremely white in color, invariably whiter than their quicklimes.

Odor. Except for highly carbonaceous species, most limestones are odorless. Quick and hydrated limes possess a mild odor that is characteristic but difficult to describe except that it is faintly musty or earthy, not offensive.

Texture. All limestones are crystalline, but there is tremendous variance in the size, uniformity, and arrangement of their crystal lattices. The crystals of the minerals calcite, magnesite, and dolomite are rhombohedral; those of aragonite are orthorhombic. The crystals of chalk and of most quick and hydrated limes are so minute that these products appear amorphous, but high powered microscopy proves them to be cryptocrystalline. Hydrated lime is invariably a white, fluffy powder of micrometer and submicrometer particle size. Commercial quicklime is used in lump, pebble, ground, and pulverized forms.

There is considerable variance in the porosity of limestones, thus the bulk densities generally are 2000–2800 kg/m^3 (125–175 lb/ft^3). The density of some chalk limestones are even less. Dolomitic stones average 2–3% higher densities than high calcium ones. Depending on the physical size of the quicklime particles and their divergent porosities, bulk densities are 770–1120 kg/m^3 (48–70 lb/ft^3), and densities of their hydrates 400–640 kg/m^3 (25–40 lb/ft^3). Again, dolomitic limes average about 4% denser than their high calcium counterparts. The severity of the calcination process largely determines the porosity of a quicklime; the higher the temperature of calcination and the longer its duration, the more the porosity declines.

Specific gravities of pure and commercial limes and limestones are shown:

Material	Specific gravity
calcite	2.7112
aragonite	2.929
high calcium limestones	2.65–2.75
dolomitic limestones	2.75–2.90
chalk	1.4–2.0
pure calcium oxide	3.34
high calcium quicklimes	3.2–3.4
dolomitic quicklimes	3.4–3.6
high calcium hydrated lime	2.3–2.4
dolomitic hydrated lime	2.4–2.9

Hardness. Most limestone is soft enough to be readily scratched with a knife. Pure calcite is standardized on Mohs' scale at 3; aragonite is harder, 3.5–4. Dolomitic limestone is generally harder than high calcium. Dead-burned or sintered limes are 3–4 on this scale, whereas most commercial soft-burned quicklimes are 2–3 (see HARDNESS).

Strength. The compressive strength of limestone varies tremendously, having values from 8.3 to 196 MPa (1,200–28,400 psi). Marble generally has the highest value and chalk and calcareous marl the lowest.

Luminescence. Limestone possesses only limited luminescent qualities, ranging from very faint or none with the impure types. However, quicklime is very luminescent at calcining temperatures, hence the term limelight.

Thermal Properties. Because all limestone is converted to an oxide before fusion or melting occurs, the only melting point applicable is that of quicklime. These values are 2570°C for CaO and 2800°C for MgO. Boiling point values for CaO are 2850°C and for MgO 3600°C. The mean specific heats for limestones and limes gradually ascend as temperatures increase from 0 to 1000°C. The ranges are as follows: high calcium limestone, 0.19–0.26; dolomitic quicklime, 0.19–0.294; dolomitic limestone, 0.206–0.264; magnesium oxide, 0.199–0.303; and calcium oxide, 0.175–0.286.

In the hydration of quicklime, considerable heat is generated: for $Ca(OH)_2$, 63.6 kJ/mol (488 Btu/lb) of quicklime; and for $Mg(OH)_2$, 32.2–41.8 kJ/mol (247–368 Btu/lb). The heat of solution for $Ca(OH)_2$ is 11.7 kJ/mol (67.8 Btu/lb). The value for MgO is immeasurable because MgO is virtually insoluble.

Solubility. High calcium limestone is only very faintly soluble in water. In cold CO_2-free water it is often regarded as insoluble. Between 17 and 25°C its solubility is only 14–15 mg/L. As the temperature increases, so does the solubility until at 100°C solubility reaches 30–40 mg/L. This faint solubility at elevated temperatures accounts for the accretion of a primarily $CaCO_3$ scale in steam boilers. Carbon dioxide exerts a mild solvent action on $CaCO_3$ increasing the solubility in direct proportion to the increase of CO_2 pressure as shown in Figure 1. The maximum solubility of $CaCO_3$ is 3.93 g/L at 5.7 MPa (56 atm) CO_2 pressure and 18°C. At a CO_2 pressure of 101.3 kPa (1 atm), the solubility ranges between 1.3 and 0.765 g/L between temperatures of 9–35°C, the converse of CO_2-free water, because the solubility declines as the temperature increases. Argonite solubility values are slightly greater than those of calcite. However, $MgCO_3$ is much more water soluble than $CaCO_3$, with or without CO_2. On an equivalence basis, the $MgCO_3$ is about 15–20 times more soluble.

There are no solubility values for quicklime because the oxide is hydrated to its hydroxide before dissolving. The magnitude of solubility of a high calcium hydrate on a CaO basis is 1.330 g/L (or 0.13%) of saturated solution at 10°C in distilled water. Thus lime is about 75 times as soluble as high calcium limestone on a comparable basis and can be regarded as slightly soluble at low temperatures (5). Contrary to limestone in CO_2-free water, the solubility of hydrate is in inverse proportion to temperature, decreasing with rising temperatures. Figure 2 displays how temperature changes influence lime's solubility. Fractional percents up to 5–10% of many inorganic salt solutions, such as $CaCl_2$, NH_4Cl, NaCl, etc, increase lime's solubility in varying degrees up to threefold. Alkalies, notably Na_2CO_3 and NaOH, exert an adverse effect, rendering lime almost totally insoluble at elevated temperatures. However, the greatest stimulants to solubility are certain organic compounds, such as glycerol, phenol, and sugar. In a 35% sugar solution at 25°C, 10.1 g of CaO/100 cm^3 can be dissolved, nearly 100 times the solubility of lime in distilled water.

Data on the solubility of magnesium hydroxide in water are not all in agreement, but the solubility is extremely low. The extent of $Mg(OH)_2$ solubility is 10 mg/L, which is about 1/100 the solubility of $Ca(OH)_2$. In concentrated solutions of NH_4Cl and NH_4CO_3, the solubility of $Mg(OH)_2$ is markedly increased, but

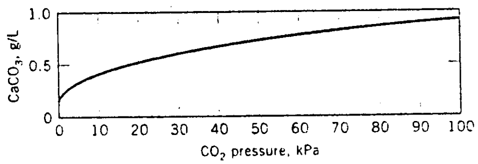

Fig. 1. Influence on aqueous $CaCO_3$ solubility of increasing fractional CO_2 pressure at constant temperature of 25°C. To convert kPa to mm Hg, multiply by 7.5.

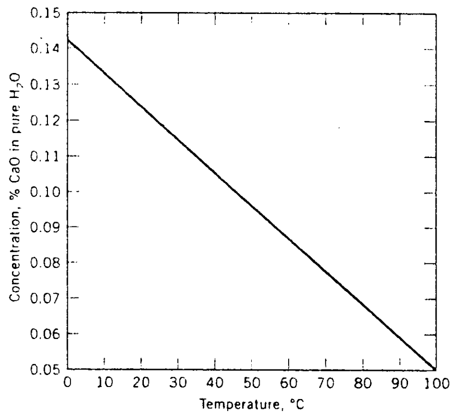

Fig. 2. The water solubility of lime which decreases with rising temperatures.

in no instance does its solubility equal that of $MgCO_3$ in water heavily permeated with CO_2. Dolomitic hydrates are slightly less soluble than high calcium hydrates, but much nearer the latter in value than $Mg(OH)_2$, because the presence of MgO and $Mg(OH)_2$ does not impede the dissolution of its $Ca(OH)_2$ constituent.

Plasticity. An innate characteristic of a lime putty of paste-like consistency is it plasticity or its ability to be molded under pressure and to retain its altered shape without deformation. This rheological property is important for structural uses of lime in masonry mortar and plaster (7). Although no completely satisfactory method for measuring plasticity has been developed, North America has a standardized Emley Plasticimeter test. This test simulates the action of a plasterer applying a lime finish coat to an absorbent base using a trowel. A special machine that measures the resistance of a lime putty of standard consistency against a rotating disk is used. If a lime has an Emley plasticity value of 200 or more, it is judged satisfactory for all structural purposes. Limes vary widely in the degree of plasticity they impart. Generally, dolomitic limes develop greater plasticity than high calcium types in the United States, but this marked superiority does not occur in other countries. The ASTM specification on physical tests of limes (C110) describes this test and other physical tests pertaining to building lime, such as water retentivity, pitting and popping, and soundness.

Stability. All calcitic and dolomitic limestones are extremely stable compounds, decomposing only in fairly concentrated strong acids or at calcining temperatures of 898°C for high calcium and about 725°C for dolomitic stones at 101.3 kPa (1 atm). A very mild destabilizing effect is caused by CO_2-saturated water, as described in the preceding section on solubility. Aragonite, however, is not as stable as calcite. In sustained contact with moisture, it tends to revert to calcite through recrystallization. At a temperature of 400°C it is transformed irreversibly to the more stable form of calcite. Dolomite and magnesite are the equal of calcite in stability.

Quicklime and hydrated lime are reasonably stable compounds but not nearly as stable as their limestone antecedents. Chemically, quicklime is stable at any temperature, but it is extremely vulnerable to moisture. Even moisture in the air produces a destabilizing effect by air-slaking it into a hydrate. As a result, an active high calcium quicklime is a strong desiccant (qv). Probably hydrate is more stable than quicklime. Certainly hydrated lime is less perishable chemically because water does not alter its chemical composition. However, its strong affinity for carbon dioxide causes recarbonation. Dolomitic quicklime is less sensitive to slaking than high calcium quicklime, and dead-burned forms are completely stable under moisture-saturated conditions. Except for dead-burned dolomite, all limes are much more reactive with acids than limestone. The high calcium types are the most reactive.

Chemical Reactions. *Neutralization.* In water, lime ionizes readily to Ca^{2+}, Mg^{2+}, and OH^-, forming a strong base or alkali. Both $Ca(OH)_2$ and $Mg(OH)_2$ are strong diacid bases neutralizing such strong monobasic acids as HCl and HNO_3, yielding neutral salts and heat.

$$Ca(OH)_2 + 2\,HCl \longrightarrow CaCl_2 + 2\,H_2O + 115\text{ kJ } (27{,}400\text{ cal})$$

$$Mg(OH)_2 + 2\,HNO_3 \longrightarrow Mg(NO_3)_2 + 2\,H_2O + 115\text{ kJ } (27{,}400\text{ cal})$$

For H_2SO_4, a dibasic acid, the molar ratio is one-to-one:

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,H_2O + \text{heat}$$

The neutralizing power of lime and limestone and other alkalies is compared in Table 2 (8). Of all these alkalies, MgO is the strongest base, followed by CaO. Thus neutralization of a given acid requires less dolomitic limestone or lime than high calcium limestone or lime.

pH. As Figure 3 indicates, lime solutions develop a high pH of slightly under 12.5 at 25°C and approach 13 at maximum solubility at 0°C. Using even the barest trace of lime a pH of 11 is easily achieved, causing a precipitous rise

Table 2. Basicity Factors of Common Alkaline Reagents[a]

Alkali	Descriptive formula	Basicity factor[b]
dolomitic quicklime	$CaO{\cdot}MgO$	1.110
high calcium quicklime	CaO	0.941
dolomitic normal hydrate	$Ca(OH)_2{\cdot}MgO$	0.912
dolomitic pressure hydrate	$Ca(OH)_2{\cdot}Mg(OH)_2$	0.820
high calcium hydrate	$Ca(OH)_2$	0.710
sodium hydroxide	NaOH	0.687
dolomitic limestone	$CaCO_3{\cdot}MgCO_3$	0.564
sodium carbonate	Na_2CO_3	0.507
high calcium limestone	$CaCO_3$	0.489

[a] These factors were determined on representative commercial samples, except those of sodium hydroxide and sodium carbonate, which were calculated.
[b] On a basis of pure CaO = 1.000.

on the pH scale from 7. The pH of limestone is much lower. Calcium carbonate attains a pH of 8–9 and dolomitic stone a pH of about 8.5–9.2.

Causticization. Lime, particularly the high calcium type, reacts with carbonates such as Na_2CO_3 and Li_2CO_3 to form other hydroxides and carbonates through double decomposition or metathesis reactions as follow:

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

The $CaCO_3$ precipitate is easily separated from the other, soluble reactant.

Silica and Alumina. The manufacture of Portland cement is predicated on the reaction of lime with silica and alumina to form tricalcium silicate [*12168-85-3*] and aluminate. However, under certain ambient conditions of compaction with sustained optimum moisture content, lime reacts very slowly to form complex mono- and dicalcium silicates, ie, cementitious compounds (9,10). If such a moist, compact mixture of lime and silica is subjected to steam and pressure in an autoclave, the lime–silica reaction is greatly accelerated, and when sand and aggregate is added, materials of concrete-like hardness are produced. Limestone does not react with silica and alumina under any circumstances, unless it is first calcined to lime, as in the case of hydraulic lime or cement manufacture.

Other Reactions. Dry hydrated lime adsorbs halogen gases, eg, Cl_2 and F_2, to form hypochlorites and fluorides. It reacts with hydrogen peroxide to form calcium peroxide, a rather unstable compound. At sintering temperatures, quicklime combines with iron to form dicalcium ferrite.

Limestone Production. Because more than 99% of U.S. limestone is sold or used as crushed and broken stone, rather than dimension-stone, most of the description of limestone's extraction and processing herein focuses on the former (Fig. 4). Most stone is obtained by open-pit quarrying methods. Underground

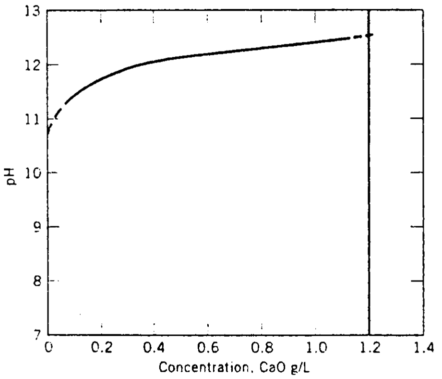

Fig. 3. The pH values of $Ca(OH)_2$ solutions of varying concentrations of CaO in water at 25°C. The solid vertical line represents the maximum solubility of $Ca(OH)_2$ solutions at 25°C.

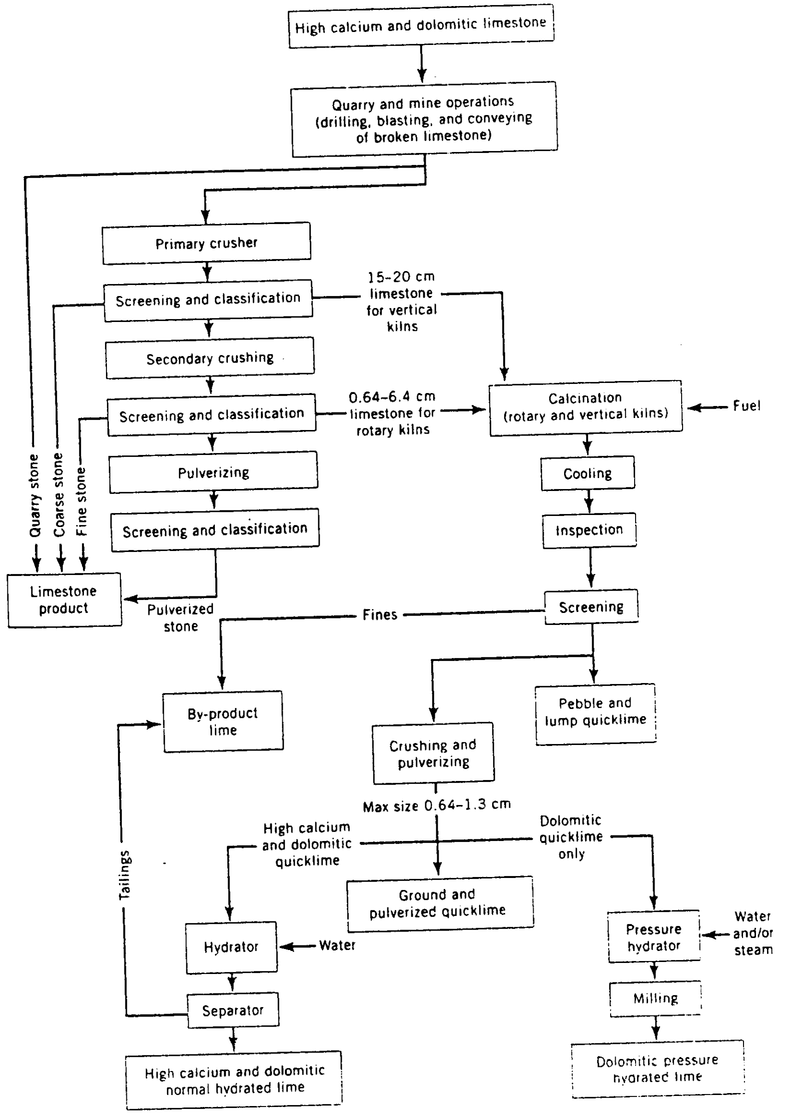

Fig. 4. Simplified flow sheet for lime and limestone products.

mining is pursued by some important operations, but the tonnage quarried exceeds that mined by nearly 20-fold. There is, however, a slight trend toward increased mining which should continue.

Stone Extraction. Quarries vary greatly in depth, from 4.5–7.5 m to deep quarries of up to 100 m. The first step in quarrying is stripping of the soil and loose rock that overlays the limestone deposit. Very rarely is limestone discovered in bare outcrop. If the overburden is thick, more than 5 m, irregular in thickness, and containing rock pinnacles and cavities, stripping can be so arduous and costly that mining may be more feasible. A variety of earth-moving equipment and methods are used in stripping. Washing soil away hydraulically was practiced historically, but because of cost and environmental constraints is seldom used. Much of the overburden is used for building roads, quarry ramps, and protective berms.

After the bedrock is exposed and clean, the next procedure is drilling. The productivity of large rotary and percussion drilling rigs is such that these rigs have largely replaced lower capacity well drills.

Diameters of the holes vary from 5–25.4 cm. Drilling perpendicularly to the deposit is preferable but in folding or tilted beds inclined drilling is often practiced. Spacing of the holes and borehole diameters depend on the hardness and fracturing characteristics of the stone, and desired top size for the primary crusher.

Most limestone quarries use either 100% ammonium nitrate [*6484-52-2*] (fertilizer grade) and fuel oil (ANFO), or a combination of ANFO and ammonium or gelatin dynamite, for blasting (see EXPLOSIVES AND PROPELLANTS, EXPLOSIVES). After blasting, oversized boulders usually are reduced to manageable sizes by drop ball cranes.

Quarries that excavate soft stone, notably marl or chalk, do not drill or blast, but extract the stone using heavy-duty rippers and scrapers. In the Middle West and Florida, lake marls and soft coralline limestone are dredged in a process much like stripmining.

Environmental regulations compel operations to abate dust, control wastewater discharge, and abide by noise-control regulations (11) (see AIR POLLUTION CONTROL METHODS; NOISE POLLUTION AND ABATEMENT METHODS). Drilling dust is eliminated by fabric filters that are a part of modern drilling rigs. Soil banks are planted with vegetation to reduce dust and erosion; trees, snow fences, and berms serve as wind barriers at vulnerable locations.

Most underground limestone mines (6) in the United States are relatively shallow room- and pillar-mines of 3–30 m depth. Thick 2 m supporting pillars are preserved at 7.5–10.6 m centers with 10.5–25 m high roofs or ceilings. However, some deep mines, reminiscent of coal (qv) operations, reach depths of 300 m with stope-mining techniques from a central vertical shaft. Because stone extracted from deep mines is often too costly to compete at the marketplace, it is generally mined for captive consumption, ie, for making higher priced products, eg, lime, chemicals.

Stone Processing. Next to blasting, primary crushing is the most effective method of reducing stone size (see SIZE REDUCTION). For maximum productivity it is essential that the primary crusher size be correlated with that of the bucket of the loader or shovel employed in the quarry or mine. Otherwise production is lost through large stone obstructions causing jamming delays in the crusher.

Primary crushers are of two basic types: compression or impact. Compression crushers typified by the jaw, cone, and gyratory primary crushers, operate by the slow application of pressure which causes the rock to crack and rupture. In contrast, impact crushers, on which impact breakers and hammer mills are predicated, subject the stone to sharp, rapid, repeated blows. Selection of the crusher type is contingent on the hardness and fracturing characteristics of the limestone, plant capacity, and the desired size or gradation. In general, compression types are favored for the hardest, most abrasive, and largest stone sizes, the impact type for the smaller sizes, and the gyratory type for plants of highest capacity. Depending on type, primary crushers yield product sizes of 3.8–25 cm. Crusher capacities range broadly from 90 to 450 t/h.

Impact crushers that rotate at speeds of 250–1000 rpm fracture the stone by collision of the rock against breaker bars or other rocks. Cubical shapes of stone predominate. The jaw and particularly the gyratory crushers yield a higher proportion of flat, elongated shapes. Often secondary crushing is unnecessary with impact types, but it is necessary with the larger top sizes used in jaw crushers and gyratory crushers. Special hammer mills, a modified gyratory and cone crusher, are often used for secondary crushing.

If a plant crushes to obtain stone of 0.6 and 7.6 cm for lime-kiln feed, coarse aggregate, or fluxstone, much undersized material is also produced. Oversized material can be reduced by recycling through the crusher system, but the subsized stone, called spall, is wasted in a spall pile. Such spalls have potential value as by-products for use as, eg, asphalt (qv) filler.

For fine pulverization, both dry and wet processes are utilized, but increasingly the dry process is more popular because wet grinding ultimately requires drying and is much more energy intensive. A sensitive fan swirls the dust sizes into the air separator and permits coarse particles to recycle to the grinding mill or be rejected as tailings; the fines are drawn into cyclones where the dust is collected.

Many different pulverizers are used by the industry. For sand-sized particles, hammer, cage, and rod mills are utilized; for soft stone, roller mills are preferred; for dust and very fine sizes, ball, tube, pebble, rod, and compartmented mills are used.

Crushed stone is conveyed by a rubber-belt conveyor and bucket elevator. Fine stone and dust are conveyed by enclosed screw conveyors, air slides, or pneumatic air systems into storage bins and tank trucks for shipment. For screening, changeable vibratory screens predominate for all sizes from 23 cm to 0.074 mm (200 mesh). Most stone is stored uncovered on the ground in conical stockpiles, supplied by radial belt conveyors. Such a conveyor can maintain four stockpiles of different sized stone. Large commercial plants typically stockpile stone in 10 sizes: 12.7 × 7.6 cm, 7.6 × 5.0 cm, 5.0 × 2.5 cm, 2.5 × 1.9 cm, 1.9 × 1.3 cm, 1.3 × 1.0 cm, 1.0 × 0.6 cm, 0.6 × 0.3 cm, limestone sand, 0.25–1 mm (10–60 mesh), and agstone or 90%–0.14 mm (100 mesh).

To comply with stringent specifications, some plants beneficiate the semiprocessed stone by removing clay and soil clinging to limestone. Several wet methods are used: washing, scrubbing, flotation, and heavy-media separation are used for removing silica, ie, chert and quartz. Optical mineral sorters use compressed air to deflect stone particles deviating from a preset color standard; and hand-picking from conveyor belts is still practiced by some plants.

Since 1960, portable stone-processing plants have grown steadily. Although such units are relatively small, companies utilize them to supplement the permanent facilities at times of peak demand or to provide stand-by capacity.

The main environmental problem is dust control, which requires collection of particulate emissions from point sources and suppression of fugitive dust from a multitude of areas (12). Rotary dryers for drying stone, now operated by few plants, produce by far the most visible and concentrated emission, requiring use of multiple cyclones plus a baghouse or high energy wet scrubber to meet standards. Other point sources of particulates are at each stone-transfer junction, ie, crushers, grinders, conveyors, screens, and loading. Such dust can be quelled by use of multiple-jet water sprays to keep the stone moist. Special wetting agents are applied to the water to enhance dustproofing while conserving water. Plants desiring a dry product install protective hoods, baffles, or enclosures at each transfer point. A few plants collect emissions from each transfer point and convey the dust to a single large wet scrubber for treatment. This is the most costly method.

Most fugitive dust is derived from spillage of stone fines and overburden soil from conveyors, bucket elevators, loading spouts, trucks, etc; from stockpiled-processed stone and spall piles that become air-dried and then wind-blown; and from truck traffic and wind on plant roads. Spillage can be minimized by a variety of practices including not overloading conveyor belts, elevators, and trucks; better coordination of the stone-feed flow; reducing conveyor gravity drops; use of enclosures at vulnerable transfer points; use of retractable loading spouts that fit tightly in circular ports of tank trucks; liberal application of rainbird-type jet-spray systems on stockpiles; watering unpaved areas; removing dust from paved surfaces with vacuum-cleaning equipment; reducing truck speed; or using pneumatic pumplines in place of trucks. Successful dust abatement requires a well-supervised, unremitting campaign, supported by all levels of management.

Dimension-Stone Production. The production of dimension stone for facing buildings, tombstones, and varied ornamental effects is totally different from that of crushed stone. No blasting is done. Stone is cut from the quarry floor in huge blocks of approximately 1.2 × 15 – 30 m having a depth of 3 m, using either a channeling machine or a wire saw. Skilled, experienced workers break the stone free by wedging and subdivide the block into smaller mill blocks of 3 × 1.2 × 0.9 m by cutting and wedging. The smaller blocks are hoisted from the quarry with a crane and transported to the mill shop for further cutting and finishing or shipment to other stone finishers.

All products are specially made to comply with exacting specifications on dimensions, shape, finish, and appearance. Finishing stone requires precision sawing and such skills as planing, joining, milling, turning, fluting, and carving. Even packing and shipping the finished product requires a skilled artisan.

The limestone industry has achieved a high degree of mechanization since the 1960s, counteracting to some extent the general cost of inflation. The principal factors behind the productivity gains and cost saving have been use of larger earth-moving equipment in stripping operations; improvement in speed, diameter, and depth of drilling with large rotary- and percussion-type drilling rigs equipped for inclined drilling; expanded use of delayed action blasting; widespread substitution of ANFO for dynamite in blasting; use of mechanical or hydraulic breakage in place of secondary blasting; use of large shovels or buckets for quarry loading; greater use of front-end loaders for quarry loading instead of shovels; large capacity primary crushers; increasing use and efficiency of conveying systems, reducing truck hauling in quarries; vibratory screens replacing revolving screens; increased diesel conversion of the electric power generation for the whole plant; individual hoisting, earth-moving, and truck equipment; use of portable stone plants, providing greater production flexibility; and increased use of computerized control systems in stone processing.

Lime Manufacture

Most lime plants worldwide produce their own kiln feed from a contiguous quarry or mine, and are thus integrated lime producers. However, several unintegrated lime plants located on the Great Lakes obtain kiln feed by boat from large commercial quarries in northern Michigan. Most of these plants, among the largest in U.S. lime production, are situated in the Chicago and Detroit areas and in northern Ohio.

Theory of Calcination. The reversible reaction involved in the calcination and recarbonation of lime–limestone is one of the simplest and most fundamental of all chemical reactions. In practice, lime burning can be quite complex, however, and many empirical modifications are often necessary for efficient performance.

There are three essential factors in the thermal decomposition of limestone: (*1*) the stone must be heated to the dissociation temperature of the carbonates; (*2*) this minimum temperature (but in practice a higher temperature) must be maintained for a certain duration; and (*3*) the carbon dioxide evolved must be removed rapidly.

At calcination temperatures of 925–1340°C, dissociation of the limestone proceeds gradually from the outer surface of the stone particle inward, like a growing veneer or shell. Actually initial surface dissociation can occur under certain conditions, such as fractional atmospheric pressures below the dissociation point at 101.3 kPa (1 atm). However, for dissociation to penetrate the interior of the stone particle, attainment of temperatures often considerably higher than the dissociation point is necessary. Generally, the larger the diameter of the stone particle, the higher is the temperature required to calcine its center. The CO_2 expelled has a longer distance to travel and often considerable internal pressure is exerted as the gas forces its escape. If dissociation of the particle is incomplete, there remains in the center of the particle a core of uncalcined carbonate stone that may range in size from that of a grain of rice to that of an acorn, depending on the linear dimensions of the fraction and the extent to which calcination is complete. Such a core is usually not deleterious, but it does dissipate the concentration of the available lime. Its presence is inevitable with under-burned lime.

On the other hand, if the stone is calcined under severe calcining conditions, ie, high temperature and long retention, the lime may become hard-burned or even dead-burned at sintering temperatures. Under these conditions the stone shrinks by 25–50% of its original size. This shrinkage densifies the resultant lime, narrowing and occluding its micropores and fissures, so that the reactivity of the lime is reduced in varying degrees and extinguished with dead-burned dolomite. Chemical reactivity is usually measured by the rapidity with which lime hydrates in water. Densification of the quicklime particles is caused by the accretion of large crystallites from the stone's original minute crystals. As a result, in hard- and dead-burned limes the crystal lattice is much more compact, and the oxide molecules are in very intimate proximity (7,13).

Both of the above extremes are undesirable for most lime uses. Usually, the objective is to produce a completely calcined but soft-burned lime having no core or no more than 1–2% core. Such limes are more porous and chemically reactive.

Certain stifled calcination conditions can cause recarbonation in which CO_2 is readsorbed on the lime's surface. This can seriously diminish the quality and concentration of the lime. The possibility of recarbonation underscores the importance of rapid expulsion of the CO_2 gas during calcination.

Some limestones, more often the coarse crystalline types, can never be calcined successfully. Such stone tends to decrepitate during preheating or calcination into fine particles that interfere with this pyrochemical reaction. The adaptability of a stone for calcination can only be ascertained with surety by empirical methods. Possibly the greatest influence on lime quality is the size gradation of limestone. Narrow gradations, such as 10 × 20 cm, 2.5 × 5 cm, 1.3 × 0.6 cm, etc, or even narrower ranges, are more conducive to uniform calcination. As an example, if the size ranges between 1.25–15 cm, the small size would tend to be severely over-burned, or the large size would be incompletely calcined if the small size was properly burned. At constant temperature, the rate of calcination varies inversely with the size of the stone, increasing with smaller fractions.

Raising the temperature completes calcination more effectively than lengthening its duration. Generally, impurities complicate the process and impair lime quality more in a quantitative than qualitative manner. Impurities, such as silica, alumina, and iron, tend to combine chemically with lime, except at low calcining temperature, forming silicates, aluminates, and ferrites, and vitiating further the concentration of free lime. The total loss of available CaO, however, approximates 11–12% as a result of lime-fluxing these impurities.

Thermal Requirements. To produce a ton of lime theoretically requires 1.79 and 1.90 t of high calcium and dolomitic stone, respectively. Practically, at least 2 t of stone is needed to produce 1 t of lime, because some stone is lost as dust during the process. To heat the stone to the dissociation point, ca 1.70 GJ/t (1.46×10^6 Btu/short ton) for high calcium and 1.45 GJ/t (1.25×10^6 Btu/short ton) are required for dolomitic quicklimes. However, temperature, usually a higher than the theoretical one, must be maintained until dissociation is terminated. This additional thermal requirement is estimated at 3.22 and 3.02 GJ/t (2.77 and 2.60×10^6 Btu/short ton) for high calcium and dolomitic stones, respectively. In addition, some heat loss is inevitable in lime manufacture, such as heat of evaporation of moist limestone and/or coal, radiation and convection through the kiln structure, retention in the discharged lime, exhaust gases, and

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incombustible dusts. The thermal

theoretical heat requirement ×
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Often, maximum thermal operat
lime quality. Usually this problen
conditions between these two ext
Kilns. *Rotary Kilns.* As of
about 90% of commercial lime ca
rotary kilns. The rotary is not n
although a company in Germany
That company currently operates
kilns. South Africa has a high pe
three of 1000 t/d, and one at 150
Canada also have large rotary kil
producer operating a 1300 t/d rot
of four 1000 t/d rotary kilns, and
as capacities have increased, the
shortened from 90–127.5 to 45–
2.1–3 to 4.8–5.1 m. The diamete
1:12 in modern rotary kilns.
Helping to propel capacitie
proved preheaters, which partial
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fuel consumption a similar percen
that enhance efficiency and lime
internals as metal refractory tref
and lifters.
The exterior of the kiln is h
interior is lined with 15–24 cm r
is shown in Figure 5. Kilns are i
and revolve on trunnions at 1–2
a kiln from the preheater or silo
at the lower end. Cooling air is
calcining zone of the kiln next to
providing heat recuperation. The
the flow of kiln feed to the char
for the preheater. Most U.S. rota
adaptable to gas and oil firing. O
as the kiln feed tumbles gently
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of 0.625–1.88 cm, 1.88–3.75 cm
Rotary kilns produce the g
uniform quality. There are, how
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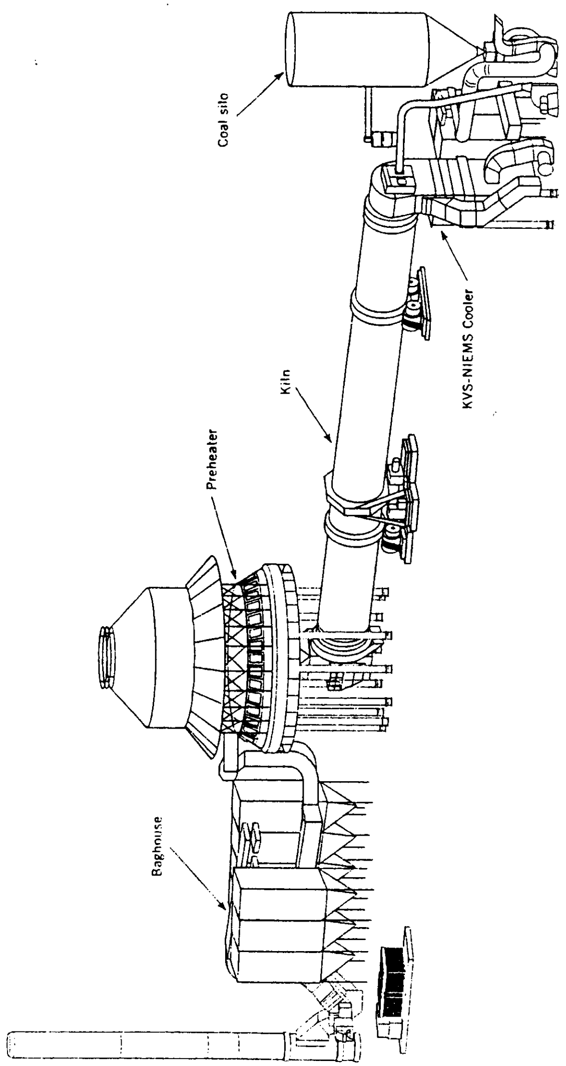

Fig. 5. Schematic of the Kennedy van Saun (KVS) patented low pressure drop (LPD) preheater/rotary kiln lime calcining system available in sites ≥1100 t/d. Courtesy of KVS.

expensive dust collection system. Energy consumption ranges widely from ca 6.4 to 9.3 GJ/t (5.5 to 8 × 10^6 Btu/short ton). The minimum energy value applies to high capacity rotary kilns with the most advanced preheaters, internal accessories, and baghouses. The highest value applies to old, low capacity kilns with no preheater and a minimum of internal accessories. Of these energy values, 90% is for fuel and 10% is electricity, mainly for dust collection.

The average dust loading in rotary kilns is 10% of the kiln feed or approximately 20 kg/t of lime, allowing for a ratio of limestone to lime of 2 on a weight basis. Primary collection of particulates is accomplished with multiple cyclones that entrap about 85% of the dust loading. A secondary system is necessary to abate most of the remaining dust. Of the secondary systems in use, the baghouse is the predominant type, followed by the wet scrubber, electrostatic precipitator, and gravel bed filter (see AIR POLLUTION CONTROL METHODS).

Vertical Kilns. Outside the United States, particularly in developing countries, the vertical kiln is the most commonly used. One reason for the decline in use in the United States is the energy crisis of the 1970s, when supplies of natural gas and fuel oil, the principal fuel for vertical kilns, became stringent and prices escalated rapidly. The vertical kiln has made a slight comeback in the United States, however, through the introduction of the Maerz parallel flow regenerative kiln.

There are many vertical kiln types and designs having widely varying efficiency. All of these kilns have four imaginary zones or sections, as depicted in Figure 6. In the preheating zone, recirculated exhaust gases preheat the stone, preparatory to calcination in the adjacent zone. The calcining zone is the calcination chamber where 95% of lime burning occurs. The lower portion of this zone is called the finishing zone where calcination is completed and where fuel ports for firing are situated. Cool air enters the cooling zone from the base of the kiln or discharge point and by natural, induced, or forced draft flows upward countercurrent to the lime descending through the kiln. The air cools the lime for discharge onto conveyors below, and the air recoups much heat from the red-hot lime as secondary combustion air for the calcining above.

Significant improvements in vertical kiln performance (14) during the 1970s and 1980s have increased capacities to 600–800 t/d, reduced energy consumption to 4.2–4.6 GJ/t (3.6–4.0 Btu/short ton) of lime, and improved product quality. Energy values include an estimated 5% for electricity. The most efficient vertical kilns are of Austrian and German origin: the Maerz or parallel-flow regenerative kiln (Austrian) and the double-inclined, Ring or Beckenbach annular shaft kilns (German). These kilns are widely used in Europe and Japan, but only two, the Maerz parallel-flow gas-fired kiln and the Beckenbach, are in operation in North America. These kilns develop tremendous heat recuperation.

The parallel-flow kiln operates with two or three independent shafts within one large refractory-lined shell. As one shaft is calcining, the waste hot gases are preheating the kiln feed in an adjoining shaft. Thus calcining, discharging, charging, and preheating are performed cyclically, programmed at preset intervals of 10–15 min. At each cycle, firing lances automatically are switched to an adjacent shaft with its preheated stone charge; ducts conveying the hot exhaust gases are similarly reversed. During each cycle's transition period, precise increments of kiln feed are provided by a mobile overhead weight hopper that

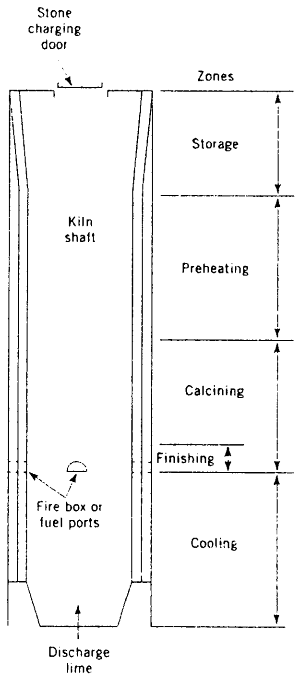

Fig. 6. Zonal section of a vertical kiln.

maintains constant levels. This kiln operates at relatively low temperatures of 950–1050°C with kiln feed of 2.5–15 cm, but usually a size ratio of only 1:3.

The double-inclined kiln calcines even smaller sized stone of 1.88–3.75 cm and at reduced capacity with stone of only 0.63 cm minimum size. Most of these kilns operate using gaseous or oil fuels, including propane. An exception is the double-inclined kiln, which appears to operate at optimum efficiency with a mixture of fuel, ie, 60–75% natural gas or oil and 40–25% coke, although it can operate on 100% gas or oil.

Another thermally efficient kiln is the modern mixed-feed vertical kiln in which coke is admixed with 8.5–20 cm lump limestone and charged into the top of the vertical kiln by a mobile, overhead charging system. However, use of this kiln is waning since the quality of mixed-feed kiln lime does not equal that of the other three kilns described above, owing to ash contamination from the coke and poorer reactivity and to the higher cost of coke in most areas.

Low capacity shaft kilns, direct-fired manually with bituminous coal, which were extant during 1900–1940, largely disappeared following World War II because of their high thermal and labor costs, poor lime quality, and offensive emission of black smoke. Another kiln that was phased out in the United States after World War II is the producer-gas (indirect-fired) kiln. The bituminous coal fuel was burned in a special firebox exterior to the kiln with low heat value gases charged into the calcining zone. These gases did not match natural gas in lime-burning performance, because they possess only 20–30% as much heat value as natural gas. After the energy crisis of 1973, this fuel was carefully reconsidered as a substitute for scarce natural gas and oil, but was judged uneconomical and unfeasible for lime production in the United States.

Many kilns that formerly were direct coal-fired or producer-gas verticals were retrofitted to natural gas firing with center-burners and after World War II, dramatically improving lime quality, kiln capacity, and fuel efficiency. By the 1960s, this improved vertical kiln had lost favor to rotary and other special kilns because of the supply and cost problems of oil and gas in the United States and the spectacular improvement in rotary kiln performance. Many natural gas-fired center burners were permanently closed and dismantled because they could not be converted to coal. However, the reverse occurred in Europe where the extensive oil and gas discoveries heightened interest in the new, advanced vertical kilns.

Miscellaneous Kilns. A U.S. kiln, the Fluo-Solids, appears to be another vertical kiln type, but this is its only similarity. It operates on a different principle. It utilizes as kiln feed only a discrete granulation of 0.225–2.4 mm (65–8 mesh) sizes. Delicately controlled by air and exhaust gas pressure, the kiln feed of granules is fluidized as a dense suspension. Because it is instrumented, this kiln can produce a very reactive lime at better than average thermal efficiency. The kiln, however, has limited utility because the cost of obtaining the kiln feed with many hard, compact limestones is prohibitive.

The Calcimatic is a patented kiln of Canadian origin that is radically different from other kiln types. It consists of a circular traveling hearth of variable speed, supported on two concentric tiers of rollers. Kiln feed of 12.7 mm is fed onto the hearth in a 2.5–10 cm bed from a preheater chamber. The kiln is usually fired with natural gas or fuel oil, although the option of using pulverized coal has also been developed. After great interest, resulting in sales of many units throughout the world, the popularity of the Calcimatic has ebbed because of disappointment in the unit's mediocre thermal efficiency.

Calcination Products. Tables 3 and 4 summarize the analyses and forms of commercial quicklime in the United States (1). In addition to conventionally calcined dolomitic quicklime, a special refractory lime is made by sintering or dead-burning granules of high quality dolomitic limestone in a rotary kiln at 1650°C. Iron oxide (5–8%) is added to the feed to stabilize the product against hydration. The grayish brown dustless granules produced are used only for lining open-hearth and electric steel furnaces or as raw materials for refractory brick and other products.

Rotary kilns and, to a lesser extent, Fluo-Solids kilns are used to calcine a wet precipitated calcium carbonate filter cake in the kraft or sulfate paper-pulp process (15). Lime is regenerated for use as a causticization reagent in recovering caustic soda for pulp digestion. Losses in lime recovery are replaced by purchased lime (see PAPER; PULP).

Table 3. Analyses of Commercial Quicklimes

Component	High calcium,[a] %	Dolomitic,[a] %	Component	High calcium,[a] %	Dolomitic,[a] %
CaO	93.25–98.00	55.50–57.50	Al_2O_3	0.10–0.50	0.05–0.50
MgO	0.30–2.50	37.60–40.80	H_2O	0.10–0.90	0.10–0.90
SiO_2	0.20–1.50	0.10–1.50	CO_2	0.40–1.50	0.40–1.50
Fe_2O_3	0.10–0.40	0.05–0.40			

[a] Values given are typical values and do not necessarily represent minimum and maximum percentages.

Table 4. Physical Forms and Sizes of Quicklime

Physical forms	Physical size, mm (mesh size)	Derivation
lump	63–255	vertical kiln
pebble	6.3–63	rotary, speciality kilns; crushed lump
ground		
100%	< 2.38 (−8)	Fluo-Solids; screening, grinding
40–60%	< 1.49 (−10)	
pulverized		
100%	< 0.84 (−20)	pulverizing; screened dust
80–90%	< 1490 (−10)	
pellets (briquettes)	16.4–55.7[a]	screened fines and dust
dead-burned dolomite	0.84–9.5 (20–2)	iron-stabilized, dead-burned dolomite granules (screened)

[a] Size is given in cm^3.

Hydrated Lime Manufacture

Although most lime is sold as quicklime, production of hydrated lime is also substantial. This product is made by the lime manufacturer in the form of a fluffy, dry, white powder, and its use obviates the necessity of slaking. Small lime consumers cannot economically justify the additional processing step that hydration entails.

The manufacture of hydrated lime proceeds by the slow addition of water to crushed or ground quicklime in a premixing chamber or a vessel known as a hydrator, both of which mix and agitate the lime and water. The amount of water added is critical. Too much water makes it impossible, or too costly, to produce the desired dry form; too little water leaves hydration incomplete, causing degraded quality, namely, chemical instability and structural unsoundness.

More than the theoretical amount (24.5%) of moisture is necessary to counteract the loss of moisture as steam generated by the appreciable heat of hydration. In practice, about 50–65% water is added, depending on the degree of reactivity of the quicklime and its physical size. The finest particles hydrate most rapidly. After hydration, the slightly moist slaked lime is propelled by an enclosed screw-conveyor to an air separator, where the coarse fractions are largely removed as tailings. This step enhances the fineness of the powder, upgrading its chemical purity, and dries the powder further. The hydrate may be further refined, or conveyed to a silo for bagging in 22.7 kg paper sacks, or for bulk truck or rail-car shipment.

The above hydration procedure applies to high calcium and normal dolomitic hydrates (ASTM type N), but the latter is usually incompletely hydrated. Only 10–20% of its MgO component is actually hydrated. All of the CaO hydrates readily. To hydrate the MgO substantially, other hydration measures are employed to produce a highly hydrated dolomitic lime (ASTM type S (Special)). For some dolomitic hydrates, retention in silos in a moist condition for 2–3 d produces the highly hydrated condition. But for most such hydrates it is necessary to employ autoclaves in lieu of normal hydrator machines that operate at atmospheric pressure. At 276–690 kPa (40–100 psi), hydration is completed in this vaporous, hotter atmosphere in less than an hour. The steam and pressure catalyze the hydration of the MgO. After autoclaving, the hydrates are usually subjected to other milling practices in addition to air separation, such as tube milling to enhance the plasticity of the resulting hydrate.

In the United States most commercial hydrates easily conform to the minimum basic requirement of no more than 0.5% retained on 590 μm (30 mesh) screen and no more than 15% retained on a 74 μm (200 mesh) screen. Typical analyses of hydrates are contained in Table 5.

Table 5. Chemical Analyses of Commercial Hydrates

Component	High calcium hydrate, wt %	Highly hydrated dolomitic, wt %
CaO	71–74	45–41
MgO	0.5–2	25–30
H_2O	24–25	27–28
CO_2	0.3–0.7	0.3–0.7
SiO_2	0.2–0.5	0.2–0.5
R_2O_3	0.1–0.3	0.1–0.3

Economic Aspects

Limestone. In the crushed, broken, and pulverized stone industry, limestone (including dolomite) is predominant, accounting for 71% of the tonnage which includes granite, basalt, trap rock, sandstone, and other miscellaneous rock. Its total of 710 × 10^6 t in 1991 makes limestone the third greatest commodity in tonnage in the United States after coal (qv) and sand and gravel. In addition, three other sources of calcium carbonate are produced, including marl, shell, and marble, for which production was 5.7, 5.0, and 3.4 × 10^6 t in 1991, respectively. The United States is clearly the largest limestone producing country, followed by the former USSR, Japan, and Germany. Most countries produce their own limestone requirements.

The average value of limestone in 1991 was $4.73/t, an increase in value of about 50% from 1979. In 1995, the average value was $5.1/t. Table 6 gives the average value of the limestone according to usage. Use of crushed and broken U.S. limestone has grown rapidly since World War II. The all-time record year for U.S. limestone was 1987 when production reached 763 × 10^6 t. Construction aggregate, although declining in volume, still dominates all uses. Transportation

Table 6. U.S. Limestone Average Value, 1991

Material	Value, \$/t	Material	Value, \$/t
cement manufacture	3.45	limestone sand	4.90
riprap	4.52	asphalt filler	8.17
concrete and roadstone	5.03	glass manufacture	11.14
flux stone	5.17	coal-mine dusting	17.05
agricultural liming	5.21	mineral food	11.93
lime manufacture	6.09	SO_2 removal	6.14
limestone whiting	17.78		

plays a principal role in limestone cost and availability. In 1991, modes of transportation for all crushed stone (typical for limestone), based on 67% return, were truck, 72.8%; railroad, 5.5%; water, 6.3%; other modes, 2.5%; and used on-site, 12.9%.

Table 7 presents 1991 statistics on limestone and dolomite uses, and includes production from 2338 U.S. plants (16). Generally the growth markets for uses have been in construction aggregate, Portland cement and lime manufacture, industrial fillers, mineral feed, and stack-gas desulfurization that utilizes limestone wet scrubbing. Declining markets have been iron and steel fluxing, fertilizer filler, pulp and paper, rock-wool manufacture, refractories, and agricultural liming.

Lime. The total tonnage of quicklime and hydrated lime sold and used in 1992 was 16.2 × 10^6 t. Captive lime accounted for 11% of this total, nearly the same percentage as captive limestone. Captive lime production decreased drastically since the 1970s, falling from 6.7 × 10^6 t in 1973 to 1.82 × 10^6 in 1992. Whereas commercial lime production was at an all time high in 1992, total lime (commercial lime plus captive lime) was 18% below that of the all time record of 19.8 × 10^6 t, set in 1973.

More than 90% of all lime uses are in the chemical and metallurgical areas, and lime is the fifth largest chemical in the United States, behind sulfuric acid and certain industrial gases such as oxygen. Although steel manufacture is still the greatest use of lime, many established and developing environmental applications are growing rapidly.

There were 113 commercial and captive lime plants in the United States as of 1993. Of these plants, the 10 largest produce about 35% of total lime output. Ohio is the largest lime producing state, followed by Pennsylvania, Missouri, Kentucky, Alabama, Texas, Illinois, Indiana, Virginia, and Arizona.

The former USSR was the leading lime-producing country in 1991, producing 26 × 10^6 t; followed by China, 18.5 × 10^6 t; and the United States, 15 × 10^6 t; Germany, 9.2 × 10^6 t; Japan, 9.0 × 10^6 t; Mexico, 6.5 × 10^6 t; and Brazil, 5.5 × 10^6 t.

Except for two countries, there is very little world trade in lime. The largest importer is the Netherlands, which is nearly devoid of limestone and thus imports about 10^6 t annually from Belgium and Germany. The other net importer of consequence is the United States, which imports ca 150,000 t/yr or about 1% of U.S. production. About 85% of the U.S. imports are from Canada; the balance is from Mexico.

Categories for total lime usage in 1991 are presented in Table 8. Steel and environmental uses predominate, accounting for 30 and 24% of the total, respectively.

In 1991, the average value per metric ton of lime in bulk was reported to be \$78.44 for agricultural lime, \$68.12 for construction lime, \$54.90 for chemical lime, and \$82.62 for refractory lime. The average value for total lime was \$57.02/t.

Table 7. Crushed Limestone and Dolomite Sold or Used by Producers in the United States, 1991

	Limestone		Dolomite	
Material	Quantity, t × 10^3	Value, \$ × 10^3	Quantity, t × 10^3	Value, \$ × 10^3
coarse (+1.25 cm) aggregate				
macadam	2,983	13,392	111	531
riprap and jetty stone	13,531	61,269	1,163	7,379
filter stone	4,590	21,259	122	653
other coarse aggregate	179	774	^{a}	^{a}
coarse aggregate, graded				
concrete aggregate, coarse	61,419	300,273	7,604	42,104
bituminous aggregate, coarse	40,923	208,579	7,137	43,572
bituminous surface-treatment aggregate	18,539	93,027	2,349	12,094
railroad ballast	4,133	18,216	1,009	4,392
fine (−0.95 cm) aggregate				
stone sand				
concrete	12,076	62,338	1,178	6,988
bituminous mix or seal	10,377	47,634	4,034	22.532
screening, undesignated	13,514	56,166	1,294	10,220
other fine aggregate	108	398		
coarse and fine aggregates				
graded road base or subbase	104,802	428.122	9,809	47.279
unpaved road surfacing	19,466	86,798	688	2,825
terrazzo and exposed aggregate	1,425	9,388	4	102
crusher run or fill or waste	21,010	88,367	2,038	8,624
other construction materials	9,673^{b}	44,020^{b}	3,497^{c}	20,002^{c}
roofing granules	755	4,657	^{a}	^{a}
agricultural				
agricultural limestone	14,163	74,041	2,287	20,371
poultry grit and mineral food	2,257	26,999	^{d}	^{d}
other agricultural uses	690	3,676	88	1.143
chemical and metallurgical				
cement manufacture	71,832	248.780		
lime manufacture	16,305	99.632	611	3.507
dead-burned dolomite manufacture			1,371	5.733
flux stone	3,635	18,803	752	2.751
chemical stone	294	1,614	^{d}	^{d}
glass manufacture	269	3.009	^{d}	^{d}
sulfur oxide removal	2.040	12.551		

Table 7. *(Continued)*

Material	Limestone Quantity, $t \times 10^3$	Limestone Value, $\$ \times 10^3$	Dolomite Quantity, $t \times 10^3$	Dolomite Value, $\$ \times 10^3$
special				
mine dusting or acid water treatment	659	11,250	200	1,542
asphalt fillers or extenders	1,448	11,861	482	4,159
whiting or whiting substitute	533	9,489	[d]	[d]
other fillers or extenders	2,753	41,851	297	3,593
other miscellaneous uses				
chemicals	505	3,120	[d]	[d]
magnesia (dolomite)	16	30		
other uses not listed	235[e]	3,672[e]	230	3,157
unspecified[f]				
actual	148,595	748,891	6,807	32,457
estimated	49,880	242,494	197	846
Total[g]	*655,622*	*3,106,400*	*55,338*	*308,600*

[a] Included with other construction materials.

[b] Includes other graded coarse aggregate, dam construction, drain fields, building products, pipe bedding, and waste material.

[c] Includes building products.

[d] Included in other uses not listed.

[e] Includes abrasives, paper manufacture, and refractory stone (including ganister).

[f] Includes production reported without a breakdown by end use and estimates for nonrespondents.

[g] Data may not add to totals shown because of independent rounding.

The price of lime doubled during the 1970s, owing to the rapidly escalating fuel prices brought on by the Arab oil embargo. This was followed by a leveling of prices during the 1980s, to around \$56.00/t (the highest rate was \$57.87/t in 1986). However, when comparing prices based on constant 1991 dollars, prices actually decreased steadily from 1979 to 1991, finishing the period down about 30%.

Uses

Limestone. *Construction.* Generally, for highway and building construction, limestone that is clean, strong, durable, sound (free from incipient cracks), and dense is preferred. This is particularly true with respect to use as a coarse aggregate. Most engineers purchase limestone on specifications based largely on the physical properties of the stone. Many of these specifications differ widely, particularly with respect to the exact application of the stone and to a lesser extent by geographical location. Many tests and specifications are published by ASTM, AASHTO, the National Institute of Standards and Technology, and others. Generally, the presence of alkalies, soluble sulfides, gypsum, and organic matter in the stone is objectionable to most users. Another important consideration is the physical size and range of particle gradation of the limestone. As a result, many types of limestone are rejected for one or more construction uses when unable to meet these requirements.

Table 8. Lime Sold or Used by Producers in the United States, $t \times 10^3$[a]

Industry	1990 Sold	1990 Used	1990 Total[b]	1991 Sold	1991 Used	1991 Total[b]
		Chemical and industrial				
alkalies	[c]	[c]	96	[c]	[c]	80
aluminum and bauxite	141		141	145		145
copper ore concentration	[c]	[c]	338	[c]	[c]	371
food products, animal or human	19		19	20		20
glass	90		90	152		152
magnesia from seawater or brine	[c]	[c]	592	[c]	[c]	523
oil well drilling	11		11	11		11
oil and grease	[c]	[c]	17	[c]	[c]	[c]
ore concentration, other	300		300	343		343
paper and pulp	[c]	[c]	1,148	[c]	[c]	1,125
precipitated calcium carbonate	[c]	[c]	230	[c]	[c]	270
steel						
BOF	[c]	[c]	3,660	[c]	[c]	3,770
electric	[c]	[c]	884	835		835
open-hearth	111		111	44		44
sugar refining	27	569	596	26	669	694
tanning	24		24	19		19
other[d]	8,091	1,069	2,194	7,116	982	1.958
Total[b]	*8,814*	*1,637*	*10,452*	*8,711*	*1,651*	*10,360*
		Environmental				
acid water, mine or plant	259		259	314		314
sewage treatment	424		424	473		473
flue gas sulfur removal	1,518		1,518	1,565		1,565
water purification	972		973	1,032		1,032
other[e]	587	9	596	408	5	413
Total[b]	*3,758*	*9*	*3,768*	*3,792*	*5*	*3.797*
		Construction and other				
soil stabilization	610		610	648		648
finishing lime	145		145	96		96
mason's lime	[c]	[c]	230	[c]	[c]	168
other[f]	268		268	269		269
Total[b]	[c]	[c]	*1,253*	*1,013*	[c]	*1,181*
agriculture	43		43	48		48
refractory lime (dead-burned dolomite)	[c]	[c]	342	[c]	[c]	308
Grand total[b]	*14,040*	*1,818*	*15,858*	*13,875*	*1.819*	*15,694*

[a] Excludes regenerated lime; includes Puerto Rico.

[b] Data may not add to totals shown because of independent rounding.

[c] Included in "other" category.

[d] Includes briquetting, brokers, calcium carbide, chrome, citric acid, commercial hydrators, desiccants, ferroalloys, fiber glass, glue, insecticides, ladle desulfurizing, magnesium metal, metallurgy, pelletizing, pharmaceuticals, petrochemicals, rubber, silica brick, soap wire drawing, and uses[c] in chemical and industrial lime only.

[e] Includes industrial solid waste treatment, industrial wastewater treatment, scrubber sludge solidification, and other environmental uses.

[f] Includes asphalt antistripping.

Table 9 shows the dominance of limestone over other types of crushed stone as an aggregate.

Concrete Aggregate. A versatile application for coarse limestone aggregate is in Portland cement concrete, either job-mixed or ready-mixed for a wide variety of concrete applications, such as footings, poured foundations, paving, curbs, structural products, etc. Limestone sand also provides a satisfactory fine aggregate, but usually it is more costly than conventional sand from local pits.

Roadstone. The greatest tonnage of aggregate is consumed in highway construction for the subgrade or subbase and base course, surface aggregate for unpaved macadam roads, coarse and fine aggregate for asphalt paving mixes of varying thicknesses for the wearing surface and/or black base, and bituminous macadam and other types of asphalt surfaces, such as sheet asphalt and cold-mix. Screenings of < 6 mm are favored in water-bound macadam roads. Most of this limestone aggregate is subject to the Los Angeles abrasive resistance test for durability.

Railroads also require coarse and fine aggregate of physical strength and durability similar to concrete and roadstone for road beds. Railroads prefer gradation of 19–63.5 mm as coarse aggregate.

Riprap. Heavy, irregular limestone fragments, ranging in size from 25–30 cm to large boulders are used for dam spillways; construction of docks, piers, and breakwaters; and rustic massive rock barriers and dry rock retaining walls. When the size of riprap is specified, its price rises sharply.

Asphalt Filler. One of the preferred mineral-dust fillers for asphalt-paving mixtures is pulverized limestone meeting a fineness requirement of at least 60–75% minus 0.074 mm (200 mesh). The limestone fines greatly reduce the size and extent of voids in the mixture, providing a more stable, water-resistant, denser-graded aggregate for mixing with the asphalt cement. Usually, it enhances toughness and resistance to softening in hot weather (see ASPHALT).

Limestone Sand. A discrete gradation of substantially 2.38–0.225 mm (8–65 mesh) size provides a versatile fine aggregate or sand for road mixtures, concrete, plaster, or any construction use supplied by silica sand. The only disadvantage is that in many areas conventional sand is less costly.

Table 9. Crushed Stone Sold or Used in the United States, 1991

Stone	Number of quarries	Quantity, t × 10^3	Value, \$ × 10^3	Unit value, \$/t
limestone[a]	2,201	655,578	3,106,444	4.74
dolomite	137	55,336	308,556	5.58
calcareous marl	15	5,175	13,769	2.66
shell	14	4,959	44,376	8.95
marble	46	3,400	83,335	24.51
granite	492	149,050	864,374	5.80
traprock	561	75,593	485,223	6.42
sandstone and quartzite	235	25,855	137,683	5.32
miscellaneous stone	312	25,616	143,061	5.58
Total	*4,013*	*1,000,534*	*5,186,800*	*5.18*

[a] Includes reporting for limestone–dolomite when no distinction is made between the two.

Miscellaneous. Granules of limestone and oyster or clam shell are generally a second-choice mineral aggregate for roofing granules. Siliceous rocks and slag, however, provide most of this requirement. Larger aggregate is used in built-up roofs. Limestone wastes or spalls are used as fill for swamps and low lying areas.

Building Materials. Portland Cement Manufacture. The second greatest use of limestone is as raw material in the manufacture of Portland cement (10). The average limestone factor per ton of Portland cement is 1.0–1.1 t of pulverized limestone. The limestone, calcined to lime in the cement rotary kiln, combines with silica and alumina to form tricalcium silicate and tricalcium aluminate and other lesser cementing compounds (see CEMENT). Most cement companies operate captive limestone quarries.

A second form of limestone is finely pulverized limestone for masonry cement. This form is achieved by intergrinding roughly equal parts of limestone and cement clinker in a ball mill to which an air-entraining agent is added.

Concrete Products. Limestone aggregate is used competitively with other aggregate in the manufacture of molded, reinforced, and prestressed concrete products in the form of block, brick, pipe, panels, beams, etc.

Insulation. Impure siliceous limestone and blast-furnace slag are the main raw materials for making rock-wool insulation bats and pellets (see INSULATION, THERMAL).

Fillers. Micronized carbonate whiting is the preferred mineral fill for putty and caulking compounds based on linseed oil or plastic, and vinyl-based floor coverings. It comprises 20–60% of the raw material mix (see FILLERS).

Calcium Silicate Products. Quicklime is used as the cementitious binder in making autoclaved building materials based on calcium silicate, ie, sand–lime brick, cellular (or foam) concrete block and insulation material, and the former USSR extremely dense and reinforced silicate–concrete building materials. Lime reacts with fine silica in the autoclave under steam and pressure to form strong dicalcium silicate cement compounds, representing a type of cementless concrete because no Portland cement is used in the mix. Use of these building materials is growing steadily in Germany, Scandinavia, the Netherlands, the eastern European countries, Australia, Canada, and Japan, but little use is made of them in the United States. They are economically useful, can be mass produced, and are of stable quality. By increasing the foaming agent in cellular concrete, an extremely lightweight insulation, microporite, can be produced. Only lime (no limestone) is used in these products.

Mineral Feed. Mineral feed supplements for domestic animals and fowl usually contain a pure form of pulverized limestone. In fact, some state laws require the supplement to be at least 35% available calcium. Other sources of calcium are bone meal and dicalcium phosphate. Use as mineral feed has been a steadily growing market for limestone. The material is ground to 90% minus 0.15 mm (100 mesh) or 80% minus 0.9074 mm (200 mesh), is low in silica, and has strict tolerances on arsenic and fluorine (see FEEDS AND FEED ADDITIVES).

Lime. *Building.* Lime, in hydrated form, is used in lime–cement–sand mortar of various proportions to provide plasticity, high water retentivity, and bond strength (17). In the United States, nearly all of the mason's lime used is

ASTM Type S hydrated lime. It is applied to mortar in several ways: (*1*) one bag each of lime and Portland cement with six parts sand by volume is added to the mortar mixer at the job site; (*2*) 5–10% of hydrated lime is added to some masonry cements and packaged for later mixing with sand (in a 1:3 proportion) and water; (*3*) at a central mixing plant, lime putty made from quicklime is mixed with a measured amount of sand and water, and delivered to the project as ready-mixed mortar or ready to use (mixed) in drums; (*4*) lime, cement, and sand are dry-mixed and delivered to the job in bulk, optionally with all mortar handling and mixing equipment on a rental basis; (*5*) pulverized quicklime is slaked at the job site, and the resulting putty is then mixed with cement and sand.

Any of these mortars can be used for unit masonry or for stucco (exterior plaster). The finish coat in conventional interior plastering is composed of either neat lime putty or a sanded putty, gauged with Keene's cement or gypsum-gauging plaster. The former is called a whitecoat finish; the latter a sand-float finish.

Lime–Soil Stabilization. Lime–soil stabilization (18) has been successfully applied to all types of roads from farm to market to interstate freeways; to parking lots, airport runways, building foundations; in embankments and earth dams, railroad beds, and irrigation canal linings; and to river levees. Lime's reaction is with silica, derived from clay in the soil, drastically lowering the soil's plasticity index and increasing the compacted soil's stability and strength. Lime also expedites construction by drying up saturated subgrades. It is applied in the subbase (subgrade) and/or base course. Where soils are deficient in clay, lime is applied with flyash which generates the desired lime–silica reaction (19). Lime, flyash, and aggregate are premixed in a central mixing plant and then spread on roadways like base material. Compaction and moist-curing follow (see SOIL STABILIZATION).

Lime stabilization originated in Texas after World War II, and now it is used throughout the world. Lime is most commonly applied at a 4 wt % application or ca 11 kg/m^2 (20 lb/yd^2) for 15 cm of compacted depth. It can be applied dry as hydrated lime or granular quicklime or as a wet slurry. Distribution of the latter form is dustless. Copious amounts (as much as 5–10%) of water are always needed in excess of the optimum moisture content of the soil. Then, a requisite for success is intimate mixing with a rotary mixer, followed by compaction to a minimum of 95% Proctor density.

Technology has developed for lime to stabilize soil at a considerable depth (20). The U.S. method is called lime slurry pressure injection, with lime slurry being injected *in situ* to 3–6.6 m depth through lances on a grid-pattern but there is no mixing of lime and soil. Both Japan and Sweden have developed techniques using specially constructed machines to inject dry quicklime and then mixing the lime, soil, and water to depths of 11 m or more under critical hydraulic conditions.

Lime–Asphalt Treatment. Hydrated lime has become an important additive for use in hot mix asphalt pavements. The lime is added at a 1–1.5% rate to the asphalt mix, primarily as an antistripping agent to reduce moisture damage. In this application, lime helps provide a more permanent bond between the asphalt and aggregate. In addition, lime also reduces long-term age hardening and low temperature cracking, thereby adding to the durability of the pavement.

Agricultural Uses. Liming Soils. Over 95% of limestone's consumption in agriculture is direct application of limestone to the soil (21). Acid soils are neutralized (sweetened) with lime, raising the pH values of the soil to a 6–7 range, the optimum level for most crops (see FERTILIZERS). Liming also provides two important plant nutrients, calcium and magnesium, for the soil as well as beneficial trace elements contained in limestone. Liming counteracts acidity generated by some nitrogen fertilizers such as ammonium nitrate and sulfate, improves soil tilth, and elevates the organic content of the soil.

Rates of applications of lime vary greatly depending on many factors, but range from 0.1 to 0.9 kg/m^2 (0.5 to 4 short ton/acre). Liming is beneficially practiced during all seasons of the year. In evaluation of a liming material, two critical factors are percentage CaO and particle size. Purity signifies a higher concentration of lime and fine particles, ie, 0.14–0.25 mm (60–100 mesh) react with soil acids much faster than coarse particles.

More than 99% of liming in the United States occurs in the eastern half of the country; in the west, soils are alkaline. In 1991, 16.4 × 10^6 tons of liming material was used in the United States, about half the amount used during the record year of 1976, when federal subsidies for liming were in effect.

Fertilizer Filler. Fertilizer-mixing plants use ground limestone as a filler. Unlike inert fillers, limestone and dolomite provide calcium and magnesium as plant nutrients and acid-neutralizing values to the mix. Dolomitic stone is preferred because it is less reactive than high calcium limestone.

Chemical and Industrial Uses. Iron and Steel Metallurgy. As a flux in the refining of metals, limestone is essential in producing pig iron. In the blast furnace, limestone reacts with impurities in the iron ore and fuel, mainly silica and other acid oxide components, creating a blast-furnace slag that is separated from the molten iron. Pulverized fluxstone is contained in a self-fluxing sinter, a concentrated iron ore agglomerate. Owing to improved iron ore beneficiation methods, the limestone to pig iron factor is only about 120 kg/t (240 lb/short ton) (see IRON; STEEL).

In producing steel from pig iron (hot metal) and steel scrap, quicklime is the main flux employed. In the basic oxygen furnace (BOF) which comprises about two-thirds of the steel in the United States, the average factor of lime in a ton of BOF steel is about 60 kg. These furnaces employ a mixture of high calcium and dolomitic pebble quicklime, averaging about 20% dolomitic, the latter being used primarily to extend lining life. In the Q-BOP furnace, pulverized quicklime is charged into the bottom of this oxygen-blown furnace. The other principal lime consuming furnace is the electric furnace which is charged with steel scrap. The basic open-hearth furnaces have been largely phased out; these use more limestone than lime as flux. In the United States, about 30% of total lime is used as steel flux. The percentage is somewhat higher in Japan and most European steel-producing nations.

In Germany and Japan, pulverized quicklime is used in making self-fluxing sinters, partially replacing limestone. Granular dead-burned dolomite is still used to protect the refractory lining of open-hearth and electric furnaces, but not the basic oxygen furnace. Refractory lime has declined with the obsolescence of the open hearth, and is primarily used in making tar bonded refractory brick for the BOFs. Other minor uses of lime by the steel industry include coating pig and slag-casting molds with lime whitewash to prevent sticking; as a lubricant for coating wire in wire drawing; in pickle-liquor and plating-waste treatment, as a neutralizer and precipitant; and in ammonia recovery from coke-oven gases.

Nonferrous Metallurgy. Lime and limestone are required in many strategic nonferrous metallurgical processes (22). All seawater, brine, or bittern processes for magnesium metal and magnesia manufacture require either high calcium or dolomitic quicklime (see MAGNESIUM AND MAGNESIUM ALLOYS). In the Bayer process, lime is used for causticization and desilification in the manufacture of alumina for reduction to aluminum metal (see ALUMINUM AND ALUMINUM ALLOYS). Limestone is also used instead of lime in an alumina process adaptation called the sinter process. The second largest metallurgical use for lime is in the beneficiation of copper ore by flotation (qv), where it is used for neutralization and to maintain proper pH control (see COPPER). Limestone serves as a flux in smelting copper, lead, zinc, ferrosilicon, and antimony from their ores. Lime is the key reagent for recovering uranium from gold slimes in South Africa, and in Canada and the United States lime neutralizes acid wastewater in acid extraction of uranium from its ore. Lime also aids in the recovery of nickel and tungsten by chemical processes after smelting, in the flotation of gold and silver, and in the sintering of low carbon ferrochrome.

In gold and silver production, lime is used to control the pH in both heap and vat leaching processes which utilize sodium cyanide solutions. Lime helps maintain the pH of the cyanide solution between 10 and 11, thereby maximizing gold recovery and preventing the formation of dangerous hydrogen cyanide gas. Because the United States is now one of the world's leading gold producers, this development has spurred lime usage in the western states and also in South Carolina.

Environmental Uses. Next to steel fluxing, environmental uses of lime are the biggest market, accounting for 24% of total lime consumption. These uses include air pollution control, water, sewage, and industrial wastewater treatment, hazardous waste treatment, etc.

Air Pollution Control. Both lime and limestone are increasingly and competitively used for desulfurizing stack gases from utility and industrial plants that operate coal-burning boilers (23). This developing technology has resulted in stack gas scrubbing becoming the second largest market for lime, comprising about 1.75×10^6 t in 1992. The use of high purity limestone for scrubbing has also increased considerably, largely owing to its much lower material cost than lime. However, lime has nearly twice the SO_2 neutralizing capacity and produces less waste because the stoichiometrics of lime use are 100–110% compared to 140–150% for limestone. Lime is also more chemically reactive. Thus capital investment costs for limestone scrubbers are considerably higher than for lime scrubbers. More and larger treatment equipment would be required for the former, as well as the need for larger waste disposal areas.

Most of the stack gas scrubbing is handled by wet scrubbers utilizing slurries containing 10–15% lime solids, and attaining SO_2 efficiencies as high as 99%. Dry scrubbers are also being used in which lime slurry is pumped into a spray dryer. These are used with low sulfur coals, produce a dry waste product, and operate at 70–90% sulfur removal efficiency. Recently, two other techniques have been tried, namely, dry injection of hydrated lime into the top of the boiler, and also into the downstream exhaust ducts. The passage of the Clean Air Act Amendments should lead to a large increase in use of lime for scrubbing by the mid-1990s (see also COAL CONVERSION PROCESSES, CLEANING AND DESULFURIZATION).

Other developing or potential applications for lime are neutralization of tail gas from sulfuric acid plants, neutralization of waste hydrochloric and hydrofluoric acids and of nitrogen oxide (NO_x) gases, scrubbing of stack gases from incinerators (qv), and of course, from small industrial coal-fired boilers.

Water Treatment. Potable water treatment (24) is the third largest tonnage use of lime. Approximately 1.1×10^6 t/yr are used for water softening, purification through coagulation, and high pH retention. In water softening, lime removes the temporary (bicarbonate) hardness, and when soda ash is added, permanent hardness is also removed. In clarification using alum and iron salts as coagulants, lime maintains the optimum pH for removing turbidity from river and lake water sources. Similar water treatment methods are applicable to industrial boiler and process waters and to the recovery of waste-process water for recycling.

In recent years, lime treatment has been advocated for corrosion control by removing lead and copper from distribution systems, mainly by raising the pH to around 7.5, which prevents these heavy metals from solubilizing. This type of treatment is applicable to all water supplies, and especially for small systems. It involves the use of hydrated lime, generally delivered in bags (see WATER).

Industrial Wastewater Treatment. Industrial wastewaters require different treatments depending on their sources. Plating waste contains toxic metals that are precipitated and insolubilized with lime (see ELECTROPLATING). Iron and other heavy metals are also precipitated from waste-pickle liquor, which requires acid neutralization. Akin to pickle liquor is the concentrated sulfuric acid waste, high in iron, that accumulates in smokeless powder ordinance and chemical plants. Lime is also useful in clarifying wastes from textile dyeworks and paper pulp mills and a wide variety of other wastes. Effluents from active and abandoned coal mines also have a high sulfuric acid and iron oxide content because of the presence of pyrite in coal.

For neutralization, both lime and limestone are used, but limestone is only effective in under-neutralization to pH 6–6.5. In complete- or over-neutralization to pH 9–10, necessary for precipitating ferrous iron and other heavy metals, only lime is effective (25).

Sewage Treatment. In the abatement of stream pollution, wastewater from sewage plants must meet stringent standards that increasingly require chemical treatment, usually including lime. Lime treatment precipitates phosphates and most heavy metals. It also aids clarification by coagulating a high percentage of solid and dissolved organic compounds, thereby reducing biological oxygen demand (BOD). When lime raises the pH to 11–12, most bacteria and viruses are destroyed, as well as odor. The high pH also helps to volatilize ammonia, a nitrogen-plant nutrient (26).

Solid-Waste Disposal. Heavy lime treatment of sewage sludge quells obnoxious odors, sterilizes or destroys pathogens, and precipitates toxic heavy metals. Thus sludge is stabilized for safe disposal as landfill or for beneficial disposal on agricultural land. This use of lime in sewage sludge treatment is being spurred on by passage in 1992 of the Federal 503 Sludge Regulation. This law recognizes lime pasteurization (in Class A treatment) in which the sludge is treated to pH > 12 for two hours, at a temperature of 70°C for 30 minutes, this can be accomplished by using quicklime. The sludge can then be used as a safe soil amendment.

Hydrated lime is also used to stabilize the calcium sulfite–sulfate sludge derived from thickeners at SO_2 scrubbing plants that use limestone–lime. Hydrated lime (2–3%) is added to react with the gypsum sludge and flyash or other added siliceous material. Under ambient conditions the lime and silica serve as a binder by reacting as calcium silicates so that the material hardens into a safe, nonleaching, stable, sanitary landfill or embankment fill.

Filter Beds. The sprinkling filter beds of sewage plants are composed of closely screened mineral aggregate of 38–64 mm or 51–76 mm that meet a severe soundness test. Much of this requirement is supplied by dense, fine-grained, hard limestone and dolomite.

Chemicals Manufacture. Lime Manufacture. Limestone is consumed at the rate of 32–34 × 10^6 t/yr in the manufacture of lime. About 75% of the tonnage is captively produced in the United States. The balance is shipped from quarries in northern Michigan and British Columbia in large ore boats or barges. The limestone:lime ratio is ca 2:1.

Alkalies. In the 1960s, 3.2–34 × 10^6 t/yr of lime was captively produced by the U.S. alkali industry for manufacturing soda ash and sodium bicarbonate via the Solvay process. Electrolytic process caustic soda and natural soda ash (trona) from Wyoming have largely replaced the Solvay process. Three of the trona producers in Wyoming now purchase quicklime for producing caustic soda.

Calcium Carbide. Until the 1940s, calcium carbide, which is made by interacting quicklime and coke in an electric furnace, was the only source of acetylene. Although much more acetylene is now derived from natural gas, calcium carbide is still being produced, using 0.9–1.0 t of quicklime to make 1 t of carbide (see CARBIDES).

Plastics. The fastest-growing use of whiting (microcarbonate fillers) is in the plastics industry where dry, pulverized limestone is used intensively for most types of plastics. Other carbonate fillers, precipitated calcium carbonate, oyster shell, marble, and wet-ground limestone, are also used.

Miscellaneous. Both whiting and hydrated lime are used as diluents and carriers of pesticides, such as lime–sulfur sprays, Bordeaux, calcium arsenate, etc. The most widely used bleach and sterilizer, high test calcium hypochlorite, is made by interacting lime and chlorine (see BLEACHING AGENTS). Calcium and magnesium salts, such as dicalcium phosphate, magnesium chloride, lithium salts, etc, are made directly from calcitic and dolomitic lime and limestone. Two types of magnesia, caustic-calcined and periclase (a refractory material), are derived from dolomitic lime. Lime is required in refining food-grade salt, citric acid, propylene and ethylene oxides, and ethylene glycol, precipitated calcium carbonate, and organic salts, such as calcium stearate, lactate, caseinate, etc.

Other Industrial Uses. Pulp and Paper. Limestone is the traditional alkaline medium for the sulfite pulp process in preparing the calcium bisulfite pulp-cooking liquor. The main application of quicklime is in the sulfate pulp process for causticizing the waste black liquor to regenerate caustic soda for reuse in

digesting the pulp. The sulfate pulp industry captively produces several million tons of lime per year from the waste calcium carbonate sludge resulting from the causticizing reaction, with the commercial lime industry supplying about one million tons per year as make-up lime.

The latest development in paper making has been the switch from the acid to alkaline pulping process, which reduces production costs and results in stronger, longer lasting paper. Although ground limestone is used in the alkaline process, the growth is primarily the result of the installation of economical satellite precipitated calcium carbonate (PCC) plants at the paper mills (27). The PCC serves as both a filler and coating material for making fine white grades of paper. There are about 40 satellite PCC plants in the United States and Canada built since 1986 and producing more than 0.8 t/yr of PCC. This use is now being extended overseas.

Glass Manufacture. Both high calcium limestone and dolomite are high volume batch ingredients for many types of glass (qv), television picture tubes, flat glass (for windows, automotive glass, and mirrors), light bulbs, food and beverage containers, glass tableware, and glass fiber (for reinforcement and insulation). The glass fiber industry generally uses quicklime, whereas dried, double-screened limestone or dolomite is generally used in other glass products. Because magnesium oxide enhances durability and weatherability, dolomite (or dolomite along with limestone) is specified for nearly all glass types except one-use nonreturnable beverage containers. Glass companies require raw materials that are consistent in sizing and chemistry after shipment. They have established very strict limits for both the iron content of the ore itself (typically < 0.1%, but as low as 0.06%), and for contaminating metallic material like stainless steel or aluminum.

Industrial Fillers. Whiting is widely used in paints as a filler and pigment extender. A high reflective white color is a requisite for paint. Both ultrafine and relatively coarse carbonate fillers are incorporated in rubber products. The latter type of a nominal 0.074 mm (200 mesh) size is for inexpensive rubber products.

Coal-Mine Dusting. A steady market for pulverized limestone is in dusting coal mines with a noncombustible mineral dust as a federally mandated mine safety requirement. Of all mineral dusts, limestone is by far the most commonly used (60–75% 0.074 mm (200 mesh)). Consumption in 1991 was 0.7 × 10^6 t.

Sugar. Lime is an essential reagent in refining sugar (qv). There is a vast difference in the use of lime in beet and cane sugar. In beet sugar, the lime factor is 0.25 t/t of sugar; in cane sugar, it is only 4.5–5.4 kg/t. Because all beet sugar refineries require an abundance of carbon dioxide in the process, invariably every plant has on-site lime kilns for captive lime and CO_2 even though the kilns are operated only in the autumn after the beet harvest for ca 1–2 mo. Most beet-sugar plants purchase their limestone kiln feed.

Petroleum. Apart from its use in petrochemicals manufacture, there are a number of small, scattered uses of lime in petroleum (qv) production. These are in making red lime (drilling) muds, calcium-based lubricating grease, neutralization of organic sulfur compounds and waste acid effluents, water treatment in water flooding (secondary oil recovery), and use of lime and pozzolans for cementing very deep oil wells.

Other. Lime is also used in leather (qv) tanning for dehairing hides, in the manufacture of some paint and ceramic pigments, and for glue and gelatin from packinghouse wastes, in controlled atmospheric storage of fresh fruit as a CO_2 absorbent, in making monocalcium phosphate for baking powder, and as a binder for making refuse-derived fuel pellets.

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K. A. GUTSCHICK
National Lime Association

LINCOSAMINIDES. See ANTIBIOTICS, LINCOSAMINIDES.

LINEN. See FIBERS, VEGETABLE.

LINOLEIC ACID, LINOLENIC ACID. See CARBOXYLIC ACIDS.

LINSEED. See FIBERS, VEGETABLE.

LINSEED METAL, LINSEED CAKE. See FEEDS AND FEED ADDITIVES.

LINT. See COTTON.

LINTERS. See CELLULOSE; VEGETABLE OILS.

LIPASES. See ENZYME APPLICATIONS, INDUSTRIAL.

LIPIDS. See FATS AND FATTY OILS; VEGETABLE OILS.

LIPOSOMES. See DRUG DELIVERY SYSTEMS.

LIPSTICK. See COSMETICS.

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STEPHEN G. HIBBINS
Timminco Metals

CALCIUM CHANNEL ANTAGONISTS. See CARDIOVASCULAR AGENTS.

CALCIUM COMPOUNDS

SURVEY

The chemical element calcium [*7440-70-2*], Ca, atomic number 20, is an alkaline-earth metal which is fifth in abundance among all elements (ca 4%) and the third most abundant metal found in the earth's crust (1). It is too reactive to be found naturally in the free state, but its compounds are widespread as the minerals listed in Table 1 indicate. Calcite [*13397-26-7*], $CaCO_3$, found as limestone, marble, and chalk, makes up approximately 7% of the earth's crust. Gypsum [*13397-24-5*], $CaSO_4{\cdot}2H_2O$, fluorspar or fluorite [*7789-75-5*], CaF_2, and dolomite [*16389-88-1*], $CaCO_3{\cdot}MgCO_3$, are other minerals that occur in sufficient quantities to serve as sources for elemental calcium. Lime feldspar [*1302-54-1*] (anorthite), $CaAl_2Si_2O_8$, accounts for more than half of the feldspars, which in turn make up some 60% of igneous rocks, eg, basalt and granite (2).

Table 1. Calcium-Containing Minerals

Mineral	CAS Registry Number	Molecular formula
marble		$CaCO_3$
limestone		$CaCO_3$
calcite	[*13397-26-7*]	$CaCO_3$
dolomite	[*17069-72-6*]	$CaCO_3{\cdot}MgCO_3$
gypsum	[*13397-24-5*]	$CaSO_4{\cdot}2H_2O$
anhydrite	[*14798-04-0*]	$CaSO_4$
fluorspar	[*7789-75-5*]	CaF_2
fluorapatite	[*1306-05-4*]	$Ca_5F(PO_4)_3$
hydroxylapatite	[*1306-06-5*]	$Ca_5OH(PO_4)_3$
selenite	[*15698-85-8*]	$CaSO_4{\cdot}2H_2O$
anorthite	[*1302-54-1*]	$CaAl_2Si_2O_8$

The oceans contain vast quantities of ionic calcium, Ca^{2+}, to the extent of 400 mg/L of seawater (3). Calcium is present in living organisms as a constituent of bones, teeth, shell, and coral. It is essential to plant as well as animal life.

Limestone and marble have been mined as building materials and the oxide of calcium, lime [*1305-78-8*], has been used in the manufacture of mortar for centuries (see BUILDING MATERIALS, SURVEY; LIME AND LIMESTONE). Lime-burning was one of the first industries in the American colonies, where calcining of limestone was accomplished in kilns dug out of the sides of hills.

As befits the electron configuration of elemental calcium, the metal is very reactive, readily losing two valence electrons to form the dispositive ion. In aqueous solution and in its compounds, Ca^{2+} is colorless. Most calcium compounds are white, unless the cation is paired with a colored anion. The ion has only a weak tendency toward covalent bond formation.

Calcium reacts readily with water, oxygen, sulfur, and the halogens to form the respective ionic compounds calcium hydroxide [*1305-62-0*], $Ca(OH)_2$, calcium oxide [*1305-78-8*], CaO, calcium sulfide [*20548-54-3*], CaS, and the calcium halides, CaX_2, where X = F [*7789-75-5*], Cl [*10035-04-8*], Br [*7774-34-7*], or I [*10102-68-8*]. This reactivity of the metal prevents it from being kept in air for any appreciable length of time. At elevated temperatures, calcium also combines directly with nitrogen, hydrogen, and carbon to form calcium nitride [*12013-82-0*], Ca_3N_2, calcium hydride [*7789-78-8*], CaH_2, and calcium carbide [*75-20-7*], CaC_2, respectively.

Inorganic Compounds

Calcium Carbonate. Limestone is the most widely used of all rocks, as such for dimension stone or aggregate in concrete and road building, or as an industrial chemical and precursor of lime and hydrated lime. Calcium carbonate acts as a base in its application as a soil conditioner (agricultural lime is actually limestone), neutralizer of surface waters, industrial acid neutralizer, and in a limestone slurry as a stack gas scrubber to remove SO_2 (see SULFUR REMOVAL AND RECOVERY). Fluidized-bed combustion of coal using an admixture of pulverized limestone can be used to trap SO_2 before it reaches the exhaust stacks (see COAL CONVERSION PROCESSES). Precipitated calcium carbonate [*741-34-1*], formed from carbonating suspensions of calcium hydroxide, is finding application as a mineral filler to give brightness and opacity to acid-free paper (4). Limestone is also used as a metallurgical flux.

Lime and Hydrated Lime. Lime, CaO, production in the United States in 1990 amounted to 15,820 metric tons ranking it fifth in tonnage of manufactured chemicals (5). More than 90% of the lime consumed in the United States is used for basic or industrial chemistry. It is produced by thermal decomposition (calcination) of calcium carbonate in various forms including limestone, marble, chalk, oyster shells, and dolomite. Although some purposes require 100% CaO lime, quicklimes used industrially almost always contain impurities such as MgO, SiO_2, Fe_2O_3, Al_2O_3, H_2O, and CO_2 (6). Quicklime containing less than 5% MgO is classified as high calcium lime, that which contains between 5 and 35% MgO, usually between 5 and 10%, is classified as magnesian lime, and lime containing more than 35% MgO, typically between 35 and 40%, is classified as dolomitic lime. Lime is strongly alkaline and has a negative temperature coefficient of solubility.

The hydrolysis process, ie, reaction with water, for lime is called slaking and produces hydrated lime, $Ca(OH)_2$. Calcium hydroxide is a strong base but has limited aqueous solubility, 0.219 g $Ca(OH)_2$/100 g H_2O, and is therefore often used as a suspension. As an alkali it finds widespread industrial application because it is cheaper than sodium hydroxide.

Mortar. Mortar, principally slaked lime and sand, sets because of the evaporation of water, the deposition of calcium hydroxide, and the absorption of water by the bricks or cement blocks, followed by hardening as a result of the absorption and reaction of carbon dioxide.

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

Metallurgy. Calcium oxide reacts readily with acid anhydrides:

$$CaO + SO_3 \longrightarrow CaSO_4$$

Reactions of this type are important in high temperature metallurgical processes in which CaO, which may be produced by decomposition of $CaCO_3$, reacts with and removes acidic impurities, eg, in the pig-iron blast furnace (6).

$$CaO \text{ (from limestone)} + SiO_2 \longrightarrow CaSiO_3 \text{ (blast furnace slag)}$$

In modern steel (qv) manufacture, pebble quicklime is used as a flux in the basic oxygen, basic open-hearth, basic Bessemer, and basic electric furnaces.

Treatment of Industrial Wastes. The alkaline nature and inexpensive price of lime make it ideal for treatment of acid waste liquors (6), including waste pickle liquids from steel plants, wastes from metal plating operations, eg, chrome and copper plating, acid wastes from chemical and explosives plants, and acid mine wastewaters.

Great quantities of stack gases containing acidic substances such as H_2S and SO_2 are produced in the smelting and refining of nonferrous metals such as copper, zinc, and lead obtained from sulfide ores. These can be trapped by stack gas scrubbers as a fine spray of lime, or limestone slurry in water is passed down the stack while the hot acidic gases are passing upwards. Control of emission of acid gases, primarily sulfur dioxide, from fossil fuel power plants is also accomplished with $Ca(OH)_2$ scrubbers (see AIR POLLUTION CONTROL METHODS). By-product calcium sulfite [*10257-55-3*], $CaSO_3$, from this process must be dewatered (see DEWATERING) and eventually disposed of on land.

Cement (qv) and lime-based technologies are used to immobilize fly ash, cement kiln dust, ground blast furnace slag, and the sludges of sulfides, hydroxides, and phosphates of heavy metals, but not organic wastes that inhibit the setting process. Treatment of the concrete clinker with a sealant may be beneficial when acid leaching is a potential problem (7). Quicklime may be useful in chemically treating polychlorinated biphenyls (PCBs). The success of lime treatment of PCBs has been questioned, however (8).

Treatment of Municipal and Industrial Water Supplies. Hard water (qv) contains dissolved solids, chiefly calcium and magnesium salts. Water hardness results in the formation of insoluble curd from soap, decreased efficiency of detergents, and in the formation of mineral deposits that coat the surfaces of hot water systems, thereby clogging pipes and reducing heating efficiency. Feedwater softening treatment is necessary for boiler water and for water used in dyeing and other textile processing operations. On a large scale, the lime water-softening process is used to remove calcium and magnesium ions from water:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\ CaCO_3(s) + 2\ H_2O$$

$$MgX_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2(s) + CaX_2$$

Magnesium deficiency is easily corrected if the soil is acidic by using a high-magnesium (dolomitic) limestone to raise soil pH (see discussion of soil acidity below). Otherwise, Sul-Po-Mag is one of the best choices for correcting such a deficiency.

Calcium deficiencies are usually associated with low pH soils and soils with low CECs. The best remedy is usually to lime and build up the soil's organic matter. However, some important crops, such as peanuts, potatoes and apples, commonly need added calcium. Calcium additions also may be needed to help alleviate soil structure and nutrition problems of sodic soils (see below). In general, if the soil does not have too much sodium, is properly limed and has a reasonable amount of organic matter, there will be no advantage to adding a calcium source, such as gypsum. However, soils with very low aggregate stability may sometimes benefit from the extra salt concentration associated with surface gypsum applications. This is not a calcium nutrition effect, but a stabilizing effect of the dissolving gypsum salt. Higher soil organic matter and surface residues should do as well as gypsum to alleviate this problem.

Sulfur deficiencies are common on soils with low organic matter. Some soil testing labs around the country offer a sulfur soil test. (Those of you who grow garlic should know that a good supply of sulfur is important for the full development of garlic's pungent flavor — so garlic growers want to make sure there's plenty available to the crop.) Much of the sulfur in soils occurs as organic matter, so building up and maintaining good amounts of organic matter should result in sufficient sulfur nutrition for plants. Although reports of crop response to added sulfur in the Northeast are rare, it is thought that deficiencies of this element may become more common now that there is less sulfur air pollution originating in the Midwest. Some fertilizers used for other purposes, such as Sul-Po-Mag and ammonium sulfate, contain sulfur. Calcium sulfate (gypsum) also can be applied to remedy low soil sulfur. The amounts used on sulfur-deficient soils are typically 20 to 25 lbs. sulfur/acre.

Zinc deficiencies occur with certain crops on soils low in organic matter and in sandy soils or those with a pH near neutral. Zinc problems are sometimes noted on silage corn when manure hasn't been applied for a while. It also can be deficient following topsoil removal from parts of fields as land is leveled for furrow irrigation. Sometimes, crops outgrow the problem as the soil warms up and organic sources become more available to plants. Zinc sulfate (about 35 percent zinc) applied to soils is one of the materials used to correct zinc deficiencies. If the deficiency is due to high pH, or if an orchard crop is zinc-deficient, a foliar application is commonly used. If a soil test before planting an orchard reveals low zinc levels, zinc sulfate should be soil-applied.

Boron deficiencies show up in alfalfa when growing on eroded knolls where topsoil and organic matter have been lost. Root crops seem to need higher soil boron levels than many other crops. Cole crops, apples, celery and spinach are also sensitive to low boron levels. The most common fertilizer used to correct a boron deficiency is sodium tetraborate (about 15 percent boron). Borax (about 11 percent boron), a compound containing sodium borate, also can be used to correct boron deficiencies. On sandy soils low in organic matter, boron may be needed on a routine basis.

Manganese deficiency, usually associated with soybeans and cereals on high pH soils and vegetables grown on muck soils, is corrected with

Magdoff, Van Es 2000

New Jersey Department of Health and Senior Services

HAZARDOUS SUBSTANCE FACT SHEET

Common Name: **CALCIUM HYDROXIDE**

CAS Number: 1305-62-0
DOT Number: None

RTK Substance number: 0322
Date: February 1989 Revision: April 1998

HAZARD SUMMARY

- **Calcium Hydroxide** can affect you when breathed in.
- Skin contact can cause irritation and burns.
- **Calcium Hydroxide** can cause severe eye irritation and burns.
- Breathing **Calcium Hydroxide** can irritate the nose, throat and lungs causing coughing, wheezing and/or shortness of breath.

IDENTIFICATION

Calcium Hydroxide is a soft, white, powdery material with a bitter taste. It is used in mortar, plaster, cement, and other building and paving materials.

REASON FOR CITATION

- **Calcium Hydroxide** is on the Hazardous Substance List because it is regulated by OSHA and cited by ACGIH and NIOSH.
- Definitions are provided on page 5.

HOW TO DETERMINE IF YOU ARE BEING EXPOSED

The New Jersey Right to Know Act requires most employers to label chemicals in the workplace and requires public employers to provide their employees with information and training concerning chemical hazards and controls. The federal OSHA Hazard Communication Standard, 1910.1200, requires private employers to provide similar training and information to their employees.

- Exposure to hazardous substances should be routinely evaluated. This may include collecting personal and area air samples. You can obtain copies of sampling results from your employer. You have a legal right to this information under OSHA 1910.20.
- If you think you are experiencing any work-related health problems, see a doctor trained to recognize occupational diseases. Take this Fact Sheet with you.

WORKPLACE EXPOSURE LIMITS

OSHA:	The legal airborne permissible exposure limit (PEL) is **15 mg/m^3** for TOTAL DUST and **5 mg/m^3** for RESPIRABLE DUST averaged over an 8-hour workshift.
NIOSH:	The recommended airborne exposure limit is **5 mg/m^3** averaged over a 10-hour workshift.
ACGIH:	The recommended airborne exposure limit is **5 mg/m^3** averaged over an 8-hour workshift.

WAYS OF REDUCING EXPOSURE

- Where possible, enclose operations and use local exhaust ventilation at the site of chemical release. If local exhaust ventilation or enclosure is not used, respirators should be worn.
- Wear protective work clothing.
- Wash thoroughly immediately after exposure to **Calcium Hydroxide**.
- Post hazard and warning information in the work area. In addition, as part of an ongoing education and training effort, communicate all information on the health and safety hazards of **Calcium Hydroxide** to potentially exposed workers.

This Fact Sheet is a summary source of information of all potential and most severe health hazards that may result from exposure. Duration of exposure, concentration of the substance and other factors will affect your susceptibility to any of the potential effects described below.

HEALTH HAZARD INFORMATION

Acute Health Effects

The following acute (short-term) health effects may occur immediately or shortly after exposure to **Calcium Hydroxide**:

* Skin contact can cause irritation and burns.
* **Calcium Hydroxide** can cause severe eye irritation and burns with possible permanent damage.
* Breathing **Calcium Hydroxide** can irritate the nose, throat and lungs causing coughing, wheezing and/or shortness of breath.

Chronic Health Effects

The following chronic (long-term) health effects can occur at some time after exposure to **Calcium Hydroxide** and can last for months or years:

Cancer Hazard

* According to the information presently available to the New Jersey Department of Health and Senior Services, **Calcium Hydroxide** has not been tested for its ability to cause cancer in animals.

Reproductive Hazard

* According to the information presently available to the New Jersey Department of Health and Senior Services, **Calcium Hydroxide** has not been tested for its ability to affect reproduction.

Other Long-Term Effects

* **Calcium Hydroxide** has not been tested for other chronic (long-term) health effects.

MEDICAL

Medical Testing

Before beginning employment and at regular times after that, for those with frequent or potentially high exposures, the following are recommended:

* Lung function tests.

Any evaluation should include a careful history of past and present symptoms with an exam. Medical tests that look for damage already done are not a substitute for controlling exposure.

Request copies of your medical testing. You have a legal right to this information under OSHA 1910.20.

Mixed Exposures

* Because smoking can cause heart disease, as well as lung cancer, emphysema, and other respiratory problems, it may worsen respiratory conditions caused by chemical exposure. Even if you have smoked for a long time, stopping now will reduce your risk of developing health problems.

WORKPLACE CONTROLS AND PRACTICES

Unless a less toxic chemical can be substituted for a hazardous substance, **ENGINEERING CONTROLS** are the most effective way of reducing exposure. The best protection is to enclose operations and/or provide local exhaust ventilation at the site of chemical release. Isolating operations can also reduce exposure. Using respirators or protective equipment is less effective than the controls mentioned above, but is sometimes necessary.

In evaluating the controls present in your workplace, consider: (1) how hazardous the substance is, (2) how much of the substance is released into the workplace and (3) whether harmful skin or eye contact could occur. Special controls should be in place for highly toxic chemicals or when significant skin, eye, or breathing exposures are possible.

In addition, the following control is recommended:

* Where possible, automatically transfer **Calcium Hydroxide** from drums or other storage containers to process containers.

Good **WORK PRACTICES** can help to reduce hazardous exposures. The following work practices are recommended:

* Workers whose clothing has been contaminated by **Calcium Hydroxide** should change into clean clothing promptly.
* Do not take contaminated work clothes home. Family members could be exposed.
* Contaminated work clothes should be laundered by individuals who have been informed of the hazards of exposure to **Calcium Hydroxide.**
* Eye wash fountains in the immediate work area should be provided for emergency use.
* If there is the possibility of skin exposure, emergency shower facilities should be provided.
* On skin contact with **Calcium Hydroxide**, immediately wash or shower to remove the chemical. At the end of the workshift, wash any areas of the body that may have contacted **Calcium Hydroxide**, whether or not known skin contact has occurred.
* Do not eat, smoke, or drink where **Calcium Hydroxide** is handled, processed, or stored, since the chemical can be swallowed. Wash hands carefully before eating or smoking.

PERSONAL PROTECTIVE EQUIPMENT

WORKPLACE CONTROLS ARE BETTER THAN PERSONAL PROTECTIVE EQUIPMENT. However, for some jobs (such as outside work, confined space entry, jobs done only once in a while, or jobs done while workplace controls are being installed), personal protective equipment may be appropriate.

OSHA 1910.132 requires employers to determine the appropriate personal protective equipment for each hazard and to train employees on how and when to use protective equipment.

The following recommendations are only guidelines and may not apply to every situation.

Clothing

* Avoid skin contact with **Calcium Hydroxide**. Wear protective gloves and clothing. Safety equipment suppliers/manufacturers can provide recommendations on the most protective glove/clothing material for your operation.
* All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day, and put on before work.

Eye Protection

* Wear dust-proof goggles and face shield when working with powders or dust, unless full facepiece respiratory protection is worn.

Respiratory Protection

IMPROPER USE OF RESPIRATORS IS DANGEROUS. Such equipment should only be used if the employer has a written program that takes into account workplace conditions, requirements for worker training, respirator fit testing and medical exams, as described in OSHA 1910.134.

* NIOSH has established new testing and certification requirements for negative pressure, air purifying, particulate filters and filtering facepiece respirators. The filter classifications of dust/mist/fume, paint spray or pesticide prefilters, and filters for radon daughters have been replaced with the N, R, and P series. Each series has three levels of filtering efficiency, 95%, 99%, and 99.9%. Check with your safety equipment supplier or your respirator manufacturer to determine which respirator is appropriate for your facility.
* If while wearing a filter, cartridge or canister respirator, you can smell, taste, or otherwise detect **Calcium Hydroxide**, or in the case of a full facepiece respirator you experience eye irritation, leave the area immediately. Check to make sure the respirator to face seal is still good. If it is, replace the filter, cartridge, or canister. If the seal is no longer good, you may need a new respirator.
* Be sure to consider all potential exposures in your workplace. You may need a combination of filters, prefilters, cartridges, or canisters, to protect against different forms of a chemical (such as vapor and mist) or against a mixture of chemicals.
* Where the potential for high exposure exists, use a MSHA/NIOSH approved supplied-air respirator with a full facepiece operated in the positive pressure mode or with a full facepiece, hood, or helmet in the continuous flow mode, or use a MSHA/NIOSH approved self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.

QUESTIONS AND ANSWERS

Q: If I have acute health effects, will I later get chronic health effects?

A: Not always. Most chronic (long-term) effects result from repeated exposures to a chemical.

Q: Can I get long-term effects without ever having short-term effects?

A: Yes, because long-term effects can occur from repeated exposures to a chemical at levels not high enough to make you immediately sick.

Q: What are my chances of getting sick when I have been exposed to chemicals?

A: The likelihood of becoming sick from chemicals is increased as the amount of exposure increases. This is determined by the length of time and the amount of material to which someone is exposed.

Q: When are higher exposures more likely?

A: Conditions which increase risk of exposure include <u>dust releasing operations</u> (grinding, mixing, blasting, dumping, etc.), <u>other physical and mechanical processes</u> (heating, pouring, spraying, spills and evaporation from large surface areas such as open containers), and <u>"confined space" exposures</u> (working inside vats, reactors, boilers, small rooms, etc.).

Q: Is the risk of getting sick higher for workers than for community residents?

A: Yes. Exposures in the community, except possibly in cases of fires or spills, are usually much lower than those found in the workplace. However, people in the community may be exposed to contaminated water as well as to chemicals in the air over long periods. Because of this, and because of exposure of children or people who are already ill, community exposures may cause health problems.

The following information is available from:

New Jersey Department of Health and
Senior Services
Occupational Disease and Injury Services
Trenton, NJ 08625-0360
(609) 984-1863

Industrial Hygiene Information

Industrial hygienists are available to answer your questions regarding the control of chemical exposures using exhaust ventilation, special work practices, good housekeeping, good hygiene practices, and personal protective equipment including respirators. In addition, they can help to interpret the results of industrial hygiene survey data.

Medical Evaluation

If you think you are becoming sick because of exposure to chemicals at your workplace, you may call a Department of Health and Senior Services physician who can help you find the services you need.

Public Presentations

Presentations and educational programs on occupational health or the Right to Know Act can be organized for labor unions, trade associations and other groups.

Right to Know Information Resources

The Right to Know Infoline (609) 984-2202 can answer questions about the identity and potential health effects of chemicals, list of educational materials in occupational health, references used to prepare the Fact Sheets, preparation of the Right to Know survey, education and training programs, labeling requirements, and general information regarding the Right to Know Act. Violations of the law should be reported to (609) 984-2202.

DEFINITIONS

ACGIH is the American Conference of Governmental Industrial Hygienists. It recommends upper limits (called TLVs) for exposure to workplace chemicals.

A **carcinogen** is a substance that causes cancer.

The **CAS number** is assigned by the Chemical Abstracts Service to identify a specific chemical.

A **combustible** substance is a solid, liquid or gas that will burn.

A **corrosive** substance is a gas, liquid or solid that causes irreversible damage to human tissue or containers.

DEP is the New Jersey Department of Environmental Protection.

DOT is the Department of Transportation, the federal agency that regulates the transportation of chemicals.

EPA is the Environmental Protection Agency, the federal agency responsible for regulating environmental hazards.

A **fetus** is an unborn human or animal.

A **flammable** substance is a solid, liquid, vapor or gas that will ignite easily and burn rapidly.

The **flash point** is the temperature at which a liquid or solid gives off vapor that can form a flammable mixture with air.

HHAG is the Human Health Assessment Group of the federal EPA.

IARC is the International Agency for Research on Cancer, a scientific group that classifies chemicals according to their cancer-causing potential.

A **miscible** substance is a liquid or gas that will evenly dissolve in another.

mg/m^3 means milligrams of a chemical in a cubic meter of air. It is a measure of concentration (weight/volume).

MSHA is the Mine Safety and Health Administration, the federal agency that regulates mining. It also evaluates and approves respirators.

A **mutagen** is a substance that causes mutations. A **mutation** is a change in the genetic material in a body cell. Mutations can lead to birth defects, miscarriages, or cancer.

NAERG is the North American Emergency Response Guidebook. It was jointly developed by Transport Canada, the United States Department of Transportation and the Secretariat of Communications and Transportation of Mexico. It is a guide for first responders to quickly identify the specific or generic hazards of material involved in a transportation incident, and to protect themselves and the general public during the initial response phase of the incident.

NCI is the National Cancer Institute, a federal agency that determines the cancer-causing potential of chemicals.

NFPA is the National Fire Protection Association. It classifies substances according to their fire and explosion hazard.

NIOSH is the National Institute for Occupational Safety and Health. It tests equipment, evaluates and approves respirators, conducts studies of workplace hazards, and proposes standards to OSHA.

NTP is the National Toxicology Program which tests chemicals and reviews evidence for cancer.

OSHA is the Occupational Safety and Health Administration, which adopts and enforces health and safety standards.

PEOSHA is the Public Employees Occupational Safety and Health Act, a state law which sets PELs for New Jersey public employees.

ppm means parts of a substance per million parts of air. It is a measure of concentration by volume in air.

A **reactive** substance is a solid, liquid or gas that releases energy under certain conditions.

A **teratogen** is a substance that causes birth defects by damaging the fetus.

TLV is the Threshold Limit Value, the workplace exposure limit recommended by ACGIH.

The **vapor pressure** is a measure of how readily a liquid or a solid mixes with air at its surface. A higher vapor pressure indicates a higher concentration of the substance in air and therefore increases the likelihood of breathing it in.

>>>>>>>>>>>>>>>>>>>>>> EMERGENCY INFORMATION <<<<<<<<<<<<<<<<<<<<<<

Common Name: **CALCIUM HYDROXIDE**
DOT Number: **None**
NAERG Code: **No Citation**
CAS Number: **1305-62-0**

Hazard rating	NJDHSS	NFPA
FLAMMABILITY	0	Not Rated
REACTIVITY	Not Found	Not Rated

Hazard Rating Key: 0=minimal; 1=slight; 2=moderate; 3=serious; 4=severe

FIRE HAZARDS

* Extinguish fire using an agent suitable for type of surrounding fire. **Calcium Hydroxide** itself does not burn.
* If employees are expected to fight fires, they must be trained and equipped as stated in OSHA 1910.156.

SPILLS AND EMERGENCIES

If **Calcium Hydroxide** is spilled, take the following steps:

* Evacuate and isolate the area of the spill, and restrict persons not wearing protective equipment from area of spill until clean-up is complete.
* Collect powdered material in the most convenient and safe manner and deposit in sealed containers.
* Ventilate the area of the spill.
* It may be necessary to contain and dispose of **Calcium Hydroxide** as a HAZARDOUS WASTE. Contact your Department of Environmental Protection (DEP) or your regional office of the federal Environmental Protection Agency (EPA) for specific recommendations.
* If employees are required to clean-up spills, they must be properly trained and equipped. OSHA 1910.120(q) may be applicable.

==

FOR LARGE SPILLS AND FIRES immediately call your fire department. You can request emergency information from the following:

CHEMTREC: (800) 424-9300
NJDEP HOTLINE: (609) 292-7172

==

HANDLING AND STORAGE

* Prior to working with **Calcium Hydroxide** you should be trained on its proper handling and storage.
* **Calcium Hydroxide** must be stored to avoid contact with MALEIC ANHYDRIDE, NITROETHANE, NITROMETHANE, NITROPROPANE, NITROETHER, NITROPARAFFINS and PHOSPHORUS, since violent reactions occur.
* **Calcium Hydroxide** is not compatible with STRONG ACIDS (such as HYDROCHLORIC, SULFURIC and NITRIC).
* Store in tightly closed containers in a cool, well-ventilated area.

FIRST AID

In NJ, POISON INFORMATION 1-800-764-7661

Eye Contact

* Immediately flush vigorously with water for 45 minutes without stopping, periodically lifting upper and lower lids. If chemical particles are seen sticking to the eye after 10-15 minutes, very gently brush off with a clean cotton swab. Continue constantly until medical help is available.

Skin Contact

* Remove contaminated clothing. Wash contaminated skin with soap and water.

Breathing

* Remove the person from exposure.
* Transfer promptly to a medical facility.

PHYSICAL DATA

Water Solubility: Soluble

OTHER COMMONLY USED NAMES

Chemical Name:
Calcium Hydroxide
Other Names:
Carboxide; Hydrated Lime; Slaked Lime; Calcium Hydrate

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NEW JERSEY DEPARTMENT OF HEALTH AND SENIOR SERVICES
Right to Know Program
PO Box 368, Trenton, NJ 08625-0368
(609) 984-2202

Sixth Edition

SOILS

AN INTRODUCTION TO SOILS AND PLANT GROWTH

Raymond W. Miller
Department of Plant, Soil, and Biometeorology
Utah State University

Roy L. Donahue
Professor Emeritus
Department of Crop and Soil Sciences
Michigan State University

Joyce U. Miller
Editorial assistant

1990

PRENTICE HALL
ENGLEWOOD CLIFFS, NJ 07632

the Pacific coastal soils of the northwest, and (3) some of the mountain areas (see Fig. 7-1). For example, Logan in northern Utah averages about 400 mm (17 in.) of rainfall annually, and seldom has soils more acidic than pH 6.5. Mountains within 50 km (31 mi) will often have 750–900 mm (30–36 in.) of precipitation and soils are acidic (pH 5.0–6.0).

7:3 COMPOSITION OF LIME

Liming materials are usually the carbonates, oxides, hydroxides, and silicates of calcium and magnesium. More than 90 percent of the agricultural lime used is calcium carbonate; next used are carbonates of calcium plus magnesium (dolomitic lime); a much smaller quantity is composed of calcium oxide or calcium hydroxide. In the building trades, lime refers to calcium oxide, a caustic powder that is slaked in water for use in various brick-laying mortars. Although this material is usable as agricultural lime, it is caustic to handle and to spread.

The common liming materials used include:

1. Calcic limestone ($CaCO_3$), which is ground limestone.
2. Dolomitic limestone [$CaMg(CO_3)_2$], from ground limestone high in magnesium. Although state laws vary, the average composition of dolomitic limestone sold in the United States is 51 percent $CaCO_3$, 34 percent $MgCO_3$, and 15 percent soil and other impurities.
3. Quicklime (CaO), which is burned limestone.
4. Hydrated (slaked) lime [$Ca(OH)_2$], from quicklime that has changed to the hydroxide form as a result of reactions with water.
5. Marl ($CaCO_3$), from the bottom of small freshwater ponds in areas where the soils are high in lime. The lime has accumulated by precipitation from drainage waters high in lime. Some marls contain many shell remains from ancient marine animals, which are major sources of the carbonate.
6. Chalk ($CaCO_3$), resulting from soft limestone deposited long ago in oceans.
7. Blast furnace slag ($CaSiO_3$ and $CaSiO_4$), a by-product of the iron industry. Some slags contain phosphorus and a mixture of CaO and $Ca(OH)_2$. This product is called *basic slag* and is used primarily for its phosphorus content.
8. Miscellaneous sources, such as ground oystershell, wood ashes, and by-product lime resulting from paper mills, sugar beet plants, tanneries, water-softening plants, fly ash from coal-burning plants, and cement-plant flue dust.
9. Fluid lime, a relatively new product that is becoming popular because it can be spread with the same equipment that is used to apply fluid fertilizers. Typically, **fluid lime** is *any* suitable liming material that has a fineness of <60-mesh (250 μm). A sieve of 60-mesh means a screen with 60 divisions per linear inch in each of two directions. When applied *with* urea–ammonium nitrate fluids, only the *carbonate* form of lime should be used so ammonia is not volatilized.[1,2,3]

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[1] Gary W. Colliver, "Liquid Lime," *Crops and Soils Magazine* (Aug.–Sept. 1979). pp. 14–16.

[2] K. T. Winter et al., "Liming Has No Miracles," *Solutions* (Mar.–Apr. 1980), pp. 12, 14, 18, 24, 30, 32, 34.

[3] M. E. Sumner, H. Shahandeh, J. Bouton, D. Radcliffe, and J. Hammel, "Amelioration of an Acid

Gypsum ($CaSO_4$) is sometimes added to the soil to supply calcium, which might alleviate somewhat the toxicity from soluble aluminum. In Georgia, gypsum increased alfalfa yield 25 percent but calcium carbonate (precipitates more Al) increased it 50 percent.[4] Calcium silicate ($CaSiO_3$) slag has been used successfully as a source of silicon for rice and sugarcane. Its value as a liming material has not been demonstrated.

All the liming materials mentioned also have value for supplying either calcium or both calcium and magnesium, and in making aluminum, manganese, and iron less toxic. The choice of a particular liming material is determined by the cost in relation to its purity, the ease of handling, and the speed with which the lime reacts in the soil.

7:3.1 Chemical Guarantees of Lime

There are several methods of expressing the relative chemical value of lime. The most common ones are the following two.

Calcium Carbonate Equivalent This is sometimes known as the **total neutralizing power.** If a lime is chemically pure calcium carbonate (calcite), the calcium carbonate equivalent would be 100. If all the lime were in the calcium carbonate form, but it was only 85 percent pure, the calcium carbonate equivalent would be 85. Limestone is seldom pure because it formed in ocean bottoms and collected clay and silt sediments. Other forms of lime can be converted to the calcium cabonate equivalent by the use of atomic and molecular weights.[5] The question is: How effective is 100 g of any liming material compared to 100 g of pure $CaCO_3$?

$$\% \; CaCO_3 = \left(\frac{\text{grams of pure } CaCO_3 \text{ equal to 100 g of lime}}{\text{100 g of pure } CaCO_3}\right)(100)$$

If we are comparing CaO material,

$$CaO \text{ gram molecular weight} = 40 + 16 = 56 \text{ g}$$

$$CaCO_3 \text{ gram molecular weight} = 40 + 12 + 48 = 100 \text{ g}$$

Therefore, 56 g of CaO neutralizes the same amount of acid as does 100 g of $CaCO_3$. If we represent soil acidity by H^+,

$$CaO + HOH + 2H^+ \longrightarrow Ca^{2+} + 2HOH$$

$$CaCO_3 + CO_2 + HOH + 2H^+ \longrightarrow Ca^{2+} + H_2CO_3$$

and the H_2CO_3 breaks down into CO_2 gas and water. We can now write the relationship between CaO and $CaCO_3$:

Profile through Deep Liming and Surface Application of Gypsum," *Progress Report,* Department of Agronomy, Georgia Agricultural Experiment Station, Dec. 1985.

[4] D. L. Anderson, D. B. Jones, and G. H. Snyder, "Response of a Rice-Sugarcane Rotation to Calcium Silicate Slag on Everglade Histosols," *Agronomy Journal,* **79** (1987), pp. 531–535.

[5] The "Model Agricultural Liming Material Bill" proposes these minimum calcium carbonate equivalents: quicklime 140, hydrated lime 110, ground limestone 80, blast furnace slag 80, and ground oystershell 80. Reference: *Abstract of State Laws and ACP Specifications for Agricultural Liming Materials,* 3rd ed., National Limestone Institute, Fairfax, Va. 1977, p. 75.

$$\frac{100\text{ g CaCO}_3}{56\text{ g CaO}} = \frac{?\text{ g of CaCO}_3}{100\text{ g CaO}} \qquad 100\text{ g CaO} = 179\text{ g CaCO}_3$$

To calculate the "% $CaCO_3$ equivalent" question asked earlier,

$$\%\ \text{CaCO}_3 = \left(\frac{179\text{ g of CaCO}_3\text{ is equal to }100\text{ g CaO}}{100\text{ g of pure CaCO}_3}\right)(100)$$

$$= 179\%\text{ for CaO}$$

(see Table 7-1).

Elemental Percentage of Calcium and/or Magnesium This method of expressing lime guarantee is determined in a similar way. If pure $CaCO_3$ were to be reported as elemental calcium, the calculations would be:

$$\%\ \text{Ca} = \left(\frac{\text{atomic weight of Ca}}{\text{molecular weight of CaCO}_3}\right)(100)$$

$$= \left(\frac{40}{100}\right)(100)$$

$$= 40\%\text{ Ca equivalent}$$

7:3.2 Physical Guarantees of Lime

The chemical activity of liming material is determined by the solubility of the chemical compounds in the lime. For example, calcium oxide is more soluble than calcium carbonate, whereas calcic limestone is more soluble than dolomitic limestone; calcium silicate is the least soluble of all these liming materials. It is obvious that the finer lime particles react faster in the soil (Fig. 7-3).

TABLE 7-1 Lime Conversion Factors

To Convert from This Material[a] *(Column A)*	*To Each of These:* *Ca*	*CaO*	*$CaCO_3$*
	Multiply column A by:		
Calcium (Ca)	1.00	1.40	2.50
Calcium oxide (CaO)	0.71	1.00	1.78
Calcium hydroxide [$Ca(OH)_2$]	0.54	0.78	1.35
Calcium carbonate ($CaCO_3$)	0.40	0.56	1.00
Magnesium (Mg)	1.65	2.31	4.12
Magnesium oxide (MgO)	0.99	1.39	2.48
Magnesium hydroxide [$Mg(OH)_2$]	0.69	1.00	1.72
Magnesium carbonate ($MgCO_3$)	0.48	0.67	1.19
Dolomite, pure ($CaCO_3 \cdot MgCO_3$)	0.43	0.63	1.09

[a] *Calculated, using the following atomic weights: Calcium—40.08, oxygen—16.00, carbon—12.01, and hydrogen—1.00. For example: In line 1 above, to convert from Ca to CaO equivalent, divide the molecular weight of CaO by the atomic weight of Ca = 56.08/40.08 = 1.40. Therefore, to convert Ca to CaO, multiply the kilograms (pounds) of Ca by 1.40 to obtain equivalent kilograms (pounds) of CaO.*

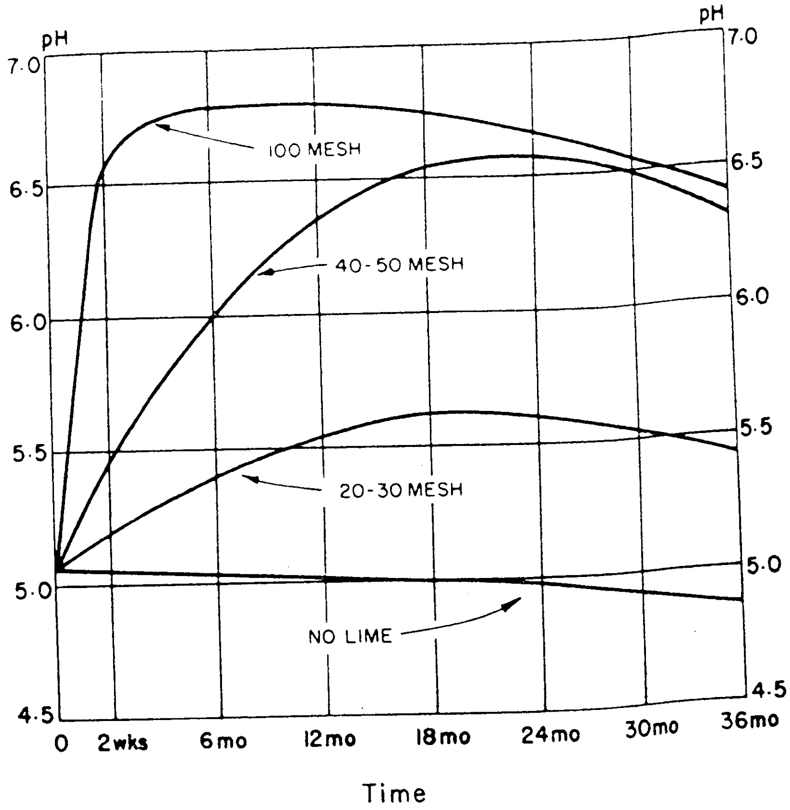

FIGURE 7-3 The finer the limestone, the more quickly it reacts with the soil to raise the pH and the quicker the calcium becomes available to the plant. A satisfactory fineness is 85 percent through a 16-mesh (1.18-mm) sieve and 30 percent through a 100-mesh (150-μm) sieve. *Note:* 20 mesh = 850 μm, 30 mesh = 600 μm, 40 mesh = 425 μm, 50 mesh = 300 μm. (*Source:* The Fertilizer Institute and Purdue University.)

There are no U.S. laws governing a commercial supplier's physical guarantee of lime, this regulation being left to the states. Thirty-nine states have lime laws, enforced by each state department of agriculture. In general, the physical guarantees of lime in the respective states may be averaged roughly in this way: *85 percent of the lime particles must pass through a 16-mesh (1.18 mm) sieve and 30 percent must pass through a 100-mesh (150 μm) sieve.*[6]

A unique technique for evaluating the *effectiveness* of liming materials is to calculate the calcium carbonate equivalent and multiply this by an arbitrary fineness factor. This **neutralizing index** gives a better evaluation of the usefulness of the material than would either factor by itself (Note 7-3). Finer material and larger calcium carbonate equivalents are more effective limes having neutralizing indexes near 70 or higher.

---

[6] Sieves are designated as number of openings per linear inch. An 8-mesh (2.36-mm) sieve has 8 openings per linear inch and a 60 mesh (25-n or 250-μm) sieve has 60 openings per linear inch.

, in Parkhurst, 1997

chloride (TTC) (produces coloured triphenylformazan together with hydrogen chloride) is not the sole hydrogen acceptor in soil. In this case, dehydrogenase activity is underestimated. Another problem with this assay is that Cu can interfere with the analytical procedure so that soils high in soil solution Cu or that received Cu-contaminated amendments will show artificially low dehydrogenase activity levels (Chander and Brookes, 1991).

Protease is often well correlated with microbial biomass (Nannipieri *et al.*, 1978; Asmar *et al.*, 1992) because it apparently exists only in microbial cells or is excreted into soil solution as an extracellular enzyme. Extracellular protease does not survive longer than six to seven days in soils (Nannipieri *et al.*, 1978; Asmar *et al.*, 1992) and apparently does not stabilize in the abiontic form. Extracellular protease activity in soil solution is highly correlated with ATP content ($r = 0.74$) and total bacteria counts ($r = 0.94$) (Asmar *et al.*, 1992). Besides showing a relationship between enzyme activity and soil biology, it also provided evidence for a functional role of extracellular enzymes as hypothesized by Burns (1982), i.e. extracellular enzymes begin hydrolysing compounds outside the cell that may be too large or insoluble for microorganisms to use directly.

Enzymes and ecological or inhibition dose models

Soil enzyme activity has potential to assess the impacts of pollutants on specific processes in soils and the ecological dose value (ED_{50}) provides a mechanism for quantifying these impacts. The ED_{50} is analogous to LD_{50} (lethal dose at 50% kill rate) used for assessing the toxicity of substances on animal and human life. Applying this to enzyme activity would mean that an ED_{50} value would be the pollutant (inhibitor) concentration required to cause a 50% inhibition of enzyme activity in soil.

This approach, first applied to soils by Babich *et al.* (1983), uses mathematical models to assess the impact of heavy metals on microbially mediated processes in soils. Two general models have been used: the sigmoidal dose-response curve model as defined by Haanstra *et al.* (1985); and the Michaelis-Menten kinetic model as defined by Babich *et al.* (1983) (see Appendix and Fig. 6.5 for details of these two models).

The sigmoidal dose-response model has been used to assess heavy metal impacts on urease (Doelman and Haanstra, 1986), phosphatase (Doelman and Haanstra, 1989), and arylsulphatase activities (Haanstra and Doelman, 1991). For example, Haanstra and Doelman (1991) found that the ED_{50} (i.e. the toxicity) of heavy metals was highest in sand and sandy loam and lowest in sandy peat soils. They were also able to discriminate toxicities among various heavy metals added to soils and changes in ED_{50} over time. They went on to suggest that this model be used to revise critical heavy metal concentration standards for soils.

Speir *et al.* (1995) argued that the Michaelis-Menten kinetic model is more appropriate for assessing toxicities than the sigmoidal dose-response model because an enzyme kinetic model has physical interpretation whereas the sigmoidal model has no physical interpretation. Secondly, they pointed out that by plotting concentrations on a logarithmic scale (as is done in the sigmoidal model), the initial section of the curve becomes greatly elongated which can mean that the lowest concentration tested may be well beyond this section of the curve. In this case, a simple plot of activity against metal concentration might have yielded a rectangular hyperbola, which would be predicted by simple kinetic models of inhibition. They were able to rank the sensitivity of soil biological properties to Cr(VI) using an ED_{50} with a Michaelis-Menten kinetic model in the following order: denitrification > dimethyl sulphoxide-reducing activity > sulphatase activity ≅ biomass C > phosphatase activity > urease activity > respiration. They were also able to identify that mineral surface areas, organic matter content, and CEC were sensitive soil properties that affected the ED_{50}.

Biol. Indicators of Soil Health

So far, this approach has been used only to assess heavy metal pollution of soils. Presumably it could be used, on a relative basis, to quantify the impact of other soil pollutants or soil perturbations (e.g. mining) on soil enzyme activities.

Enzyme Activity as a Biological Indicator of Soil Management, Pollution or Perturbations

There is growing evidence that soil biological properties are sensitive to soil management and environmental stresses (Dick, 1992). Serious attention to the role of soils in environmental issues may change previously-held environmental standards. A good example is heavy metal standards developed for municipal waste applications to soils which are based on plant uptake and animal health. As Brookes (1995) pointed out, applications of European Community standards for heavy metal concentrations of soils results in significant negative impacts on microbial biomass and activity, indicating the greater sensitivity of the soil to these impacts than of plants or animals.

The soil microbial component and soil enzyme activities are attractive as indicators for monitoring various impacts on soils because of their central role in the soil environment. An important question is what constitutes a 'significant' impact on a soil biological parameter because these properties typically vary widely under natural conditions. For example, Domsch *et al.* (1983) in their survey of reports on bacterial fluctuations under field conditions showed that reductions of 90% are common. These extremes in variation occur naturally due to fluctuations in water potential, gas exchange, and temperature. They recommended that a stress that results in full recovery in <30 days is normal but >60 days would indicate a severe impact that merits investigation. This is an important concept that needs further consideration and should be part of the criteria for developing soil health standards.

soil whereas organic amendments stimulated enzyme activities (Fauci and Dick, 1994).

Dick *et al.* (1988a), on soil samples from plots with treatments that had been in place since 1931, showed an effect of increasing rates of ammonia-based N fertilizer decreasing the activity of amidase and urease (both enzymes are involved in the N cycle). Conversely, activities of other enzymes not directly involved in the N cycle (arylsulphatase and β-glucosidase) did not correlate with N fertilizer input levels. A feedback mechanism was hypothesized as suppressing production of enzymes whose reaction product (NH_4) was continually added by inorganic fertilizers. This was later confirmed by McCarty *et al.* (1992) who showed that NH_4 repression of urease activity was real, but that the NH_4 effect was indirect and due to byproducts of NH_4 assimilation.

Phosphorus fertilization under field conditions has been shown to depress phosphatase activity in agricultural systems (Mathur and Rayment, 1977; Spiers and McGill, 1979) and forest systems (Clarholm, 1993). But this is likely to be a function of soil type as shown by Mathur and Rayment (1977) where a low organic matter soil increased phosphatase activity with P fertilization, but a soil with a higher organic matter content amended with P fertilizer showed no change in phosphatase activity. In cases of phosphatase inhibition, this has been correlated with high levels of PO_4 in soil solution (Chunderova and Zubets, 1969). Phosphate may inhibit the synthesis of microbial phosphatases and also it is known that orthophosphate is a competitive inhibitor of acid and alkaline phosphatase activity (Juma and Tabatabai, 1978).

Industrial amendments or contaminants

Large amounts of combustion by-products (fly ash) are produced by coal-fired power plants and other industries. There is growing interest in applying these to soils. These materials generally have a high pH and can contain high levels of soils. These materials generally have a high pH and can contain high levels of trace elements. Soil enzyme activities have been used to determine whether there are positive or negative effects on soils. In an acid soil (pH 4.2), McCarty *et al.* (1994) found that fly ash had a positive effect on hydrolytic enzyme activities (urease and arylsulphatase) which closely correlated with the effects of $CaCO_3$. This suggested the positive effect was due to the liming effect (increase in pH) on this acid soil. Conversely, fly ash had a negative effect on dehydrogenase activity which would indicate that the overall microbial population was being suppressed. This might suggest there was either a selective stimulation by a portion of the remaining population that produced hydrolytic enzymes or there was induction of these hydrolytic enzymes. Alternatively, the dehydrogenase assay may have been affected by Cu in the ash. Chander and Brookes (1991) found there was a chemical reaction between triphenylformazan (the end product measured in dehydrogenase activity) and Cu, meaning that soils amended with materials containing Cu severely underestimate dehydrogenase activity. Although McCarty *et al.* (1994) do not report the Cu content of the fly ash, high amounts can be present in this material (Pichtel and Hayes, 1990).

In contrast to the findings of McCarty *et al.* (1994), Pichtel and Hayes (1990) found that inhibition of phosphatase, sulphatase, dehydrogenase and invertase activities increased with increasing ash rates (0 to 20%, w/w) but that catalase activity was unaffected in a 28-day incubation. There was a corresponding decrease in respiration and total bacterial, actinomycete and fungal counts. These results are likely to be due to the high concentration of some heavy metals found in the ash (e.g. Cu, Cd, Al, Zn, Ni). The pH of this soil was 6.2 and the liming benefits of ash would not be nearly as important as in the soil used by McCarty *et al.* (1994) (their soil had a pH of 4.2 so that liming would cause significant precipitation of metals). This shows that soil type is important when determining the impact of a given soil amendment and that soil enzyme activities are generally useful in differentiating the effects of these amendments on soil health.

Disposal of pulp and paper mill effluent on agricultural land is increasing as a way to recycle these materials in an ecological manner. Kannan and Oblisami (1990) investigated the effect of pulp and paper mill effluent on an alkaline soil (pH 7.5) that was cropped to sugarcane and received paper mill effluents as an irrigation application for periods ranging from 0 to 15 years. After two years, there was > threefold increase in total C suggesting that the applied material was recalcitrant, and only invertase and dehydrogenase activities of the enzymes tested were significantly higher than the control. Phosphatase and amylase after three years and cellulase after 15 years were significantly different than the control. Of the enzymes tested, invertase was the most sensitive early indicator of changes with a 3.3-fold increase over the control after two years of paper mill effluent applications. After 15 years amylase was the highest with an 8.6-fold increase compared to the next highest activity of invertase which had a 6.6-fold increase over the control. Apparently there was a liming effect by this effluent on the soil, as soil pH increased to 8.3 after three years of effluent irrigations.

Hydrocarbons

Accidental spills or leakage from storage facilities of hydrocarbons is a common and widespread problem. Soil enzyme activities hold potential for assessing the impact of hydrocarbons on soils and the effectiveness of remediation of soils contaminated with hydrocarbons. However, there is little information on the interaction of hydrocarbons and soil enzyme activities (Song and Bartha, 1990). In one example, Song and Bartha (1990) showed that in the absence of bioremediation (addition of fertilizer, tillage, and liming), jet fuel at 50 and 135 mg g^{-1} soil, inhibited FDA hydrolysis during an 18-week incubation period (Fig. 6.3). With bioremediation, during the first two weeks, FDA hydrolysis was initially inhibited but was then stimulated reaching a peak after most of the jet fuel had been mineralized (4 and 15 weeks for 50 and 135 mg g^{-1} soil, respectively). These results support the potential for enzyme assays to monitor changes in soil health after an environmental accident. In this case, there appeared to be a

Table 9.2. Indices of the nematode faunae under various management regimes at Avon, South Australia[1].

	CC[2]	DD[3]	Pasture	Native shrub	CF[4]
Taxa identified (s)	16.0	17.0	21.0	29.0	24.0
Specimens identified (*n*)	337.0	290.0	322.0	265.0	208.0
% bacterial feeding	37.6	37.7	27.6	63.6	44.4
% fungal feeding	7.2	4.8	8.5	12.0	11.2
% predacious	–	–	–	0.3	1.6
% plant pathogenic	49.2	45.7	46.8	2.8	10.6
% plant associated	4.1	6.4	7.7	1.4	17.2
% omnivorous	1.8	5.5	9.5	19.7	15.0
Fungivores/bacterial feeder ratio	0.19	0.13	0.31	0.19	0.25
Trophic diversity (*T*)	2.56	2.77	3.15	2.18	3.66
Species richness (*SR*)	2.58	2.82	3.46	5.02	4.31
Shannon–Weaver index (H')	1.94	1.85	2.36	2.61	2.97
Evenness (J')	0.70	0.65	0.78	0.78	0.94
Simpson index for dominance (λ)	0.20	0.24	0.13	0.11	0.09
Diversity (H_2)	1.63	1.42	2.03	2.21	2.46
Maturity index (Σ MI)	2.33	2.50	2.36	2.52	3.38
Maturity index for non-parasites (MI)	2.05	2.20	2.33	2.53	2.25
Plant parasite index (PPI)	2.62	2.88	2.41	2.61	2.89

[1]Adapted from Yeates and Bird (1994); [2]conventionally cultivated wheat plots; [3]direct-drilled wheat plots; [4]wheat field subject to continuous traditional farming for a century.

near the soil surface, they may favour this trophic group. The effects of minimun tillage on plant parasitic nematodes are variable (Parmelee and Alston, 1986; Thomas, 1978; Yeates and Bird, 1994).

Freckman and Ettema (1993) studied the effect of disturbance of varying intensity, including tillage, chemical inputs and successional treatments with little human impact, on soil nematode communities. They used a variety of ecological indices (similar to those reported by Yeates and Bird, 1994; Table 9.2) to describe effects on nematode community structure. Species diversity was greatest in the successional treatments, whereas nematode abundance was highest in the high input and organic systems. Canonical discriminant analysis based on the ecological indices was shown to be a useful way to demonstrate the effects of the different degrees of disturbance on nematode communities.Yeates and Bird (1994) also reported changes in nematode communities in soils exposed to different management regimes (Table 9.2). They found that ecological indices such as species richness and the Shannon index were the best of the indices in revealing trends in the trophic structure of nematode communities. However, since several ecological indices were confounded by soil textural effects, they cautioned against using faunal indices to extract generalized trends across different soils and climatic conditions.

Long-term studies of reduced tillage and conventional tillage systems have revealed distinct differences in both biological (including microfauna) and functional processes in the soil (Beare *et al.*, 1992; Groffman *et al.*, 1986; Hendrix *et al.*, 1986; Parmelee and Alston, 1986; Roper and Gupta, 1995). Tillage generally favours organisms with short generation times, high metabolic rates and rapid dispersal (Andrén and Lagerlof, 1983). This may be why residue incorporation leads to more bacterial growth and hence increased abundance of bacterial-feeding protozoa, bacterial-feeding nematodes and enchytraeids. In contrast, under no-tillage systems fungi dominate over bacteria (because of their capacity to access limiting nutrients across the soil–residue interface) resulting in increased abundance of fungal-feeding protozoa and fungal-feeding nematodes (Andrén and Lagerlof, 1983; Gupta and van Vliet, 1996). The dynamics of the detritus food web and its influence on organic matter turnover and nutrient recycling is extensively discussed by Hendrix *et al.* (1986), Hunt *et al.* (1987), Beare *et al.* (1992) and Wardle *et al.* (1995).

Effects of organic and inorganic fertilizers

The effects of organic amendments, such as farmyard manure (FYM), on soil microfaunal populations depend largely upon the effects of the amendment on soil fertility and plant growth. The total number of protozoa and the number of active amoebae and ciliates was significantly higher in soil treated with FYM or complete mineral fertilizer than in untreated soil (Singh, 1949; Detcheva, 1965). Similarly, increases in protozoan abundance in soils treated with inorganic fertilizers (e.g. nitrogenous fertilizers) have been reported (Viswanath and Pillai, 1977; Elliott and Coleman, 1977; Lehle and Funke, 1989; Griffiths, 1990). In contrast, Solhenius (1990) and Angus *et al.* (1996) observed a reduction in the biomass of protozoa as a result of high levels of inorganic fertilizers (>100 kg N ha^{-1}) and Berger *et al.* (1986) found no significant changes in the populations of ciliates and testaceae in alpine pasture soils fertilized with 600 kg NPK ha^{-1}. These differences in fertilizer response are probably due to differences in habitat type and time between fertilizer application and sampling of the protozoan communities.

Asecht and Foissner (1991, 1992) observed, in a reforested alpine soil, that fertilizer application may cause significant changes to the relative proportions of different protozoan groups (e.g. bacterial-feeding or fungal-feeding ciliates and acidophilic or neutrophilic testaceans) present in the soil (Fig. 9.3). Changes in soil pH following fertilizer application would explain the differences in the composition of testaceans whilst an increased fungal biomass in response to the fertilizers was probably the reason for changes in the composition of ciliates. In another study, Gupta and Germida (1988) reported that application of elemental

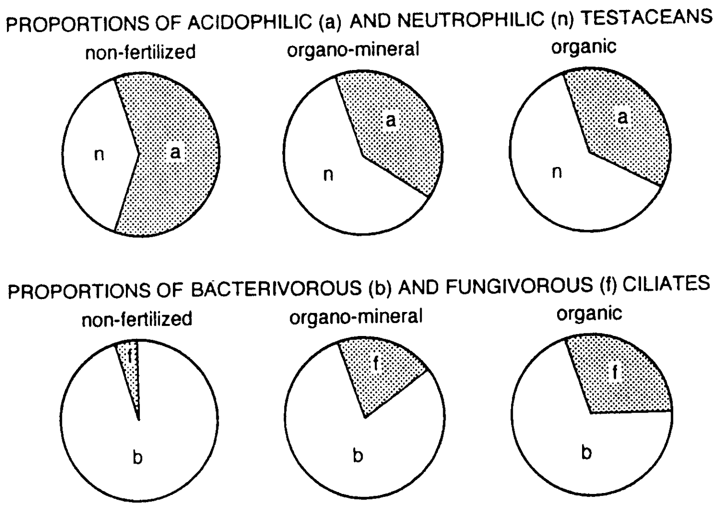

Fig. 9.3. Proportions of indicator species of protozoa (testaceans and ciliates) in a reforested and fertilized site near the alpine timberline. (Adapted from Aescht and Foissner, 1991, 1992.)

sulphur fertilizer to soil for five years resulted in a 30–71% decline in populations of bacterial feeding protozoa and a >84% decline in populations of mycophagous amoebae (MA). The changes in the populations of protozoa paralleled changes in microbial biomass and activity, especially in the case of MA. They observed a significant positive relationship ($R = 0.82$, $P < 0.01$) between fungal biovolume and populations of MA. This suggests that the amount of food available is the most important factor limiting populations of MA.

The effects of fertilizer application on nematode populations are varied and changes in both the abundance and trophic diversity of nematodes in response to fertilizers have been reported. Sohlenius and Boström (1986) and Sohlenius (1990) reported that N fertilization (120 kg N ha^{-1}) resulted in a large increase in nematode abundance compared to no N fertilization. This positive effect of N fertilization was attributed to an increase in plant production, root biomass and microbial activity in the soil. In contrast, Sohlenius and Wasilewska (1984) and Berger *et al.* (1986) observed a reduction in nematode numbers following the application of fertilizer N. Rodriguéz-Kábana (1986) reported that organic (oil cake) and inorganic amendments (300 kg N ha^{-1} as anhydrous ammonia and 130 kg N ha^{-1} as urea) were effective nematode suppressants. There was a direct relationship between the amount of protein N in the organic amendments and their effectiveness in suppressing nematode populations.

Application of both organic and inorganic fertilizers may cause significant changes in nematode trophic diversity. Generally, application of fertilizers increases the proportion of root feeders (Yeates, 1982) and bacterial feeders (Yeates, 1982; Sohlenius and Wasilewska, 1984; Sohlenius and Boström, 1986; Hyvönen and Huhta, 1989; Bohlen and Edwards, 1994) and decreases the proportion of fungal feeders and omnivores (Sohlenius and Wasilewska, 1984; Sohlenius and Boström, 1986; Sohlenius, 1990). Such trends have been found in both agricultural and forest systems. Increased plant production is considered to be the main cause for the increase in root feeding nematodes, whilst stimulation of microbial activity and bacterial populations in the rhizosphere may be responsible for the increase in bacterial feeders. Sohlenius and Boström (1986) attributed the decline in fungal-feeding nematodes to the reduction in fungal biomass in fertilized plots (Schnurer *et al.*, 1986).

De Goede *et al.* (1993) used the *c-p* triangle (which classifies nematode fauna into enrichment opportunists *c-p* 1, general opportunists *c-p* 2 and persisters *c-p* 3–5) to show changes in nematode communites following different fertilizer treatments. Ettema and Bongers (1993) also used this approach to investigate the relative abundance of nematode trophic groups in soil following manuring and/or fumigation (Fig. 9.4A). A temporary increase in food supply following manuring or fumigation caused an enrichment of opportunists (*c-p* 1) which were succeeded by *c-p* group 2 and finally supplemented by persisters (*c-p* 3–5). This type of pictorial representation of data helps to provide meaningful interpretation to large quantities of ecological data. Bongers *et al.* (1995) used a modified version of the *c-p* triangle to follow the changes in nematode diversity following eutrophication, acidification and manure application (Fig. 9.4B).

Most of the changes in protozoan and nematode abundance and trophic diversity is found to be short-term and once the effects of the C and nutrient inputs from the fertilizer application have disappeared, the microfaunal population will return to its original status, unless significant changes have occurred to the physical and chemical properties of the soil (Wodarz *et al.*, 1992; Ettema and Bongers, 1993).

Soil pH and salinity

Experimental evidence of the direct effects of pH on individual protozoan species is limited. However, many flagellates, ciliates and amoebae appear to grow over a relatively wide range of pH (pH 3.5–9.75), and protozoan populations usually respond positively and rapidly to the application of lime (Cutler and Crump, 1935; Stout and Heal, 1967; Homma *et al.*, 1983; Berger *et al.*, 1986 Foissner, 1987; Lehle and Funke, 1989). Some effects of adverse pH on protozoa include reduced activity of spore-perforating amoebae (Homma and Cook, 1985 and malformations in euglyphid testates (Rauenbusch, 1987).

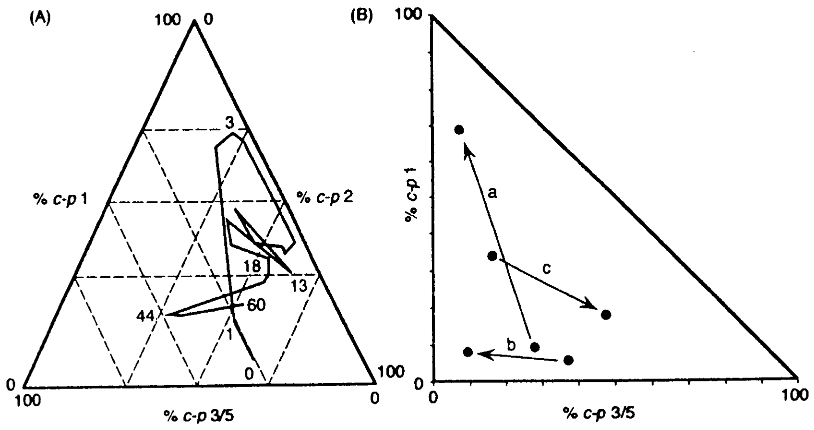

Fig. 9.4. Colonizer-persister (*c-p*) triangle showing (A) successional changes in nematode (*c-p* group) distribution in manured soil (numbers indicate weeks after manuring; Ettema and Bongers, 1993) (B) shifts during a) eutrophication, initial situation and 2 weeks after adding powdered cow-dung (Ettema and Bongers, 1990); b) artificial acidification of coniferous soil (Hyvönen and Persson, 1993) and c) recovery, 33 and 44 weeks after organic manuring (Ettema and Bongers, 1990). (Adapted from Ettema and Bongers, 1993 and Bongers *et al.*, 1995).

The available data on nematode distribution in different soils and agroecosystems indicates no direct limitation of soil pH, although liming which increased soil pH was correlated with an increase in nematode abundance (Yeates, 1981). Information of the effect of pH on the trophic diversity of nematode populations is limited. Hyvönen and Persson (1990) observed a shift in nematode composition (reduction in % abundance of *c-p* 3–5, persisters; suggesting a community under stress) following the artificial acidification of a coniferous forest soil (Fig. 9.4B).

Although most soil protozoa can adapt to a wide range of salinities (up to 45%) an increase in salinity may inhibit reproduction and cause encystment in some species (Stout, 1955). Pomp and Wilbert (1988) observed no significant correlation between the occurrence and abundance of certain ciliate species and the salt content of soils from Australia. The concentration and composition of salts in soil solution, however, has been reported to influence the trophozite form of *Naegleria gruberi* (Willmer, 1963).

Effects of pesticides

A number of studies have demonstrated negative effects of herbicides on protozoan and nematode populations (Yeates *et al.*, 1976; Popovici *et al.*, 1977; Pons and Pussard, 1980; Laminger and Maschler, 1986; Sály, 1989; Wardle *et al.*, 1995). Popovici *et al.* (1977) found a dose-dependent decline in the abundance of taxonomic groups of protozoa (e.g. flagellates, ciliates and naked amoebae) following application of the herbicide atrazine which persisted in the soils for four months; flagellates were the most sensitive group. Pons and Pussard (1980) found differences in the response of different monoxenic cultures of naked amoebae to the same herbicide, atrazine (40 mg l^{-1}). In contrast, Odeyemi *et al.* (1988) did not find any adverse effects of soil application of the herbicides Gramoxone, Dacthal, Preforan and Dual on protozoan populations. However, Pizl (1985) found that exposure of earthworms to the herbicide zeazin 50 increased their infection by monocystid gregarines (protozoa) suggesting that herbicide stress reduced the resistance of earthworms to infection.

While some direct negative effects of herbicides on nematode populations have been recorded (Wong *et al.*, 1993), many of the effects are indirect arising from the changes in the quantity and quality of plant inputs (e.g. dead organic matter from weeds) to the soil. Herbicide induced stimulation of nematode populations is attributed to the increased microbial activity from the dead weed residues (Mahn and Kastner, 1985; Edwards, 1989; Wardle *et al.*, 1995). Long-term use of herbicides, however has been shown to reduce both the abundance and diversity of nematodes in agricultural soils and vineyards (Yeates *et al.*, 1976; Ishibashi *et al.*, 1978; Wardle *et al.*, 1995).

The effects of insecticides and fungicides on protozoa (especially ciliates and testaceans) and nematodes are more pronounced than those of herbicides (Foissner, 1987; Yeates and Bongers, 1997). Petz and Foissner (1989) observed acute toxicity to the insecticide lindane in ciliates; the number and composition of the ciliate faunae remained significantly altered 90 days after its application. Negative effects of lindane on the abundance and composition of testate amoebae were also reported by Wanner (1991). Populations of fungal-feeding ciliates were significantly reduced by the application of the fungicide mancozeb (Petz and Foissner, 1989), probably through its effects on fungi. Yeates *et al.* (1991) reported that fumigation by methyl bromide eliminated nematode populations and that 166 days after fumigation nematode populations were still lower than those in untreated soils.

Effects of Sewage, Heavy Metals and Industrial Pollutants on Microfauna

Sewage effluent, sludge and heavy metals

The use of municipal sewage effluents and sludge (activated or digested) as fertilizers or soil conditioners has increased in recent years (McLaren and Smith 1996). Soil microfauna are able to adapt to effluent irrigation and associated data from species with very different life styles, especially since there are species-specific responses to environmental parameters (see below). However, samples from field sites may contain individuals whose mean weight may vary 10-fold between adults of different species and up to 100-fold between juveniles and adults within species. Thus the argument comes down to whether the impact of earthworms is best represented by a given change (e.g. a 10-fold change) in earthworm numbers or biomass.

The use of total biomass avoids the difficulties associated with earthworm size and taxonomy, and is more stable than numerical abundance as a measure of earthworm impact. For example, Williams and Doube (unpublished) examined the relationship between numbers and biomass of two species of earthworm (*Aporrectodea trapezoides* and *A. rosea*) and barley yields in a red-brown earth. They found that biomass was far superior to abundance as a predictor of the impact of earthworms on plant weight ($r = 0.88$, $P<0.001$) and grain yield ($r = 0.75$, $P<0.001$) (Fig. 11.1), supporting the view that species with similar ecological requirements (as above) may be pooled and that biomass, rather than numerical abundance, should be used as a measure of abundance. Whether it is useful to pool the biomass of species from different ecological categories is not known.

Earthworm abundance in intensively cultivated land can be very low, rendering their use as bioindicators impractical for methodical and statistical reasons (Knüsting, 1992).

Once agricultural soils have their full complement of peregrine species, can the abundances of species or groups of species (or even the composition of communities) act as an indicator of soil health? To answer this question we need to examine the factors determining the abundance of earthworms and establish whether the same factors limit sustainable crop productivity.

Determinants of Earthworm Abundance

Factors that influence the abundance of earthworms in agroecosystems include the organic matter status of the soil, soil type and depth, pH, moisture holding capacity, rainfall, temperature, cultivation, crop type and crop residues, and predation and parasitism (Curry, in press). Amongst these, the availability of organic matter is commonly the most important (Edwards and Bohlen, 1996), but other factors (e.g. pH, soil type, habitat type or predation) can also be of overriding importance in particular circumstances. Furthermore, agricultural practices (tillage, fertilizer, etc.) can also have a major influence on earthworm abundance.

Added organic matter commonly increases earthworm populations. For example, the abundance of *A. trapezoides, A. rosea* and *M. dubius* increased 2- to 10-fold when sheep dung was added to a pasture soil (Hughes *et al.*, 1994a). The abundance of the same three species increased 2- to 6-fold in response to added cereal straw in a cropping soil (Doube *et al.*, 1995) (Fig. 11.2). The type of organic matter is also important. For example, Barley (1959a) showed that *Aporrectodea caliginosa* gained weight when fed dung, maintained weight on a diet of plant foliage and lost weight when fed roots. On a regional basis, Hendrix *et al.* (1992) reported a significant positive but weak correlation between earthworm numbers and soil organic matter content across a number of ecosystem types on the Georgia piedmont, USA.

Soil pH can have an overriding influence on earthworm abundance. Jefferson (1956) measured the abundance of ten earthworm species in a field trial in which soil pH in adjacent plots differed radically. Five species made up 94.5% of those sampled and *Aporrectodea tuberculata* made up 60% of all earthworms. Earthworms were virtually absent from the highly acidic soils ($pH<4$) and alkaline soils ($pH>8$) and were most abundant in soils in the pH range 6.0–7.0 (Fig. 11.3). Earthworms were absent from plots treated with ammonium salts but were present at ca. 700 m^{-2} in adjacent untreated plots (Jefferson, 1955). It is also important to note that there were major differences between species. For example, *A. tuberculata* and, to a lesser extent, *Lumbricus festivus* and *Lumbricus rubellus* were tolerant of acidic soil conditions whereas *Aporrectodea chlorotica*, *Eisenia* (*Aporrectodea*) *rosea* and *Octalasion cyaneum* were greatly reduced in acidic soils and abundant in neutral soil (Fig. 11.3). Similarly, Edwards (1974) examined earthworm populations in the Park Grass Plots at Rothamsted, UK (trial established 1856) where liming acidic soils had created soils whose pH ranged from 3 to 8. Again earthworms were scarce or absent from soils of extreme pH. The earthworm *L. terrestris* was most abundant in soils in the range pH 7–8 whereas the other species were most abundant in the range pH 5–6.

Soil type also appears to influence earthworm numbers, dramatically in some cases (Lee, 1985; Edwards and Bohlen, 1996). Earthworms are commonly scarce in sandy soils, relatively abundant in loamy soils and scarce in some clays (e.g. krasnozems, Wylie, 1994). Plant productivity does not follow the same pattern in relation to soil type, but it is possible that, within the caveat of soil type, earthworm numbers might act as indicators of soil health.

The species composition of earthworm communities depends upon the nature of the habitat and the opportunity for new species to colonize it. For example, in New Zealand, replacing natural vegetation with pasture caused the loss of virtually all native species: these pastures remained worm-free until colonized, decades later, by introduced European pasture species (Lee, 1985). Similarly in tropical, subtropical and temperate regions, the conversion of native lands to agricultural land has seen the local demise of populations of native earthworm species and colonization by an introduced exotic species (Lavelle, 1988; Lavelle *et al.*, 1992).

Predation on earthworms can have dramatic effects on local populations (Edwards and Bohlen, 1996). For example, plovers, in a hayfield in Iceland, reduced earthworm populations (238 m^{-2}) by nearly 50% in 22 days (Bengston

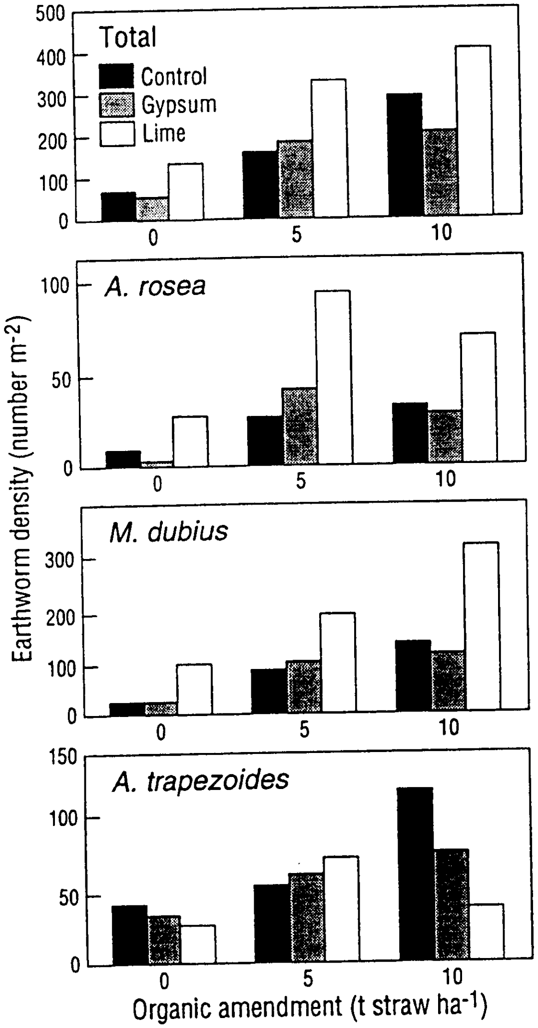

Fig. 11.2. The effect of the rate of wheat straw addition (0, 5 and 10 t ha^{-1}) and calcium (0, 2.0 t ha^{-1} year^{-1} lime, 0, 2.4 t ha^{-1} year^{-1} gypsum) on the abundance of three species of earthworm in a trial conducted in a red-brown earth at the Waite Agricultural Research Institute (from Doube *et al*., 1995).

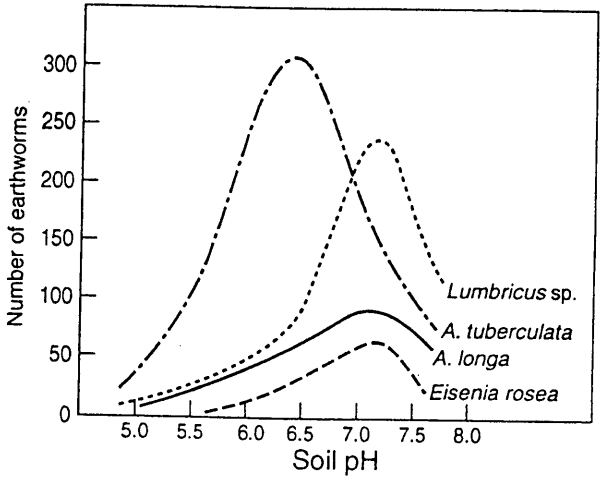

Fig. 11.3. A schematic illustration of the effect of soil pH on the relative abundance of four species of earthworm in experimental plots at Bingley, UK (redrawn from Jefferson, 1956).

et al., 1976) and Blackshaw (1990) contends that the New Zealand planarian, *Artioposthia triangulata* was responsible for the total elimination of earthworm populations from a grass field near Belfast, Northern Ireland. This species threatens earthworm populations across northern Europe (Boag *et al*., 1995). Clearly earthworm abundance will be a poor indicator of soil productivity in the presence of the flatworm or other effective predators.

The effect of agricultural practices on earthworm abundances has recently been reviewed by Fraser (1994). She concludes that the influential factors are pastoral management techniques, the sequence of crop rotation, the timing, frequency and type of cultivation used, irrigation, whether or not mulched or crop residues are returned to the soil and the use of agricultural fertilizers and/or pesticides. Commonly the extreme treatments induce a 2- to 5-fold change in earthworms abundance, but there is no evidence for corresponding changes in crop productivity.

The speed with which earthworm populations respond to favourable conditions is a vital aspect of their capacity to act as indicators. Some earthworms have low fecundity and slow growth rates (e.g. the giant Gippsland earthworm). By contrast, large changes in the abundance of the peregrine agricultural species can occur within one season. Given favourable conditions, single earthworms can produce up to several hundred cocoons per year and juveniles can reach maturity within a few months (Edwards and Bohlen, 1996). Further cocoons may remain viable in the soil, even under adverse conditions, for several years

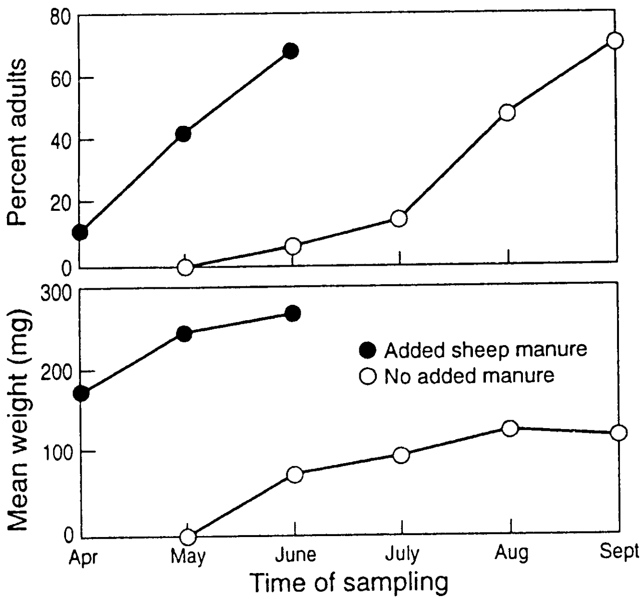

Fig. 11.4. The effect of added sheep manure on the growth and maturity of the earthworm *Microscolex dubius* in the field in the Adelaide Hills, South Australia (from Hughes *et al.*, 1994b).

(Edwards and Bohlen, 1996). Clearly peregrine earthworm species have the potential to respond rapidly when conditions for growth and reproduction change (Fig. 11.4). For example, within half a season (8 weeks) the numbers of three peregrine species had increased 2- to 10-fold following organic enrichment of the soil (Hughes *et al.*, 1994a). Similarly, Buckerfield (1996) found that earthworm populations in potato growing soils were reduced in the year immediately following potatoes but recovered to densities greater than those in adjacent pastures in the following year. Boström and Lofs-Holmin (1988) found that earthworm populations were severely reduced by rotary hoeing but their numbers had recovered one year later. In Lismore, New Zealand (Francis and Knight, 1993) and Temora, Australia (Doube *et al.*, 1994c) initial earthworm numbers following ploughing of pasture were high (850 and 410 m^{-2}, respectively) but populations decreased by 50–70% in the following 1–2 years, presumably due to a reduced food supply (Fig. 11.5) (Gupta and Kirkegaard, personal communication).

From the above it is clear that earthworm populations respond positively to many of the conservation practices in agriculture and have a capacity to respond in a time scale appropriate for an indicator (1–2 years). Numerical responses in earthworms are more intense than crop responses to environmental changes and

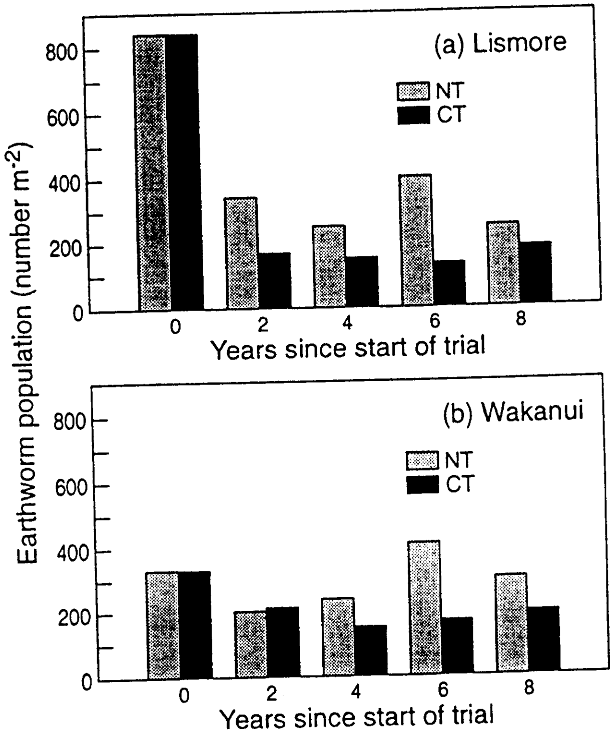

Fig. 11.5. The effects of cultivation and time on populations of earthworms at two locations on the Canterbury Plains, New Zealand (from Francis and Knight, 1993). NT, no tillage; CT, conventional tillage.

so measures of earthworm abundance could provide a sensitive indicator of soil health.

Linkages between Earthworm Abundance, Soil Properties and Plant Growth

Evaluation of the links between earthworm abundance and plant productivity (an index of soil health) is possible using data from long term field trials found in agricultural regions throughout the world. These provide ideal situations in which to investigate the linkages between soil biological parameters and soil health because long term measures of productivity and the biological condition of the soil are often available and comparisons are not confounded by

Parnes - Fertile Soil
1990

CALCIUM AND SOIL PH

A. SUMMARY

Calcium is needed in cell membranes and in the growing points of plant roots and tops. Calcium also helps to neutralize toxic materials. Retention of calcium in the soil and the effect of calcium in the control of pH depends upon the cation exchange properties of the soil.

The soil pH is directly important to the plant only to the extent of its influence on the availability of phosphorus and trace elements and indirectly because of its influence on biological activity.

Soil pH, cation exchange, and lime requirement are discussed. Table 22 is a list of calcium amendments.

B. CALCIUM IN THE PLANT

Calcium is the Servant, opening and closing doors and keeping out unwelcome intruders. Calcium seems to exist at all interfaces. For example, it is part of cell walls and controls movement into and out of the cell. Calcium is in the growing tips of the roots and tops and is part of the sticky substance that surrounds the roots and binds them to the soil. Also, calcium reacts with waste products, either precipitating them or chelating with them, rendering them harmless to the plant.

Plant roots are inefficient at absorbing calcium from the soil, about 10 times less efficient, for example, than they are at absorbing potassium. Consequently the actual amount of calcium taken up by the plant is small, despite the large quantity that may be present in the soil.

A deficiency of calcium causes dieback of all the growing tips, in both roots and tops, and causes cell membranes to lose their impermeability and to disintegrate. When calcium is deficient roots are short, thick and bulbous, symptomatic of aluminum toxicity.

C. CALCIUM IN THE SOIL

The low ability of the plant to take up calcium coincides with the large amount in most soils. Available calcium is measured in terms of thousands of pounds/acre, while other nutrients are present at hundreds of pounds/acre, and often much less. Except under conditions of severe calcium deficiency in the soil, no relation exists between the amount of calcium in the soil and the amount in the plant. Furthermore, like potassium, not much calcium is required by soil organisms.

Calcium has two major effects in the soil. One is as a bonding agent in the aggregation of soil particles, wherein it helps to bind organic and inorganic substances. It is thus important in the development of a good soil structure (see Chapter 2 for a discussion of soil structure).

The second effect of calcium is as a nutrient filler, to occupy space which otherwise would be taken up by the acid elements. The value of lime is not in the calcium it contains, otherwise gypsum would be as good as lime in raising the pH. In chemical terms, agricultural lime is calcium carbonate, and the carbonate is what causes the pH to rise. Other carbonates would raise the pH as well as lime, and some would do it faster, but they would throw the soil out of balance. Potassium carbonate, for example, would be a splendid liming agent, except that it would cause the potassium level to rise so high that the plants probably would not survive.

How does calcium serve as a filler, and what "space" does it occupy? The term "space" refers to a unique property, wherein the soil contains a vast reservoir, a "space" holding all of the mobile cations. This sense of mobility, associated with the flow of cations in and out of the reservoir, is important, and the phenomenon is known as cation exchange. Cation exchange is important not only in preventing cation nutrients from leaching but also in establishing their plant availability, the soil pH, and the quantity of limestone required to change the pH by a desired amount.

Thus it seems appropriate to discuss here cation exchange, soil pH and the effect of limestone.

D. SOIL pH AND CATION EXCHANGE

CATION EXCHANGE

Cation exchange is due to the presence of very fine clay or humus particles, which have a negative electric charge. This negative charge attracts cations, which have a positive charge, and the result is a collection of various cations floating around the particles, similar to the atmosphere floating around our planet. These particles are called micelles (short for microcells). The cations are not chemically bound to the micelles, but they are held loosely as a collection. Cations are constantly drifting back and forth between the micelles and the soil solution. Those associated with the micelles form the pool of "exchangeable" cations and those in solution the pool of "soluble" cations. In equilibrium, a balance is reached between exchangeable and soluble cations.

In most soils, the exchangeable cations dwarf the soluble cations. Soluble cations taken up by plants or those lost by leaching are replaced by exchangeable cations, with a likely change in balance at equilibrium. The application of lime and fertilizers produces cations that first enter the soil solution and then drift onto the micelles, with a corresponding change when equilibrium is reached.

The principal exchangeable cations are calcium, magnesium, potassium, and, in many areas, hydrogen and aluminum. In a soil containing mostly calcium, the majority of the exchangeable cations are calcium ions.

Exchangeable calcium, magnesium and potassium are available to plants. A plant root in the immediate vicinity of a micelle can take up one of these nutrients and substitute an equivalent amount of hydrogen ions.

The cation exchange reservoir is determined by the number of micelles. The number of cations which can be held by the micelles, or the number of cations in the reservoir, is called the cation exchange capacity, or CEC [54]. The larger the exchange capacity, the larger is the number of exchangeable cations.

A large exchange capacity, however, does not assure a fertile soil but only that the soil contains a large number of exchangeable cations. The CEC does not indicate whether the cations are nutrients. Indeed, the cations may be acid-forming non-nutrients. The purpose of adding lime and fertilizer is to replace non-nutrients with nutrients. Since the plant is less sensitive to the calcium concentration than to the other major nutrients in the soil, calcium plays the major role in maintaining the balance between acid and alkaline cations.

SOIL pH

Soil pH is an imperfect and limited concept. A discussion of why this is so may help in interpreting soil test results.

The term "pH" is chemical in origin. Its intended purpose is to indicate the hydrogen ion concentration in a water solution, converted to logarithmic units. The conversion is so arranged that pH 7 indicates a neutral solution, neither acidic nor alkaline; a lower pH means that the solution is acid and a higher pH that it is alkaline. The pH can be estimated with the help of paper strips coated with chemicals whose color depends upon the acidity of the water solution. The most accurate measurements, however, are made with a glass or plastic pH probe attached to a millivoltmeter.

So in a soil, it is the water that is important, not the soil particles.

People who first tried measuring the pH of soil simply plunged the probe into a soil sample; but the results were erratic, because the probe did not make intimate contact with the soil water. More reliable results were obtained with a paste, adding just enough water to the soil to saturate it, just before it becomes shiny with excess water. This procedure, however, is too laborious, and eventually the test was standardized by combining soil and water in a predetermined proportion, commonly but not always equal quantities by weight.

The problem is that the great majority of the acid-producing cations are exchangeable, whereas the pH meter measures the concentration of soluble hydrogen. The relationship between the two depends upon the amount of water used and its purity. The more water, the greater the dilution, the lower the concentration of soluble hydrogen ions and the higher the pH. Any salts in the water will replace some of the exchangeable acidity; consequently salty water will result in a higher soluble hydrogen ion concentration, or a lower pH. Moreover, during a dry season salts will accumulate in the soil, and when the rains come, these salts are leached out. If the pH is tested during the dry part of the season, the soil salts will dissolve in the water used to measure the pH, but they will not during the wet season, having already leached out. This means that the pH measured during a drought will be lower than the pH measured after a rainstorm.

So we should first understand that a pH meter does not measure soil pH, which is a somewhat meaningless concept, nor even the pH of the soil water, but rather the pH of the water mixed with the soil by a technician or by a machine; and secondly that this distinction produces results which depend upon the amount of water used and its saltiness. Thus different testing laboratories may give different results. Some laboratories use salted water in order to swamp out the effect of varying salt content in the soil; this produces more uniform results, but the pH is lower, by an amount which may vary between a tenth and more than a whole pH unit, depending upon the extent to which the soil has a high salt content on the one hand or is leached out on the other; the average drop in pH is about half a unit. Unfortunately, most charts and tables showing the best pH for growing specific crops are based on the pH measured in pure water, although states that measure pH in salt solution have accumulated their own data.

However, it is the best that can be done, and "soil pH" is still the most important of the simple tests of the state of the soil for growing crops. Owing partly to the variations in pH that can occur, as discussed above, people who test their soils regularly should take samples at the same time of year and during typical weather conditions.

IMPORTANCE OF SOIL pH

As it turns out, plants are not sensitive to soil acidity; what they are sensitive to is the effect of the acidity on the availability and form of plant nutrients. An acid soil inhibits the conversion of nitrogen from the ammonium to the nitrate form, and plants have evolved accordingly. Most plants prefer nitrogen in the nitrate form, but grasses and grains do best with a mixture, and blueberries require nitrogen in the ammonium form. In an acid soil, levels of aluminum and available manganese can rise to the point where they become toxic to many plants, while molybdenum may be deficient. In an alkaline soil, the availability of most trace elements may be too low for some crops. The availability of soil phosphorus [53] drops in an acid or alkaline soil.

The soil pH is also a significant factor in determining the quantity and diversity of soil organisms, and a neutral pH encourages a greater and more diverse population than a pH below 6.

Exceptions, however, do occur, because certain plants have unique trace element requirements. For example, blueberries evolved in acid soils containing large amounts of iron and ammonium-nitrogen. Grasses and other monocotyledons have a requirement and a tolerance for moderately high amounts of manganese and zinc, which are most available in acid soils.

These factors tend to govern the optimum pH levels for plants. Soil characteristics, however, may modify any conclusions. Some soils have a high aluminum content, and a higher pH may be warranted for the sake of improving the status of available phosphorus. Sandy, highly weathered and poorly buffered soils are typical of many areas of the Atlantic coast and the Southeast. These soils require more acidity for satisfactory availability of some trace elements, notably manganese, and so, in most cases, the pH of those soils should not rise above 6.0 - 6.2. On the other hand, these tendencies to favor a departure from a biologically optimum pH can be reduced or eliminated by the presence of organic matter, which can tie up aluminum and chelate many trace elements. Soil pH is not as important to plant growth when the organic content is satisfactory.

Across the country, in the Southwest and most of the West, soils are low in aluminum. Organic soils (with an organic content of 50% or more) contain little aluminum. In all these soils aluminum toxicity is unlikely, and raising the pH to avoid it is not quite so critical as it is, for example, in the weathered, high aluminum soils of New England and parts of Oregon. For organic soils, the pH is of little importance in assessing the fertility, which is fortunate, because an impractically large amount of lime would be necessary to neutralize acidity.

SOIL pH AND CALCIUM

Lime serves to increase the pH, by modifying the balance between acidity and alkalinity. The predominant sources of acidity are the acid-forming cations, hydrogen to some extent and primarily aluminum (see note [86] for an explanation). The sources of alkalinity are the "base" cations, principally the nutrients calcium, magnesium and potassium. The equilibrium between exchangeable acid and base cations determines the amount of hydrogen ions and thus the pH of the soil solution.

Accordingly, soil acidity can be neutralized with anything that supplies alkalinity. Wood ashes, for example, are excellent for neutralizing soil acidity, but they should be used only moderately. Otherwise they would add so much potassium that plants would be likely to suffer from a calcium or magnesium deficiency. The only substances that can effectively neutralize a soil without impractically disturbing the cation balance are alkaline materials containing calcium alone or calcium plus magnesium, the choice of which depends upon the magnesium status of the soil.

It is important to recognize that the pH is useful only as a flag, to indicate the status of the soil acidity. It may show us that the soil is too acid but not how excessive the acidity is. For example, a soil in Delaware with a pH of 5 will require much less lime to neutralize it than a typical soil in California at pH 5. The amount of lime required is dependent on the cation exchange capacity, or CEC. A Delaware soil with a low CEC has fewer acid cations to neutralize than a California soil at the same pH but with a higher CEC. One can think of the pH as a measure of the proportional balance between acidity and alkalinity, but this same balance can be achieved no matter how many cations are involved. We may have neutrality between 10 acid cations and 10 base cations (this is an over-simplification, but it illustrates the point), but also between 100,000 acid cations and 100,000 base cations; if, however, one soil has 19 acid cations and 1 base cation, and the other soil has 190,000 acid cations and 10,000 base cations, both may well result in the same ph, but obviously the second soil will need much more lime to neutralize it.

A high CEC may be thought a disadvantage, owing to the large quantity of lime required to neutralize it if the soil is acid. But it is actually an advantage, because this lime constitutes a reservoir against the natural acidifying tendency of the soil. A soil with a higher CEC is more strongly buffered. This is desirable in a well-maintained soil, but it may be a problem with an abandoned soil, particularly where organic matter tends to accumulate, as in the Northeast. The buffering of soil is the reason why acid rain has little effect on soil pH (see, for example, Appendix 3).

D. CALCIUM FERTILIZERS

LIST OF FERTILIZERS IN TABLE 22

Table 22 is a list of calcium fertilizers. Poultry manure, wood ashes and seashells or lobster shells are the only common organic sources of enough calcium to be useful when spread in typical amounts. All manures, however, contain a large quantity of carbonates and thus have a liming value. The actual carbonate content, however, is variable, and the liming value of manure is unpredictable. Much of the calcium in poultry manure comes from the lime in poultry feed, most of which passes through the animal. With overuse of poultry manure, there is a danger of driving the pH too high.

Legume hay contains some calcium, but the calcium has no liming value, since no carbonates are present.

Two popular waste materials for liming are clam shells and wood ashes. Clam shells are almost pure calcium carbonate, and wood ashes comprise a variety of carbonates and oxides. The lime equivalent of wood ashes shown in Table 22 takes into account the total carbonate and oxide content, not just calcium alone (see Appendix 3 for details). Clam shells have a low solubility and require several years to be completely effective. They should be ground as finely as possible for the quickest results. Wood ashes are highly soluble and are effective almost immediately. They are also caustic and should be handled with care.

In most cases, however, agricultural limestone is the most common method for adjusting the soil pH. Two kinds of limestone are available, one being primarily calcium carbonate, or calcitic limestone, and the other a mixture of calcium and magnesium carbonate, often called dolomitic or simply high magnesium limestone. Both have approximately the same liming capability.

At one time, other more soluble forms of lime were used. Burned lime, or quicklime, is calcitic limestone which has been heated in a furnace to drive out carbon dioxide, leaving calcium oxide. It is soluble and caustic. It is also difficult to spread effectively, because it tends to form flakes in the soil, which become insoluble owing to the formation of a crust of calcium carbonate on the surface. Hydrated lime, or slaked lime, is burned lime to which water has been added. It is soluble and even more caustic than burned lime. It is also unstable and eventually changes to insoluble calcium carbonate upon exposure to air. These materials are no longer in common use for agricultural purposes.

Rock phosphate and bone meal raise the pH to a modest extent, which adds to their value in a non-alkaline soil. They act more slowly than limestone, because of their lower solubility. Also, their liming value is less than is indicated on most labels. See Appendix 3 for details.

Gypsum, sometimes called land plaster, is the last material listed, and it is the only one that has no liming capability. It improves the growth of clover in an acid soil, but not as well as lime. The most likely fertilizer value of gypsum is in the sulfur it contains. Gypsum is, however, useful in improving the soil structure of alkaline soils, by facilitating the removal of excessive amounts of sodium [55].

Gypsum may possibly be helpful in acid soils with a low cation exchange capacity, by supplying calcium without raising the pH. It has been shown to counter the toxic effects of aluminum in plants; it has been used effectively in growing cranberries and on some soils in the Southeast. Why it works is not clear, but perhaps calcium and aluminum compete for uptake by plants.

Calcium chloride is another source of calcium which does not raise the pH. It is not a good soil amendment because of its potential toxicity from chlorides and its ready tendency to leach. Calcium chloride has been used as a foliar spray for fruit trees in a highly acid soil having an excess of potassium.

HOW MUCH LIME TO APPLY?

As noted earlier, the cation exchange capacity depends upon the clay and the organic matter content. In arid and semi-arid soils, the clay content is more important, but most of these soils need little or no lime. Where lime is most important, organic content is the predominant factor determining the exchange capacity. Some popular recommendations in articles and handbooks base the lime requirement only on whether the soil is sandy, silty or clayey. This may be satisfactory in some places, but it is an oversimplification and least applicable to those soils most likely to need liming.

A reliable soil test furnishes a lime recommendation that takes into account the CEC of the soil. Most state laboratories have developed accurate correlations that reflect this dependence either directly or indirectly. Many private laboratories have done so also, but some apply the results valid in one state to all others, which can lead to errors.

A defect of a soil test kit is the lack of an adequate lime recommendation, and people who use one must develop their own correlations. To start, it is best to be conservative. If, for example, the pH goal is 6.8, then no lime should be necessary if the pH is above 6. If it is below, then one ton of lime per acre, or 5 lbs/100 sq ft should be spread; it can be doubled if the organic content is known to be high. If the pH is below 5.0, two tons/acre, or 10 lbs/100 sq ft are more likely to be needed. More than two tons/acre should never be added in one year, otherwise trace elements could be tied up temporarily. In humid areas, magnesium may be low, and so the first ton of lime per acre should probably be dolomitic limestone.

Lime should be thoroughly tilled into the soil. If it is simply topdressed, it will take a long time to move down into the soil, at a rate of about one inch/year in New England [56].

The quantity of gypsum needed to neutralize sodium in an alkaline soil depends upon the sodium content, but typical quantities are of the order of several tons/acre.

TABLE 22

FERTILIZERS FOR SUPPLYING CALCIUM

Fertilizer	Calcium Content		Lime Equivalent, lb/ton
	in %	in lb/ton	
ORGANIC			
Manure			
Poultry manure-cage layer	up to 4	up to 80	
Other manures	0.2-0.4	4-8	
Legume Hay	1.4	28	
INORGANIC			
Clam & oyster shells	about 34	680	1700
Wood ashes	about 35	700	1750
Calcitic limestone	about 38	760	1900
Dolomitic limestone	about 25	500	1900
Rock phosphate			
Colloidal	21	420	800
Hard rock	33	660	1200
Gypsum	23	460	

The Dictionary of Substances and their Effects

EDITOR
M L Richardson, *BASIC, UK*

ASSOCIATE EDITOR
S Gangolli, *Consultant, UK*

ROYAL SOCIETY OF CHEMISTRY

1993

Richardson

Any other comments

Spontaneously combustible substance.

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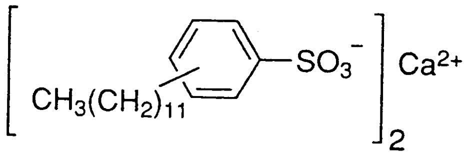
1. *EC Directive Relating to the Quality of Water Intended for Human Consumption* 1982, 80/778/EEC, Office for Official Publications of the European Communities, 2 rue Mercier, L-2985 Luxembourg

C30 Calcium dodecylbenzenesulfonate



CAS Registry No. 26264-06-2
Synonyms benzenesulfonic acid, dodecyl-, calcium salt
Mol. Formula $C_{36}H_{58}CaO_6S_2$ **Mol. Wt.** 691.07
Uses Anionic detergent. Used in toxic chemical agent decontamination emulsions.

Mammalian and avian toxicity

Irritancy

May cause skin irritation (1).

Any other adverse effects to man

Damaging potential of calcium dodecylbenzene sulfonate on humans (1).

Legislation

Limited under EC Directive on Drinking Water Quality 80/778/EEC. Calcium: guide level 100 mg l^{-1} (2).

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C31 Calcium hydroxide

$Ca(OH)_2$

CAS Registry No. 1305-62-0
Synonyms calcium hydrate; hydrated lime; Kemikal; slaked lime
Mol. Formula CaH_2O_2 **Mol. Wt.** 74.09

Uses In mortar, plaster, cement and other building and paving materials. In lubricants, drilling fluids, pesticides, fireproofing coatings, water paints. Egg preservative. Manufacture of paper pulp. Styrene butadiene rubber vulcanisation. Water treatment. Dehairing hides. Therapeutically used as an astringent.

Physical properties

M. Pt. loses water at 580°C; **B. Pt.** decomp.; **Specific gravity** 2.240.

Solubility

Water: 0.8 g l^{-1} at 0°C.

Occupational exposure

US TLV (TWA) 5 mg m^{-3}; **UK Long-term limit** 5 mg m^{-3}.

Environmental fate

Absorption

Strong interaction with humic acids (1).

Mammalian and avian toxicity

Acute data

LD_{50} oral redwing blackbird 111 mg kg^{-1} (2).
LD_{50} oral rat 7340 mg kg^{-1} (3).

Irritancy

A severe eye irritant, a skin, mucous membrane and respiratory system irritant (4).
10 mg instilled into rabbit eye caused severe irritation (4).

Sensitisation

Has been reported to cause dermatitis in humans (2).

Any other adverse effects to man

Produces third degree alkali burns (with a pH as high as 12.9) after 2 hr of contact (5).

Legislation

Limited under EC Directive on Drinking Water Quality 80/778/EEC. Calcium guide level 100 mg l^{-1} (6).

Any other comments

Use in restorative dentistry reviewed (7).
Experimental toxicology and human health effects reviewed (8).

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C35 Calcium oxide

CaO

CAS Registry No. 1305-78-8
Synonyms burnt lime; quicklime; lime; calcia; calx
Mol. Formula CaO **Mol. Wt.** 56.08
Uses Strong caustic agent. Used in bricks, plaster and other building materials. Manufacture of steel, aluminium, magnesium. Used in fungicides and insecticides. In laboratories to absorb carbon dioxide. Desiccant.
Occurrence Produced by the kiln-roasting of limestone.

Physical properties

M. Pt. 2580°C: **B. Pt.** 2850°C; **Specific gravity** 3.37.

Solubility

Organic solvent: glycerol

Occupational exposure

US TLV (TWA) 2 mg m^{-3}; **UK Long-term limit** 2 mg m^{-3}; **UN No.** 1910.

Mammalian and avian toxicity

Sub-acute data

Repeated exposure study inhalation rat 413 mg m^{-3} or a single exposure of 1026 mg m^{-3} (durations unspecified). No deaths, and no marked changes in behaviour, body weight or food intake. No significant difference in haematologic results and serum biochemical analysis or urine analysis (1).

Irritancy

Strongly caustic and may cause severe irritation of skin and mucous membranes (2). Tends to form clumps in the conjunctival sac which are dangerous and difficult to wash out (3).

Coarse dust causes skin erosion and ulceration while fine dust is injurious to the mouth, nose and eyes (4).

Prolonged exposure may cause dermatitis with desquamation and vesicular rash. Can cause severe irritation to eyes, oedema, hyperemia, lachrymation, blurred vision, corneal opacities, ulceration and perforation and loss of vision (5).

Any other adverse effects

Systemic effects include sore throat, coughing, dyspnoea and after severe exposure pulmonary oedema. Contact with moist skin can cause redness and ulceration. Fatal burns have been reported after the massive exposure. Prolonged exposure can cause inflammation and ulceration of the nasal and buccal mucosa with possible bronchial and gastrointestinal disturbances. Death results from asphyxia and circulatory collapse (5).

Legislation

Included in Schedule 6 (Release into land: Prescribed Substances) Statutory Instrument No. 472 (6).

Limited under EC Directive on Drinking Water Quality 80/778/EEC. Calcium: guide level 100 mg l^{-1} (7).

Any other comments

Reacts with water with the evolution of heat to form calcium hydroxide, thus reaction on the skin or in the mouth produces both a thermal and a caustic burn (3).

Decolmatation of lime dust and silt and increase in coarse sand was characteristic for soils of a Quercus Mongolica Forest with a *Corylus heterophylla*, *C. mandschurica*, and *Rhododendron sichtonensis* undergrowth under the impact of acid rain. The decolmatated silt formed a powdery layer on the subsoil layer. Calcium oxide occurred in organomineral forms and accumulated in humus. The most severe acidic leaching led to dispersion of the accumulated humus and its efflux in the form of low molecular compounds (8).

Experimental toxicology and human health effects reviewed (9).

Ineffective even at concentrations of 600 ppm in controlling the fish ectoparasite *Argulus sp* (10).

DNA-damaging activity of natural food additives was investigated (11).

The powdered oxide may react explosively with water.

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MANUAL FOR APPLYING FLUIDIZED BED COMBUSTION RESIDUE TO AGRICULTURAL LANDS

W.L. Stout, J.L. Hern, R.F. Korcak, and C.W. Carlson

Respectively, soil scientist, U.S. Regional Pasture Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture (ARS/USDA), University Park, PA 16802; research chemist, Appalachian Soil and Water Conservation Research Laboratory, ARS/USDA, Beckley, WV 2S802-0867; soil scientist, Fruit Laboratory, ARS/USDA, Beltsville Agricultural Research Center (BARC), Beltsville, MD 20705; and retired, formerly assistant director, Soil Management Research, BARC, Beltsville, MD 20705

Abstract

CONTENTS

Photo Caption* : *Fluidized bed combustion material applied as a surface mulch for apple orchards.

To conform to Environmental Protection Agency standards, coal-burning electric-generating plants must adopt effective methods to remove SO_2 (*For meaning of chemical symbols, see Appendix III*) from exhaust gases. One method is the atmospheric fluidized bed combustion (AFBC) process. In this process, crushed coal and a finely ground sorbent, usually limestone, are suspended or "fluidized" by jets of air. They are burned at a controlled velocity and optimum temperature. Sulfur in the coal reacts with Ca in the limestone to form gypsum, or $CaSO_4$. A part of the resulting residue is a dry granular mixture composed predominantly of CaO and $CaS0_4$, with small amounts of metal oxides.

AFBC residue contains alkaline oxides and plant nutrients that are useful in agriculture. It also has other elements that can be toxic to plants and animals if they enter the food chain in excessive amounts. To evaluate the potential benefits and hazards of AFBC residue to agriculture, the Agricultural Research Service (ARS) conducted research at several locations in the Eastern and Southeastern United States. This research was supported by the Department of Energy and the Tennessee Valley Authority National Fertilizer Development Center

This report presents guidelines for the safe and efficient use of AFBC residue in agriculture based on ARS research. The AFBC residues used in this study were the spent bed materials from experimental bubbling bed combustors. However, the guidelines should also be applicable to similar AFBC residues. This report is intended as a manual for power plant managers, consultants, and Government agency personnel who utilize AFBC residues. It does not exempt AFBC residues from guidelines established by State and Federal regulatory agencies.

AFBC residue components important to agriculture are divided into four groups (table 1)--lime, essential plant nutrients, heavy metals, and phytotoxic elements (25). This division is not absolute because some of the components can be placed in more than one group depending on their relative and absolute amounts and their interactions in the soil system.

Lime, the first group in table 1, is mainly a mixture of CaO and MgO. If the residue is quenched after combustion, these compounds revert to the hydroxide form. They also revert to the hydroxide form when they combine with water in the soil.

Lime is expressed as the neutralizing potential of the residue compared with an equal amount of ground agricultural limestone, usually $CaCO_3$. The bulk of the AFBC residue research conducted by ARS included using the lime in the residue to increase low soil pH. Based on this research, the best agricultural use of AFBC residue is as a lime source for croplands (3, 5, 25, 26), orchards (6, 9-16, 27), pastures (23), and reclaimed surface mines (4-24).

Table 1 : Variations in some chemical constituents of 9 samples of atmospheric fluidized bed combustion (AFBC) residue and soils

		AFBC residue[1]		Soils[2]	
Group	Component	Average	Range	Average	Usual range
		Percent of $CaCO_3$			
Lime	CaO and MgO	60	31-100		
		Micrograms per grams of dry material			
Essential Plant Nutrients	Ca	380,000	240,000-460,000		
	S	92,000	72,000-140,000	850	100-1,500
	Mg	7,100	5,000-12,000		
	K	2,500	500-8,000		
	P	430	380-500		400-3,000
	Fe	11,000	800-16,000		14,000-40,000
	Mn	485	210-685	850	200-3,000
	Mo	.19	.12-.28	2	.2-5
	B	110	95-170	10	2-100
	Cu	15	12-19	20	2-100
	Zn	5	29-105	50	10-300
Heavy Metals	Ni	21	13-29	40	5-500
	Pb	3.2	1.5-7.5	10	2-200
	Cd	.5		.5	.01-.70
	Cr	15	9-23	200	5-1,000
Phytotoxic Elements	Se	.29	.16-.58		.1-2
	Al	10,000	4,000-20,000		14,000-40,000

[1] From Stout, W.L., and others (25).

[2] From Baker, D.E., and L. Chesnin (2).

Essential plant nutrients (table 1) are those required for growth and reproduction of plants. The first five elements in this group (Ca, S, Mg, K, and P) are needed by plants in large amounts.

The large amounts of Ca in AFBC residues (table 1) occur not only as $Ca(OH)_2$ and CaO but also as $CaSO_4$, a compound commonly known as gypsum. Applying these compounds to acid soils has long been known to decrease soil acidity and promote root growth. This is particularly beneficial

FOURTH EDITION

Soil Fertility and Fertilizers

Samuel L. Tisdale
President (Retired), The Sulphur Institute
Formerly Professor of Soils
North Carolina State University

Werner L. Nelson
Senior Vice President, Potash & Phosphate Institute
Formerly Professor of Agronomy
North Carolina State University

James D. Beaton
Northwest Director, Potash & Phosphate Institute
Formerly Instructor of Soils
University of British Columbia

1985

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in pilot-plant and laboratory products has been 5 to 20% sulfur. The limited amount of work done with such fertilizers indicates that they are suitable sources of both phosphorus and sulfur.

A granular product based on concentrated superphosphate with an approximate analyses of 0-40-0-20(S) has been prepared by the TVA. Elemental sulfur and concentrated superphosphate are granulated using steam and water in a granulating drum. Commercial production of a similar material analyzing 0-35-0-28(S) was undertaken during the late 1960s by one manufacturer in the western United States. In spite of excellent results and farmer acceptance, production ceased after just a few years because of manufacturing and labor difficulties.

Sulfur-fortified normal superphosphates are popular in some countries such as Australia and New Zealand. Ordinary superphosphate is enriched with elemental sulfur to make mixtures containing from 18 to 35% sulfur. The added elemental sulfur is superior in its residual effect to the calcium sulfate already in the ordinary superphosphate.

There are small amounts of sulfur, normally between about 1 and 3%, in the ammonium phosphates and concentrated superphosphates which probably make minor contributions to the sulfur nutrition of fertilized crops.

Fertilizer Use Guidelines. For purposes of convenience, recommendations for the use and proper application of common sulfur-containing fertilizers are summarized in Table 8-13.

Calcium

Form Utilized by Plants. Calcium is absorbed by plants as the ion, Ca^{2+}. This takes place from the soil solution and possibly by root interception or contact exchange. The quantities of calcium required by plants can be readily transported to root surfaces by mass flow in most soils, excepting highly leached and unlimed acid soils. In soils abundant in this nutrient, excesses of it probably accumulate in the vicinity of roots.

Representative levels of calcium in the soil solution of temperate region soils are 30 to 300 ppm. In soils of higher-rainfall areas, soil solution calcium concentration will range from 8 to 45 ppm, and usually averages about 33 ppm. A level of 15 ppm Ca^{2+} in the soil solution was found by Barber at Purdue University to be adequate for high corn yields. Levels of from 100 to 300 ppm are commonly used in solution cultures. Loneragan and Snowball of the University of Western Australia demonstrated that Ca^{2+} concentrations of between 100 to 400 ppm in flowing culture solutions were sufficient for high yields of 30 grasses, cereals, legumes, and herbs.

The presence of concentrations of calcium in the root medium higher than are necessary for proper plant growth will normally have little effect on its uptake. This is because the calcium content of plants is largely genetically controlled. Although the Ca^{2+} concentration of the soil solution is frequently about 10 times greater than that of K^+, its uptake is usually lower than that of K^+. Capacity of plants for uptake of Ca^{2+} is limited because it can be absorbed only by young root tips in which the cell walls of the endodermis are still unsuberized.

Source of Soil Calcium. The calcium concentration of the earth's crust is about 3.64% and it is more common than most other plant nutrients. Soils vary widely in calcium content with extremely sandy soils of humid regions containing very low amounts of this nutrient. Its concentration in calcium carbonate free soils of humid temperate regions of the world normally ranges from approximately 0.7

to 1.5%. Highly weathered soils of the humid tropics may contain as little as 0.1 to 0.3% calcium. Calcium levels in calcareous soils vary from less than 1 to more than 25%. Values of more than approximately 3% indicate the presence of calcium carbonate.

The calcium present in soils, exclusive of that added as lime or in fertilizer materials, has its origin in the rocks and minerals from which the soil was formed. The plagioclase mineral, anorthite ($CaAl_2Si_2O_8$), is the most important primary source of calcium. Other minerals in this group, including impure albite, are of less significance. Pyroxenes (augite) and amphiboles (hornblende) are fairly common in soils and also contain calcium. Small amounts of calcium may also originate from biotite, epidote minerals, apatite, and certain borosilicates.

Calcite ($CaCO_3$) is often the dominant source of calcium in soils of semiarid and arid regions. Dolomite [$Ca,Mg(CO_3)_2$] may also be present in association with calcite. In some arid-region soils, calcium sulfate or gypsum ($CaSO_4{\cdot}2H_2O$) may be present. Calcium is liberated when these various minerals disintegrate and decompose.

The fate of released calcium is less complex than that of potassium. Calcium ions set free in solution may (1) be lost in drainage waters, (2) absorbed by organisms, (3) adsorbed onto surrounding clay particles, or (4) reprecipitated as a secondary calcium compound, particularly in arid climates. As far as is known, there is no conversion in the soil of calcium to a form comparable to fixed or slowly available potassium.

As a general rule, coarse-textured, humid-region soils formed from rocks low in calcium-containing minerals are low in their content of this element. Soils that are fine-textured and formed from rocks high in the calcium-containing minerals are much higher in their content both of exchangeable and total calcium. However, in the humid region even soils formed from limestones are frequently acid in the surface layers because of the removal of calcium and other basic cations by excessive leaching. As water containing dissolved carbon dioxide percolates through the soil, the carbonic acid so formed displaces calcium (and other basic cations) in the exchange complex. If considerable percolation of such water through the soil profile takes place, soils gradually become acid.

The calcium content of soils of the arid regions is generally high, regardless of texture, as a result of low rainfall and little leaching. Many of the soils of the arid regions actually have within their profiles secondary deposits of calcium carbonate or calcium sulfate.

Deficiencies of calcium leading to yield reductions are rather rare in agricultural soils, since most acid soils usually contain sufficient amounts of this nutrient for plant growth. More common are indirect calcium deficiencies caused by its shortage in fruit and storage organs which grow rapidly but with restricted internal supplies of calcium.

Behavior of Calcium in Soil. The calcium in acid, humid-region soils occurs largely in the exchangeable form and as undecomposed primary minerals. In most of these soils calcium, aluminum and hydrogen ions are present in the greatest quantity on the exchange complex. Like any other cation, the exchangeable and solution forms are in dynamic equilibrium. If the activity of calcium in the solution phase is decreased, as it might be by leaching or plant removal, there tends to be replacement from the adsorbed phase. Conversely, if the activity of calcium in the soil solution is suddenly increased, there tends to be a shift of equilibrium in the opposite direction, with subsequent adsorption of some of the calcium by the exchange complex.

In soils not containing calcite, dolomite, or gypsum, the amount of calcium in the soil solution is dependent on the amount of exchangeable calcium present. Soil

TABLE 8-14. Effect of Calcium Concentration and pH in Subsurface Nutrient Solution on Soybean Taproot Elongation in the Nutrient Solution

Experiment 2					*Experiment 3*		
pH	*Ca Concentration Added (ppm)*	*Taproot Elongation Rate * (mm/hr)*	*Taproot Harvest Length † (mm)*	*Oven Dry Wt/mm (mg)*	*pH*	*Ca Concentration Added (ppm)*	*Taproot Elongation Rate (mm/hr)*
5.6	0.05	2.66	461	0.20	4.75	0.05	0.11
	0.50	2.87	453	0.23		0.50	0.91
	2.50	2.70	455	0.32			
4.5	0.05	0.04	24	0.54	4.0	2.50	0.44
	0.50	1.36	270	0.26		5.00	1.26
	2.50	2.38	422	0.31			
LSD	5%	0.35	62				0.75
	1%	0.54	97				1.13

* Elongation rate during first 4 hr in solution.
† Harvested 7½ days after entering the solution.
Source: Lund, *Soil Sci. Soc. Am. J.*, **34**:457 (1970).

factors of the greatest importance in determining the availability of calcium to plants are the following:

1. Total calcium supply.
2. Soil pH.
3. Cation exchange capacity.
4. Percent calcium saturation of soil colloids.
5. Type of soil colloid.
6. Ratio of calcium to other cations in solution.

Total supply of calcium in very sandy acid soils with low cation exchange capacities can be too low to provide sufficient available calcium to crops. On such soils supplemental calcium will be needed to supply calcium, as well as to correct the acidity.

High H^+ activity occurring at low soil pH will impede calcium uptake. Lund of the USDA at Auburn University found in short-term split-root experiments that much higher calcium concentrations were required for soybean root growth as the pH was lowered from 5.6 to 4.0 (Table 8-14).

In acid mineral soils calcium is not readily available to plants at low base saturation. For example, a soil having only 2000 lb of exchangeable calcium per acre but representing a high degree of saturation of a low cation exchange capacity might well supply plants with more of this element than one containing 8000 or 9000 lb of exchangeable calcium per acre but saturating a lower percentage of a higher cation exchange capacity. The degree of calcium saturation is of considerable importance in this respect, for as the amount of this element held in the exchangeable form by soil colloids decreases in proportion to the total exchange capacity of the colloidal complex, the amount of calcium absorbed by plants decreases.

An exchange complex dominated by calcium is usually associated with higher crop yields. Many crops will respond to calcium applications when the degree of calcium saturation of the exchange capacity falls below 25%. High calcium saturation is indicative of a favorable pH for growth of most plants and for microbial activity. Also, a prominence of calcium will usually mean low concentrations of undesirable exchangeable cations such as Al^{3+} in acidic soils and Na^+ in sodic soils.

Calcium saturations of below 40 to 60% and aluminum saturations of 40 to 60% have lowered cotton yields. Soybeans are reported to suffer calcium deficiency at calcium saturations of 20% or less and aluminum saturations of 68% or more. Near normal growth of sugarcane in Hawaii is possible with 12% calcium saturation of exchange complexes in volcanic soils.

The type of clay influences the degree of calcium availability; 2:1 clays require a much higher degree of saturation for a given level of plant utilization than 1:1 clays. Montmorillonitic clays require a calcium saturation of 70% or more before this element is released sufficiently rapidly to growing plants. Kaolinitic clays, on the other hand, are able to satisfy the Ca^{2+} requirements of most plants at saturation values of only 40 to 50%.

Increasing aluminum concentration in the soil solution has been found to reduce calcium uptake by various plants, including corn, cotton, soybeans, and wheat. The depressing action of aluminum on rate of calcium uptake by wheat is evident in Figure 8-16. Evans and Kamprath at North Carolina State University showed that the concentration of aluminum in the soil solution of mineral soils is determined by the percent saturation of the effective cation exchange capacity with exchangeable aluminum. With organic soils, they observed that the amount of exchangeable aluminum rather than the percent saturation was more important in determining the amount of aluminum in the soil solution.

Calcium availability and its uptake by plants are also influenced by the ratios between calcium and other cations in the soil solution. A calcium/total cation ratio of 0.10 to 0.15 is desirable for development of cotton roots. Elongation of soybean taproots proceeded most satisfactorily when the Ca/(Ca + Mg + K) ratios in nutrient cultures were between 0.10 and 0.20. Blossom-end rot, a calcium-deficiency disorder in tomatoes, can be prevented by maintaining calcium/soil solution salt ratios in the range 0.16 to 0.20.

Form of Inorganic Nitrogen. While Ca^{2+} uptake is depressed by NH_4^+, K^+, Mg^{2+}, Mn^{2+}, and Al^{3+}, its absorption is increased when plants are supplied

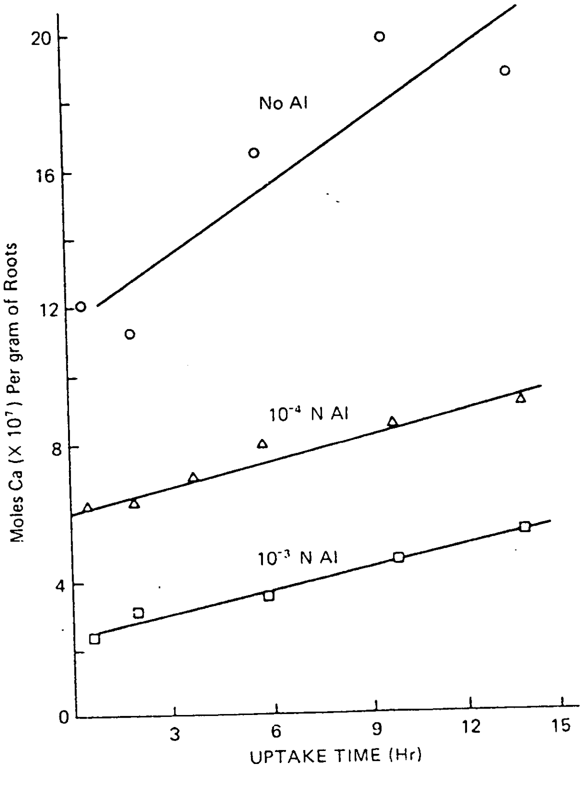

FIGURE 8-16. Influence of $AlCl_3$ on the rate of calcium uptake from 10^{-3}N $CaCl_2$ by excised wheat roots as determined by Ca^{45} measurements. [Johnson and Jackson, *Soil Sci. Soc. Am. J.*, **28**:381 (1964).]

with NO_3^--N. A high level of NO_3^- nutrition stimulates organic anion synthesis and the resultant accumulation of cations, particularly Ca^{2+}.

Leaching Losses of Calcium. Where leaching occurs, sodium is lost most readily from soil but the quantities of calcium lost are much greater. Calcium is often the dominant cation in drainage waters, springs, streams, and lakes. Leaching losses of calcium usually vary from 75 to 200 lb/A per year.

Plant Factors. Mention was made earlier of the restricted zone of calcium uptake at root tips. Conditions impairing the growth of new roots will reduce access of plant roots to calcium and thus induce deficiency. Also, problems related to inadequate calcium uptake are more likely to occur with plants that naturally have poor or small root systems than with those possessing more highly developed rooting systems.

Special attention must be given to the calcium requirements of certain crops, including peanuts, tomatoes, and celery, which are often unable to obtain sufficient calcium from soils supplying adequate calcium for most other crops. Proper calcium nourishment is also important for crops such as alfalfa, cabbage, potatoes, and sugar beets, which are known to have high requirements for this nutrient.

Calcium Fertilizers. Calcium is not normally formulated as such into mixed fertilizers but rather is present as a component of the materials supplying other nutrients, particularly phosphorus. Normal superphosphate and triple superphosphate contain 18 to 21 and 12 to 14% calcium, respectively. Calcium concentration in calcium nitrate is about 19%. Synthetic chelates such as CaEDTA contain approximately 3 to 5% calcium, while some of the natural complexing substances used as micronutrient carriers have varying calcium levels usually ranging from 4 to 12%.

The primary sources of calcium are the liming materials such as calcite, dolomite, hydrated lime, precipitated lime, and blast furnace slag which are applied to neutralize soil acidity. In situations where calcium is required without the need for correcting soil acidity, gypsum is a favorite source of calcium. Chelated calcium can also be foliarly applied to crops lacking this element but not suffering from soil acidity.

Gypsum ($CaSO_4 \cdot 2H_2O$) has been used as a fertilizer for a long time. It was applied in the early Greek and Roman times and was also used extensively in Europe in the eighteenth century. Deposits are found at several locations in the United States and Canada and in many other areas of the world. Large amounts of by-product gypsum are on hand as a result of the manufacture of phosphoric acid.

Gypsum is a source of calcium for peanuts in the United States and is applied directly to the plant in early bloom. In several African countries, for example, Nigeria, Senegal, and Upper Volta, the gypsum contained in the superphosphate applied to this crop is as valuable for its sulfur content as it is for calcium. Large acreages of soil in these countries are severely sulfur deficient. Gypsum has little effect on soil reaction, hence may have some value on crops that demand an acid soil, yet need considerable calcium. It is widely used on the alkali soils of the West. The calcium replaces sodium on the exchange complex, and the sodium sulfate is carried out in the drainage water. This replacement serves to flocculate the soil and make it more permeable to water.

Magnesium

Form Utilized by Plants. Magnesium is absorbed by plants from the soil solution as the ion Mg^{2+}. Like calcium, plant magnesium needs of plants in most soils can be satisfied by the amounts transported by mass flow. Lesser amounts

Liming Materials

The materials commonly used for the liming of soils are the oxides, hydroxides, carbonates, and silicates of calcium or calcium and magnesium. The presence of these elements alone does not qualify a material as a liming compound. In addition to these cations, the accompanying anion *must* be one that will reduce the activity of the hydrogen and hence aluminum in the soil solution.

The reaction mechanisms of liming materials with acid soils are complex. For most of the common liming materials to be described later these reactions begin with the neutralization of H^+ ions in the soil solution by either OH^- or SiO_3^{2-} ions furnished by the liming material. The basic reaction of a liming material when added to the soil can be illustrated with the case for calcium carbonate. In water, $CaCO_3$ behaves as follows:

$$CaCO_3 + H_2O \longrightarrow Ca^{2+} + HCO_3^- + OH^-$$

$$H^+(\text{soil soln.}) + OH^- \longrightarrow H_2O$$

The rate of the reaction above, and thus of the solution of $CaCO_3$, is directly related to the rate at which the OH^- ions are removed from solution. As long as sufficient H^+ ions are in the soil solution, Ca^{2+} and HCO_3^- ions will continue to go into solution. When the H^+ ion concentration is lowered, however, solution of the Ca^{2+} and HCO_3^- ions is reduced.

In acid soils, the concentration of the H^+ ions in solution is related to the hydrolysis of Al^{3+} or hydroxyaluminum or hydroxy-Fe^{3+} ions. Their hydrolysis in turn is influenced by the amount of clay and organic matter in the system. The continued removal of H^+ from the soil solution will ultimately result in the precipitation of the aluminum and iron ions and their replacement on the adsorption sites with calcium and/or magnesium and other basic cations. When the exchangeable aluminum and the hydroxyaluminum and hydroxy-Fe^{3+} have been precipitated as $Al(OH)_3$ and $Fe(OH)_3$, the soil acidity that remains arises from the other sources mentioned earlier in this chapter.

As the neutralization of soil solution H^+ by a material is necessary for it to be classed as a liming agent, gypsum ($CaSO_4{\cdot}2H_2O$) and other neutral salts cannot qualify as such. In fact, the addition of neutral salts will actually lower soil pH. Their addition, especially as in band placement, results in replacement of adsorbed Al^{3+} in a localized soil zone, sometimes with a significant lowering of the pH in this region.

Calcium Oxide. This is the only material to which the term *lime* may be correctly applied. Calcium oxide (CaO), known also as unslaked lime, burned lime, or quicklime, is a white powder, quite disagreeable to handle. It is manufactured by roasting calcitic limestone in an oven or furnace. The carbon dioxide is driven off, leaving calcium oxide. The purity of the burned lime depends on the purity of the raw material. This product is shipped in paper bags because of its powdery nature and its caustic properties. When added to the soil, it reacts almost immediately.

When unusually rapid results are required, either this material or calcium hydroxide should be selected. Complete mixing of calcium oxide with the soil may be difficult, however, for immediately after application absorbed water causes the material to form flakes or granules. These granules may harden because of the formation on their surfaces of calcium carbonate, and in this condition they may remain in the soil for long periods of time. Only by very thorough mixing with the soil at application time can this caking be prevented.

On a pound-for-pound basis, calcium oxide is the most effective of all the liming materials commonly employed, for the pure material has a neutralizing value or calcium carbonate equivalent (CCE) of 179%, compared with pure calcium carbonate. The full significance of this last statement will become apparent when the neutralizing value of the various materials is discussed.

Calcium Hydroxide. Calcium hydroxide [$Ca(OH)_2$] is frequently referred to as slaked lime, hydrated lime, or builders' lime. Like calcium oxide, it is a white, powdery substance, difficult and unpleasant to handle. Neutralization is rapidly effected, as it is with calcium oxide.

Slaked lime is prepared by hydrating calcium oxide. Much heat is generated, and on completion of the reaction the material is dried and packaged in paper bags. The purity of the commercial product varies, but the chemically pure compound has a neutralizing value of 136, making it pound-for-pound the second most efficient of the commonly used liming materials.

Calcium and Calcium-Magnesium Carbonates. The carbonates of calcium and magnesium occur widely in nature and in a number of different forms.

Crystalline calcium carbonate ($CaCO_3$) is termed calcite or calcitic limestone. Crystalline calcium-magnesium carbonate [$CaMg(CO_3)_2$] is known as dolomite when the calcium carbonate and magnesium carbonate occur in equimolecular proportions. In other proportions they are said to be dolomitic limestones. Metamorphism of these high-grade limestones produces marble. Deposits of high-grade limestone are widespread in the United States and Canada.

Limestone is most often mined by open-pit methods. First the overburden of soil and undesirable rock is removed, after which explosives are used to blast the exposed limestone. Blasting breaks out the rock, generally in sizes that can be accommodated by the quarrying and crushing equipment. The loosened material is crushed to sizes of 1 in. or less, and the limestone is ready for grinding and pulverizing. The pulverized material is classified by passing it through one or more screens of some specified size. This is required particularly of agricultural-grade limestone, specifications for which are quite rigid. Having been thus processed, it is generally stored in the open in piles and may be shipped either in bulk or in bags.

The quality of crystalline limestones depends on the degree of impurities they contain, such as clay. The neutralizing values usually range from 65 to 70% to a little more than 100%. The neutralizing value of chemically pure calcium carbonate has been established arbitrarily at 100%, and, theoretically, chemically pure dolomite may have a neutralizing value of nearly 109%. As a general rule, however, the neutralizing value or CCE of most agricultural limestones is between 90 and 98% because of impurities.

Marl. Marls are soft, unconsolidated deposits of calcium carbonate. They are frequently mixed with earth and usually quite moist. Marl occurs in many states in the eastern part of the United States and is easily mined. The deposits are generally thin, though the layers have been known to range up to 30 ft in thickness. Marl is recovered by dragline or power shovel after the overburden has been removed. The fresh material is stockpiled and allowed to dry before being applied to the land.

Marls are almost always low in magnesium. Their value as liming materials depends on the amount of clay they contain. Their neutralizing value usually lies between 70 and 90%, and their reaction with the soil is the same as that of calcite.

Slags. Several types of material are classed as slags, three of which are important agriculturally.

Blast-Furnace Slag. Blast-furnace slag is a by-product of the manufacture of pig iron. In the reduction of iron the calcium carbonate in the charge loses its carbon dioxide, and calcium oxide then combines with the molten silica to form a slag that is tapped off and either air-cooled or quenched with water. The cooled product is ground, screened, and shipped in open cars or trucks.

As a liming material, slag behaves essentially as calcium silicate. Metasilicic acid, which is formed when the slag is added to acid soils, is weakly dissociated, and the pH of the soil is raised. The neutralizing value of blast-furnace slags ranges from about 75 to 90%. These slags usually contain appreciable amounts of magnesium. Results of field tests indicate that, when applied on the basis of equivalent amounts of calcium and magnesium, they are just as effective in producing crops as ground limestones.

Basic Slag. A second type of slag is known as basic or Thomas slag and was discussed in Chapter 6. This slag is a by-product of the basic open-hearth method of making steel from pig iron, which, in turn, is produced from high-phosphorus iron ores. The impurities in the iron, including silica and phosphorus, are fluxed with lime and slagged off. The slag is cooled, finely ground, and usually marketed in 80- or 100-lb bags. In addition to its phosphorus content, basic slag has a neutralizing value of about 60 to 70%. It is generally applied for its phosphorus content rather than for its value as a liming material, but because of its neutralizing value it is a good material to use on acid soils. Its selection in relation to other sources of phosphorus is determined by economic factors.

Electric-Furnace Slag. A third type of slag results from the electric-furnace reduction of phosphate rock in the preparation of elemental phosphorus. The slag is formed when the silica and calcium oxide fuse, and the product is thought to be largely calcium silicate. It is drawn off and quenched with water. The slag is a waste product which is marketed at a low price and usually only within a limited radius of the point of production. It contains 0.9 to 2.3% P_2O_5 and is not ground. The neutralizing value ranges from 65 to 80%. Its reaction with the soil is similar to that indicated for blast-furnace slag.

Electric-furnace slags are also produced in the manufacture of pig iron and steel. They are comprised mainly of calcium and silica and may have neutralizing values as high as 89%. The results from a long-term growth-chamber experiment presented in Table 11-3 indicate that they are effective liming agents.

TABLE 11-3. Response of Red Clover to Kimberley Electric Furnace Iron Slag and Other Liming Materials

	*Yield (g) of Oven-Dry Tissue per Pot **					
	Alouette Silt Loam			*Pitt Silty Clay*		
Liming Treatment	*30% Base Satn.*	*60% Base Satn.*	*Means*	*30% Base Satn.*	*60% Base Satn.*	*Means*
Agricultural lime	1.55*a*	1.51*a*	1.53*a*	4.29*a*	4.49*a*	4.39*a*
Slag (broadcast)	2.03	2.28	2.16	4.42*a*	4.54*a*	4.48*a*
Slag (incorporated)	2.48	3.19	2.84	4.52*a*	5.02*a*	4.77*a*
Dolomitic limestone	2.25	2.66	2.45	4.04*a*	4.94*a*	4.49*a*
Magnesium carbonate	1.58*a*	1.13*b*	1.35	4.14*a*	3.28	3.71
Marl	1.58*a*	1.66*a*	1.62*a*	4.29*a*	4.64*a*	4.47*a*
Control (no liming)	1.10	1.10*b*	1.10	2.30	2.30	2.30
Mean	1.80	1.93	1.86	4.00	4.17	4.09

* Averaged over 10 harvests and five replicates. Any two means, within a given set of means, that have the same letter are not significantly different ($P < 0.05$) by the Duncan multiple range test.

Source: Beaton et al., *Can. J. Plant Sci.*, **48**:455 (1968).

Miscellaneous Liming Materials. Other materials that are used as liming agents in localized areas close to their source include fly ash from coal-burning power generating plants, sludge from industrial water treatment plants, Cotrell lime or flue dust from cement manufacturing, sugar lime, pulp mill lime, carbide lime, acetylene lime, packinghouse lime, and so on. These by-products contain varying amounts of calcium and magnesium compounds and other materials.

Neutralizing Value or Calcium Carbonate Equivalent of Liming Materials. Liming materials differ markedly in their ability to neutralize acids. The value of limestone for this purpose depends on the quantity of acid that a unit weight of the material will neutralize. This property, in turn, is related to the molecular composition of the liming material and its purity; in other words, its freedom from inert contaminants such as clay. Pure calcium carbonate is the standard against which other liming materials are measured, and its neutralizing value is considered to be 100%. Calcium carbonate equivalent (CCE) is defined as the acid-neutralizing capacity of an agricultural liming material expressed as a weight percentage of calcium carbonate.

The molecular constitution is the determining factor in the neutralizing value of chemically pure liming materials. Consider the reactions illustrated by the following equations:

$$CaCO_3 + 2HCl \longrightarrow CaCl_2 + H_2O + CO_2 \quad (1)$$

$$MgCO_3 + 2HCl \longrightarrow MgCl_2 + H_2O + CO_2 \quad (2)$$

In each of these equations the molecular proportions are the same; that is, one molecule of each of these carbonates will neutralize two molecules of acid. However, the molecular weight of calcium carbonate is 100, whereas that of magnesium carbonate ($MgCO_3$) is only 84. In other words, 84 g of magnesium carbonate will neutralize the same amount of acid as 100 g of calcium carbonate. How much more effective then is 100 g of magnesium carbonate than the same quantity of calcium carbonate in neutralizing an acid? This is demonstrated quite easily by the following simple proportion:

$$\frac{84}{100} = \frac{100}{x}$$

$$x = 119$$

Therefore, magnesium carbonate on a weight basis will neutralize 1.19 times as much acid as the same weight of calcium carbonate; hence its neutralizing value or CCE in relation to $CaCO_3 = 100$ is $1.19/1 \times 100$, or 119%. The same procedure is used to calculate the neutralizing value of other liming materials. The neutralizing values for several compounds are shown in Table 11-4. Their use makes

TABLE 11-4. Neutralizing Value (CCE) of the Pure Forms of Some Commonly Used Liming Materials

Material	*Neutralizing Value (%)*
CaO	179
$Ca(OH)_2$	136
$CaMg(CO_3)_2$	109
$CaCO_3$	100
$CaSiO_3$	86

possible the simplest and most straightforward comparison of one liming material with another in regard to neutralizing properties. These values are one guarantee which may be made for commercial liming agents. There are other methods of expressing the value of limestones, and these are discussed next.

Calcium Magnesium. The composition of liming materials is sometimes expressed in terms of the elemental content of calcium and magnesium. Chemically pure calcite, for example, contains 40% calcium and chemically pure magnesium carbonate contains (24/84)100, or 28.6% magnesium. Obviously, to convert the percentage of calcium to its calcium carbonate equivalent it is necessary to multiply by a factor of 2.5; and to convert the percentage of magnesium to the percentage of magnesium carbonate, it is necessary to multiply by a factor of 84/24, or 3.5. If a limestone carries the guarantee in terms of the element, it is a simple matter to calculate the percentage in terms of the carbonate to which the elemental percentage is equivalent.

Calcium and Magnesium Oxide Content. The quality of a limestone may also be expressed in terms of its calcium or magnesium oxide equivalent. As an example, pure calcite is 100% calcium carbonate and contains 40% calcium. Suppose that we wished to express these quantities, not in terms of either of the constituents, but rather in terms of the oxide (CaO). Calcium oxide has a molecular weight of 56, which means of course that 16 g of oxygen is combined with 40 g of calcium. Therefore, if the calcium present in calcium carbonate were expressed as the oxide, it would contain (56/100)100, or 56% calcium oxide equivalent. Thus to convert the percentage of calcium to percentage of calcium oxide, we need only to multiply the calcium by 56/40, or 1.4; and to convert the percentage of calcium carbonate to the percentage of calcium oxide, we have but to multiply the percentage of calcium carbonate by 56/100, or 0.56. Similar figures may be derived for the magnesium-containing limestones.

Total Carbonates. Another expression of the quality of limestones is that of total carbonates. This is a summation of the percentages of the carbonates contained in a given liming material. For example, assume that a limestone contains 78% calcium and 12% magnesium carbonate. The total carbonate content would be 90%.

Conversion Factors for the Various Methods of Expression. The conversion figures for a few transformations, such as the percentage of calcium to that of calcium oxide, have been given. It is on occasion desirable to convert the percentage of magnesium oxide or magnesium carbonate to the calcium carbonate equivalent. This is illustrated in the following example. Assume that a limestone contains this guarantee:

35% CaO

15% MgO

Assume further that we wish to express this analysis in terms of the calcium carbonate equivalent. The conversion may be obtained if it is remembered that 56 g of calcium oxide is equivalent to 100 g of calcium carbonate. The percentage of calcium oxide is multiplied by 100/56, and the calcium carbonate equivalent in this sample is 35% × 1.785, or 62.5%.

How is the conversion of magnesium oxide to calcium carbonate to be handled? A glance at their molecular composition shows that 1 mole of each will neutralize the same quantity of acid. A mole, or 1 gram molecular weight, of the magnesium oxide is 40, whereas that of calcium carbonate is 100. In other words 40 g of

TABLE 11-5. Limestone Conversion Factors

Percent	*Percent*		*Factor*
Ca	to CaO	multiply by	1.40
Ca	to $Ca(OH)_2$	multiply by	1.85
Ca	to $CaCO_3$	multiply by	2.50
Mg	to MgO	multiply by	1.67
Mg	to $Mg(OH)_2$	multiply by	2.42
Mg	to $MgCO_3$	multiply by	3.50
Mg	to Ca	multiply by	1.67
Mg	to $CaCO_3$	multiply by	4.17
MgO	to $CaCO_3$	multiply by	2.50
$MgCO_3$	to $CaCO_3$	multiply by	1.19

magnesium oxide will neutralize the same amount of acid as 100 g of calcium carbonate. Therefore, all that remains is to multiply the 15% magnesium oxide in the sample by the factor 100/40, or 2.5. The result, 37.5%, is added to the 62.5% and the total neutralizing value, or calcium carbonate equivalent, for the limestone in question is 100%.

Conversion factors which make possible an expression of the value of a limestone may be determined in any way desired, provided that the content of one of the constituents is given. A few of these factors are listed in Table 11-5. The student should be able to derive them as well as others not shown.

Fineness of Limestone

Molecular constitution and freedom from inert impurities are not the only properties that limit the effectiveness of agricultural limestones. The degree of fineness is equally important, because the speed with which the various materials will react is dependent on the surface in contact with the soil. Materials such as calcium oxide and calcium hydroxide are by nature powdery, so that no problem of fineness is involved, but the crystalline limestones are an entirely different matter.

When a given quantity of crushed limestone is thoroughly incorporated with the soil, its reaction depends upon the size of the individual particles. If they are coarse, the reaction will be slight, but if they are fine, the reaction will be extensive. This is strikingly illustrated by the data in Table 11-6. It is obvious that compared to the coarser fractions, the finely ground limestone reacts rapidly with soil. These results show very clearly a steady rise in the effectiveness of the coarser fractions relative to the <100 fraction with increased exposure period in soil. Also, these relative efficiencies based on change in soil pH are influenced by the magnitude of the pH change used for making the comparisons. The coarser fractions show higher efficiencies relative to the <100 fraction the lower the reference pH.

Amounts of a particular limestone fraction needed to produce a given rise in pH 2 years after application are shown graphically in Figure 11-5. Much less of the finer fractions than of the coarser fractions is needed to achieve a certain pH, particularly at lower reference pH values.

The data shown in Table 11-6 and Figure 11-5 indicate that finely divided agricultural liming materials will produce the most rapid upward adjustments in soil pH. However, the cost of limestone increases with the fineness of grinding. What is needed is a material that requires a minimum of grinding, yet contains enough fine material to effect a pH change rapidly. As a result, agricultural limestones contain both coarse and fine materials. Many states require that 75 to 100% of the limestone pass an 8- to 10-mesh screen and that 20 to 80% pass anywhere from an 8- to 100-mesh screen. In this way there is fairly good distribution of both the coarse and fine particles.

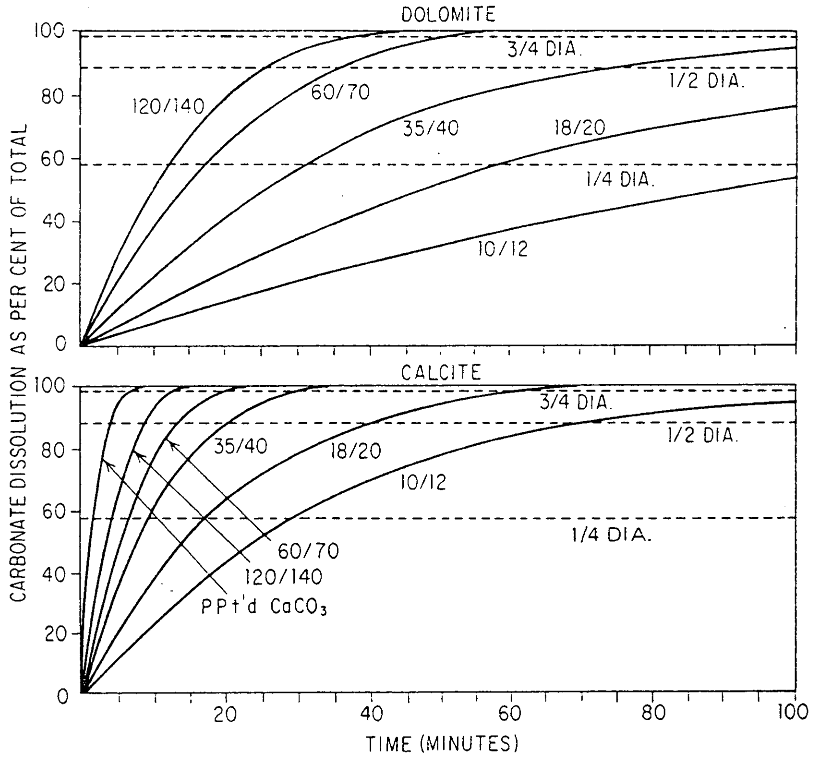

FIGURE 11-6. Reaction rates of separates of calcite and dolomite of different sizes in boiling 5 *N* NH_4Cl solution. [Shaw et al., *Soil Sci.,* **87**:262 (1959). Reprinted with permission of The Williams & Wilkins Co., Baltimore.]

Selection of a Liming Material

The quality of liming materials is determined by such properties as neutralizing value, magnesium content, degree of fineness, reactivity, and moisture content. Degree of fineness is widely recognized as a major factor in the selection of liming materials. In the United States, some states utilize a system in which particles remaining on a screen with 8 meshes to the inch are rated as totally ineffective and are given a fineness rating of 0. Particles passing through an 8-mesh sieve but collecting on a 60-mesh sieve are classified as 50% effective, while those passing through the 60-mesh sieve are considered to be 100% effective. The effectiveness factors used in Canada are 0 for particles retained on a No. 10 Tyler sieve, 40% for those which pass a No. 10 sieve but are retained on a No. 60 sieve, and 100% for those which pass a No. 60 sieve. These effectiveness ratings may not accurately represent the actual solubility of a material, but they do permit practical evaluations of the suitability of different materials.

The effective calcium carbonate (ECC) rating of a limestone or liming agent is the product of its calcium carbonate equivalent (purity) and the fineness factor. The latter is the sum of the products of the percentage of material in each of the three size fractions, specified earlier, multiplied by the appropriate effectiveness factor. Examples of two lime sources with different effective calcium carbonate contents are given in Table 11-8.

The magnesium content of limestone should also be considered. Many soils are deficient in this element, and the use of dolomitic lime is to be encouraged.

For limestones that are ground to meet local specifications and which contain roughly the same amount of magnesium, an excellent criterion of selection is the

TABLE 11-8. Fineness Effects on Effective Calcium Carbonate (ECC) Content of Two Lime Sources

	Solid Agricultural Lime	*Suspendable Lime*
Percent $CaCO_3$ equivalent	90	98
Sieve analysis		
% of 8-mesh sieve	2	0
% on 60-mesh sieve	21	2
% passing 60 mesh sieve	77	98
Calculated fineness factor		
% on 8-mesh × 0% effectiveness	2 × 0 = 0	0 × 0 = 0
% on 60-mesh × 50% effectiveness	21 × 50% = 11.5	2 × 50% = 1
% through 60-mesh × 100% effectiveness	77 × 100% = 77	98 × 100% = 98
Fineness factor (%)	88.5	99
Percent ECC = purity × fineness factor	90 × 88.5% = 79.6	98 × 99 = 97.0

Source: Murphy et al., in *Situation 1978, TVA Fert. Conf. Bull. Y-131,* Muscle Shoals, Ala.: National Fertilizer Development Center–Tennessee Valley Authority, 1978.

cost per unit of neutralizing value applied to the land, the calculation of which has already been covered. As indicated in Chapter 15, the returns per dollar spent on lime are phenomenal.

As a general rule, for the same degree of fineness, the material that costs the least per unit of neutralizing value applied to the land should be selected. Assume that there are available a calcitic limestone, CCE = 95%, and a dolomitic limestone, CCE = 105%, each with the same fineness or mechanical analysis. Assume also that they both cost $12 per ton applied to the land. Based on the neutralizing value, the first will cost 105/95 × 12 or $13.26 per ton, compared with the dolomite at $12 per ton. In addition, the dolomite supplies magnesium, which is a nutrient not overly abundant in many humid-region soils.

Whenever possible, some measure of the reactivity of the limestone, based on one of the rapid chemical methods, should be obtained. When not possible, the purchaser should be guided by the fineness of the material, its neutralizing value, its magnesium content, and the cost per ton applied to the land.

Use of Lime in Agriculture

Application of lime to acid soils in many areas of the United States and Canada produces striking increases in plant growth. The areas in the United States in which the need for liming is greatest are the humid regions of the East, South, and middle western and far western states. Soils in Canada requiring lime are confined mainly to areas of high precipitation in the Atlantic and central provinces plus the western province of British Columbia.

It is noteworthy that increasing soil acidity is a relatively new soil management problem in the inland Pacific Northwest region, which includes eastern Washington and northern Idaho. Soil acidity is also a recent problem in dryland agriculture of the Canadian prairie provinces and northeastern British Columbia, where a total of over 5.8 million acres of cultivated land have pH values of 6.0 or less.

Lime is seldom needed in those areas where rainfall is low and leaching is minimal, such as parts of the Great Plains states and the arid, irrigated saline and saline-alkali soils of the Southwest, intermountain, and far western states. This is also true for the majority of soils in the Prairie Provinces of Canada. However, the presence of lime can be helpful in the management of sodic soils.

When crop responses are obtained from the application of materials carrying the major plant nutrients, nitrogen, phosphorus, and potassium, it is assumed, and usually correctly, that the response was the direct result of overcoming a deficiency of one of these nutrient elements. Responses from the application of lime, however, may not always be attributed to the plant-nutrient value of the calcium or magnesium.

Direct Benefits. Aluminum toxicity is probably the most important growth-limiting factor in many acid soils, particularly those having pH levels below 5.0 to 5.5. Excess aluminum interferes with cell division in plant roots; fixes phosphorus in less available forms in soils and in or on plant roots; decreases root respiration; interferes with certain enzymes governing the deposition of polysaccharides in cell walls; increases cell wall rigidity by cross-linking with pectins; and interferes with the uptake, transport, and use of several elements (calcium, magnesium, and phosphorus) and water by plants. Thus it is not surprising that perhaps the greatest single direct benefit of liming acid soils is the reduction in the activity or solubility of aluminum and manganese. Both of these ions in anything other than very low concentrations are toxic to most plants. The poor growth of crops that is observed on acid soils is due largely to the large concentration of these two ions in the soil solution. When lime is added to acid soils, the activity of the aluminum and manganese is reduced and they are removed from solution. Table 11-9 illustrates the beneficial effect of liming an acid soil on growth of barley. It is readily apparent that the lime treatment raised soil pH while greatly reducing levels of extractable aluminum.

Not only are these ions toxic to plants, the presence of increasing amounts of aluminum in the soil solution also decreases the uptake of calcium and magnesium by plants. The restrictive influence of aluminum on calcium uptake by plants is demonstrated in Figures 8-16 and 11-7.

At pH 4.5 or less another benefit is the removal of H^+ toxicity, which damages root membranes and also is detrimental to the growth of many beneficial bacteria.

It has been found that different crops and even different varieties of the same crop will differ widely in their susceptibility to aluminum toxicity. Foy and his coworkers at the USDA found that different varieties of crops such as soybeans, wheat, and barley show wide ranges in their tolerance to high concentrations of aluminum in the soil solution. An example of this differential effect is shown in Figure 11-8.

Crops also vary in their tolerance to excessive amounts of manganese. For example, rapeseed or canola is very sensitive to manganese toxicity, while barley is more tolerant.

TABLE 11-9. Effects of Lime on Hudson Barley and on the pH and Level of Extractable Aluminum in Tatum Surface Soil

$CaCO_3$ Added (ppm)	*Yield of Barley Tops *,†(g/pot)*	*Soil Properties **	
		pH	*KCl-Extractable Al (meq/100 g)*
0	0.29 e	4.1	5.75
375	0.91 d	4.3	4.81
750	2.72 c	4.5	4.33
1,500	4.29 b	4.8	2.75
3,000	5.07 a	5.5	0.37

* Averages of three replications.

† Any two yields having a letter in common are not significantly different at the 5% level by the Duncan multiple range test.

Source: Foy et al., *Agron. J.*, **57**:413 (1965).

Indirect Benefits. Although the importance of calcium and magnesium in plant nutrition is not questioned, the scope of benefits derived from the application of lime where needed is much broader than would be expected from a simple response to the addition of a deficient nutrient element. Many of the indirect benefits have been covered in this text in conjunction with other topics. They are summarized here, however, and a few additional advantages are listed.

Effect on Phosphorus Availability. The relationship between the available soil phosphorus and the soil pH has been covered. At low pH values and on soils high in aluminum and iron, phosphates are rendered less available because of their reaction with these compounds. The addition of a liming agent to these soils will inactivate the iron and aluminum, thus increasing the level of plant-available phosphorus.

If the soil pH is greatly increased by the addition of excessive amounts of lime, phosphate availability will again be decreased because of precipitation as calcium or magnesium phosphates. A liming program should be planned so that the pH can be kept between 5.5 and 6.8 to 7.0 if maximum benefit is to be derived from the applied phosphate. As a usual practice, soils are not limed much above 6.5 because of the possibility of decreasing the availability of certain microelements, as discussed in a previous section.

Micronutrient Availability. The effect of soil pH on micronutrient availability was covered in Chapter 9. With the exception of molybdenum, the availability of the microelements increases with a decrease in pH. This can be detrimental because of the toxic nature of many of the elements in anything other than minute concentrations. The solubility of aluminum, iron, and manganese increases with increasing acidity. In addition to toxic effects, their presence may interfere with the absorption of calcium, magnesium, and other basic cations. The addition of adequate lime causes their inactivation, and soil at a pH value of 5.6 to 6.0 is usually most satisfactory from the standpoint of minimum toxicity and adequate availability of these elements. The effect of high pH on the availability of manganese and iron has been discussed.

Molybdenum nutrition of crops is improved by liming (see page 379) and deficiencies are infrequent in those soils limed to pH values in excess of 7.0. Because of the effect on availability of other micronutrients, liming to this value or above is not normally recommended for most crops in humid areas.

Nitrification. Most of the organisms responsible for the conversion of ammonia to nitrates require large amounts of active calcium. As a result, nitrification is enhanced by liming to a pH of 5.5 to 6.5. Decomposition of plant residues and breakdown of soil organic matter are also more rapid in this pH range than in more acidic soils. The effect of liming on both mineralization of organic nitrogen and nitrification is shown in Table 11-10. Application of lime just prior to incubation almost doubled the mineralization of organic nitrogen. However, lime added 1 or 2 years before sampling had little or no effect on release of mineral nitrogen in two of the soils. Adding lime at the start of the incubation improved nitrification, but the earlier field applications of lime had an even greater effect on nitrification in this laboratory experiment.

Nitrogen Fixation. The process of nitrogen fixation, both symbiotic and nonsymbiotic, is favored by adequate liming. With legumes, as was noted in Chapter 5, activity of some rhizobia species such as *R. meliloti* is greatly restricted by soil pH levels below 6.0 (Figure 5-2). Thus liming will increase the growth of legume plants because of the greater amount of nitrogen fixed and thereby return larger quantities of organic matter and nitrogen to the soil. With the nonsymbiotic, ni-

TABLE 11-10. Mineralization of Organic Nitrogen and Nitrification in Three Acid Soils Incubated Four Weeks With and Without Lime *

Soil	*Treatment*	*Organic N Mineralized (ppm)*	*Percent Nitrification*
Site 1 (pH 5.5, 0.20% soil N)	No lime	36a	8a
	Limed at start of incubation	61b	66b
	Limed 2 yr before in the field	33a	94c
Site 2 (pH 5.4, 0.13% soil N)	No lime	40a	7a
	Limed at start of incubation	72b	64b
	Limed 1 yr before in the field	44a	93c
Site 3 (pH 5.7, 0.83% soil N)	No lime	90a	28a
	Limed at start of incubation	177c	83b
	Limed 1 yr before in the field	134b	94c

* For each site, values not followed by the same letter are significantly different at $P = 0.05$.
Source: Nyborg and Hoyt, *Can. J. Soil Sci.*, **58**:331 (1978).

trogen-fixing organisms the greater fixation of atmospheric nitrogen taking place in adequately limed soils makes possible the more rapid conversion to humus of carbonaceous crop residues, such as those of corn and small grains. The increased level of soil nitrogen means a higher content of stable organic matter and a general increase in the fertility status of the land.

Soil Physical Condition. The structure of fine-textured soils may be improved by liming. This is largely the result of an increase in the organic matter content and to the flocculation of calcium-saturated colloids. Favorable effects of lime on soil structure include reduced soil crusting, better emergence of small-seeded crops, and lower power requirements for tillage operations. However, the overliming of Oxisols and Ultisols (liming in excess of that needed to neutralize the exchangeable aluminum) can result in the deterioration of soil structure with the consequent decrease in water percolation through such soils. This was mentioned in an earlier section of this chapter.

The presence of fine calcium carbonate particles is also known to improve the physical conditions of sodic soils. It appears that increased electrolyte concentration due to calcium carbonate dissolution is responsible for preventing clay dispersion and losses in hydraulic conductivity of such soils.

Disease. Correction of soil acidity by liming may have a significant role in the control of certain plant pathogens. An example of the beneficial effect of lime on reducing the harmful effects of clubroot is given in Table 11-11. Clubroot is a disease of cole crops which reduces yields and causes the infected roots to enlarge and become distorted. Lime does not directly affect the clubroot organism, but at soil pH greater than 7.0, germination of clubroot spores is inhibited.

On the other hand, liming will increase the incidence of diseases such as scab in root crops. Severity of take-all infection in wheat with resultant reductions in yield is known to be increased by liming soils to near neutral pH.

Application of Liming Materials

Placement. Since lime moves slowly in soils, its initial beneficial effects occur only in the immediate vicinity of application. Thus surface applications of lime without some degree of mixing in the soil are not immediately effective in correcting subsoil acidity. In several studies it was observed that 10 to 14 years were required for surface-applied lime to raise soil pH at a depth of 15 cm.

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Soils and Soil Fertility

8

Amending the Soil

Soil users who find their soils to be ideal for their needs are indeed fortunate. Usually they find that some of its characteristics are not ideal. What, then, should they do? One alternative is to use the soil in its nonideal state and accept the lowered productivity or other limitations that this imposes. Another alternative is to modify the soil in ways that make it more suitable for the intended use.

Soil modification may be aimed at some specific item of fertility such as supplementing the supply of one or more plant nutrients (Chapters 9 through 14) or it may be aimed at a more general change in the chemical and physical properties of the soil. The latter, termed *amending the soil,* is the subject of this chapter.

Some extreme cases where the soil is essentially remade are discussed in the latter part of this chapter. More generally, amending the soil involves the application of a number of tons per acre of some soil amendment to change the soil properties. Usually the direct effect is to change the soil pH. The indirect effect is to change a multitude of properties that vary with pH. Several indirect effects of pH on plant growth were discussed in Chapter 7.

Raising Soil pH

Most soils occurring in climates humid enough to grow large crops without irrigation have acid reactions (Figure 8.1). The acidity is caused by the leaching of bases by percolating water. The result is a lowered soil fertility and a less-than-ideal medium for the growth of most plants. Raising the soil pH to a reaction near neutral may be highly profitable in spite of the cost involved. This procedure is known as *liming.*

Liming will help maintain soil fertility if used in a well-managed cropping system; but in a poorly managed cropping system, liming acts as a stimulant, producing good crops immediately, followed by gradual impoverishment of fertility. An old, time-tested German expression illustrated the effect of lime used on soils without supplemental fertility practices: "Kalk macht die Vater reich aber die Sohne arm" (lime makes the fathers rich but the sons poor). Somewhat faster action but the same result are implied in another old saying: "Lime, and lime without manure, will make both farm and farmer poor." The effect of lime alone on yields is illustrated in Figure 8.2.

Liming and fertilization usually go together as complementary practices, at least in humid regions. Liming increases the usage of nutrients because more crop is harvested. Microbial activity is also favored by liming, and organic-matter decomposition is accelerated. The accelerated decomposition causes the organic-matter content of the soil to decline. Liming therefore increases the available plant nutrient supply for a time but decreases the future supply. That is why yields with liming are first higher but later lower than without liming. The lowering of yields in later years can usually be avoided by using fertilizer as well as lime. The decline in soil organic matter may be averted, or at least limited, if enough crop residues are returned to the soil from the increased production.

Fertilization often increases the need for lime. The ammonium form of nitrogen fertilizer is oxidized in the soil, and the nitrate form is produced. Ammonia is a base, but oxidizing it produces acids that lower the soil pH. An application of lime is usually required after an ammonium form of fertilizer has been used for a few years. Ammonia is

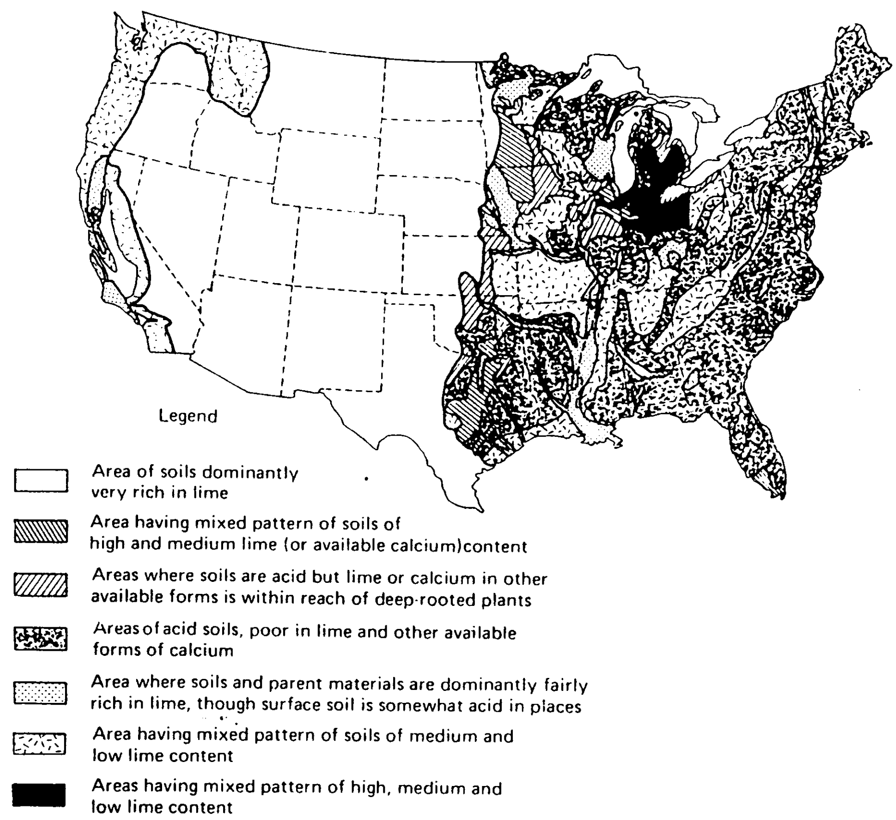

Figure 8.1. The relative lime content and acidity of the soils of the United States.

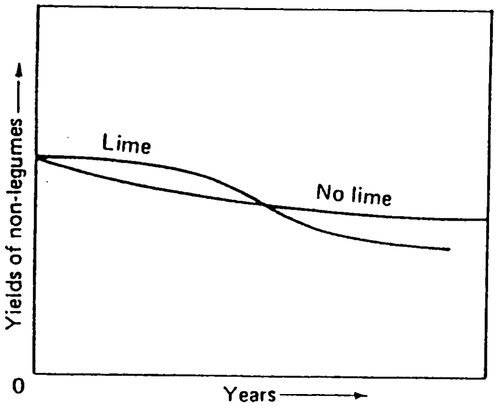

Figure 8.2. A schematic diagram showing the relative yields of limed and unlimed soils where organic matter is allowed to decline.

generally the cheapest nitrogen fertilizer, and so it is usually more economical to use ammonia and correct the acidity by liming rather than to avoid its use. Furthermore, even an organic nitrogen form such as urea acidifies the soil by the same process as ammonia.

Liming Materials

A satisfactory material for raising soil pH meets several requirements:

1. It should have a mild alkalizing (pH increasing) effect. The intent is to raise the pH to near optimum for the crop. The ideal material should have an action mild enough to cause no harm where an overdose is applied.

2. It should result in a desirable proportion of cations adsorbed on the cation-exchange sites. The added cations should be mostly Ca^{++}, although some Mg^{++} is good. Little or no Na^{+} should be included.
3. It should have a favorable effect on soil structure. The most favorable base for good soil structure is Ca^{++}.
4. It should not be too expensive.

Almost all liming material used is ground limestone rock (Figure 8.3) because it best meets the requirements. Limestone is mainly $CaCO_3$; dolomitic varieties contain some $MgCO_3$. The desired cations are supplied, and the carbonate anions cause no ill effects. The alkalizing effect is mild but effective. Few materials are cheaper or more abundant.

Some highly effective materials, such as Na_2CO_3, have too strong an alkalizing effect, supply the wrong cations, and are too expensive to be used as liming materials. Some materials, such as $CaCl_2$ and $CaSO_4 \cdot 2H_2O$ (gypsum), contain Ca^{++} but are neutral salts and have no alkalizing effect. Neutral calcium salts may be useful as calcium fertilizers on oxide clays where the pH is already satisfactory, but they are not considered to be liming materials.

The alkalizing effects of $CaCO_3$ and $MgCO_3$ are

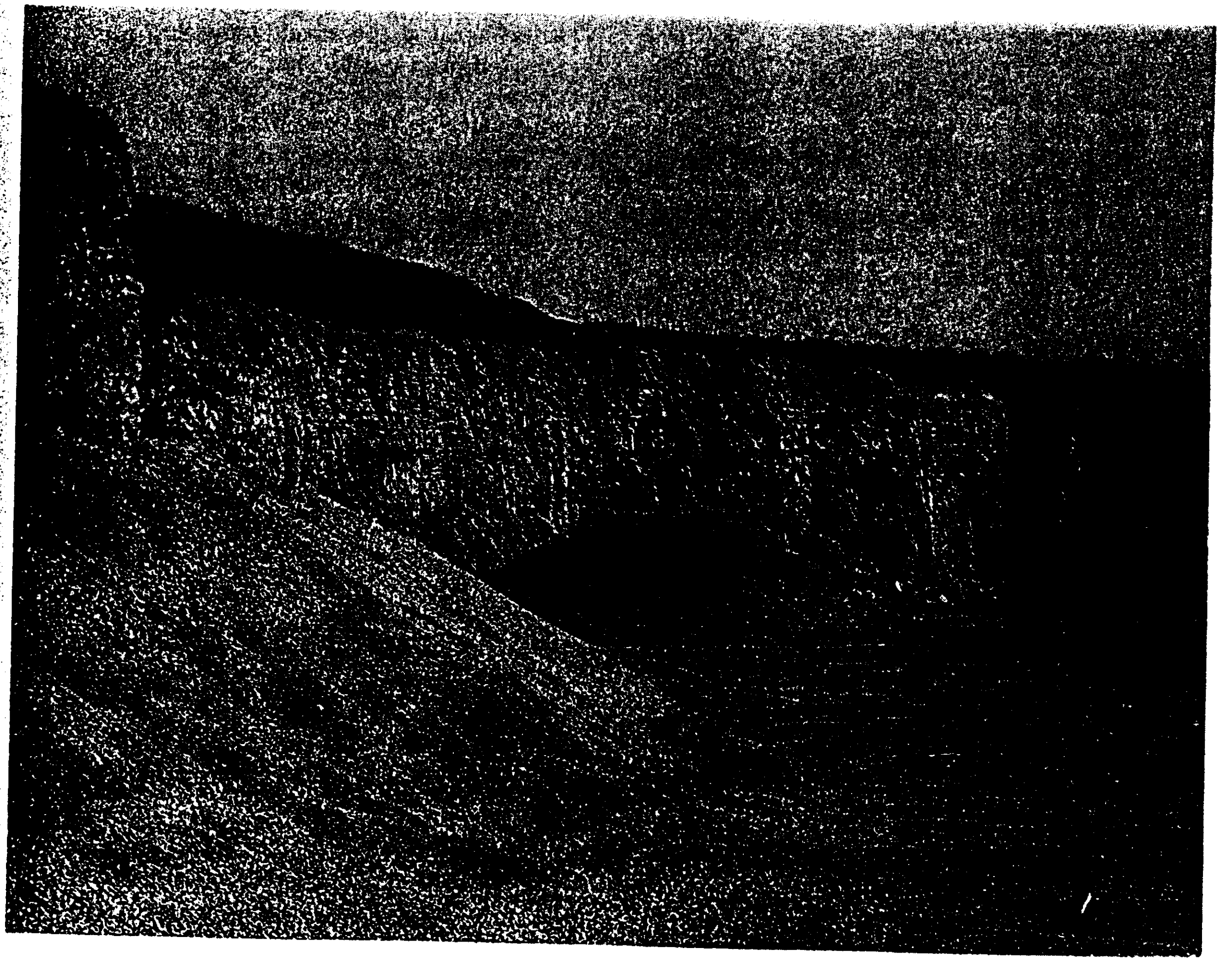

Figure 8.3. Limestone occurs in abundance under soils in many parts of the country. The ground limestone provides a cheap and abundant source of lime.

mild because they are slightly soluble salts of moderately strong bases and a weak acid. A much stronger alkalizing effect results from Na_2CO_3 because it is a highly soluble salt of a strong base and a weak acid. The effectiveness of $CaCO_3$ and $MgCO_3$ in spite of their mildness results from the escape of CO_2 gas permitting the reaction to go to completion:

$$\begin{matrix} H^+ \\ H^+ \end{matrix}\boxed{\text{micelle}} + CaCO_3 \rightarrow Ca^{++}\boxed{\text{micelle}} + H_2O + CO_2$$

Calcium Carbonate Equivalent

No two limestone deposits are alike nor are they equally effective in neutralizing soil acidity. Each material is therefore compared with pure $CaCO_3$ as a standard with an assigned value of 100 percent. Some impurities such as quartz are always present in limestone and reduce its equivalency. The presence of $MgCO_3$ in dolomitic limestone increases its equivalency because $MgCO_3$ has a lower molecular weight than $CaCO_3$; a gram of $MgCO_3$ therefore contains more molecules than a gram of $CaCO_3$. $CaCO_3$ has a molecular weight of 100. $MgCO_3$ has a molecular weight of 84. Therefore, a sample of pure $MgCO_3$ has a calcium carbonate equivalent of $100/84 = 1.19$, or 119 percent.

The use of dolomitic lime (that containing some $MgCO_3$) is particularly beneficial where magnesium deficiencies occur. Lime that contains one part $MgCO_3$ to about six parts $CaCO_3$ would provide the same ratio of Ca^{++} to Mg^{++} ions as commonly exists in highly productive unlimed soils.

Burned lime can be used instead of limestone where it is desirable to minimize weight. The heat drives off CO_2 and reduces the weight of 100 g of $CaCO_3$ to 56 g of CaO:

$$CaCO_3 \xrightarrow{\text{heat}} CaO + CO_2$$

The CaO reacts with water to produce $Ca(OH)_2$ (sometimes known as slaked lime):

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

The *calcium carbonate equivalent* (CCE) of CaO is $100/56 = 1.79$, or 179 percent. The calcium carbonate equivalents of other possible liming constituents such as MgO, $Ca(OH)_2$, $Mg(OH)_2$, and CaC_2 can be calculated from their molecular weights in similar fashion. Occasionally a source containing one or more of these compounds may be cheaper or easier to obtain locally than ground limestone. Examples of such sources are refuse lime, sugar-factory lime, water-softening-process lime, building (slaked) lime, blast furnace slag, marl, and oyster shells. However, the use of ground limestone as a liming material far exceeds all the others combined.

Effective Calcium Carbonate Equivalent

Limestone must be finely ground to be an effective liming material. The finer it is, the more quickly it reacts with the soil. Limestone pebbles over 5 mm in diameter will persist for so many years in the soil that they are ineffective for practical liming purposes; lime ground fine enough to pass through a 60-mesh sieve[1] will completely react with the soil within 3 years. Most ground limestones contain a range of particle sizes. A means of estimating the percent effectiveness of liming materials is illustrated below:[2]

Percent of material coarser than 4 mesh × 0 = 0% effectiveness
Percent of material between 4 and 8 mesh × 0.1 = % effectiveness
Percent of material between 8 and 60 mesh × 0.4 = % effectiveness
Percent of material finer than 60 mesh × 1.0 = % effectiveness

Total percent effective during first 3 years = % effectiveness

A sample of lime which all passes the 4-mesh sieve but of which 10 percent is retained on the 8-mesh sieve, 35 percent is retained on the 60-mesh sieve, and 55 percent passes through the 60-mesh sieve, gives 70 percent effectiveness during the first 3 years:

Coarser than 4 mesh	0% × 0 = 0%
Between 4 and 8 mesh	10% × 0.1 = 1%

Between 8 and 60 mesh 35% × 0.4 = 14%
Finer than 60 mesh 55% × 1.0 = 55%

Total percent effective
during first 3 years = 70%

The *effective calcium carbonate equivalent* (ECCE) or *effective neutralizing value* (ENV) depends on both the fineness and the chemical nature of the lime. If the above lime sample has a calcium carbonate equivalent of 90 percent, its ECCE is 63 percent (70 percent of 90 percent). The best way to determine the relative worth of liming materials for raising soil pH is to compare their ECCE values.

Farmers nearly always have to apply more lime than they would need of pure, finely ground $CaCO_3$. The ECCE value of the liming material permits them to calculate how much to apply. A farmer will need nearly 1,600 lb of the lime with an ECCE of 63 percent to equal 1,000 lb (or 1,600 kg to equal 1,000 kg) of pure, finely ground $CaCO_3$ (1,000 lb/0.63 = 1,587 lb).

Lime Requirement

The amount of lime needed depends on the crop, the soil, and the ECCE of the liming material. Crops differ in their needs, and there is not much reason to apply lime unless the crops to be grown in the next few years will respond. A compilation of relative yields obtained from various crops grown in Ohio at five different pH levels is shown in Table 8.1. All these crops did best at pH values near neutral (6.8 or 7.5 in these data), but there was a large difference in the sensitivity of the crops to lower pH values. Oats still produced 93 percent of their maximum yield at pH 5.0, whereas sweet clover would hardly grow at that pH.

Most legumes utilize large amounts of calcium and respond well to liming. Grasses usually obtain enough calcium for their needs even from acid soils. The main benefits of lime for grasses are through increased availability of nutrients other than calcium. A farmer growing continuous corn or wheat or some other cropping system without legumes may therefore have an alternative to liming. The farmer can supply additional nutrients as fertilizer, or else apply lime to make the nutrients that are there more available. The farmer can choose between lime and fertilizer or some combination of the two on the basis of costs and probable returns. The advantage usually swings toward more lime when there are legumes in the rotation.

Table 8.1. Relative Yields of Crops at Different Soil Reactions

	Average yields[a] at pH of				
Crop	4.7	5.0	5.7	6.8	7.5
Corn	34	73	83	100	85
Wheat	68	76	89	100	99
Oats	77	93	99	98	100
Barley	0	23	80	95	100
Alfalfa	2	9	42	100	100
Sweet clover	0	2	49	89	100
Red clover	12	21	53	98	100
Alsike clover	13	27	72	100	95
Mammoth clover	16	29	69	100	99
Soybeans	65	79	80	100	93
Timothy	31	47	66	100	95

[a] Highest yield shown as 100. All other yields are shown as percentages of the highest yield.

Certain plants are injured by the addition of lime. Such plants have frequently been called "acid-loving," but they are probably favored by the increased availability of certain nutrients, such as iron and manganese, rather than by the high concentration of H^+ ions at low pH. Table 8.2 shows a classification of plants according to probable response to the addition of lime on an acid soil. Certain berries and flowers may be injured by liming; strawberries and watermelons usually show no effect. By far the majority of plants show some degree of positive response to liming.

White potatoes thrive on soils high in lime, but so do the actinomycetes that cause potato scab. Potatoes tolerate acid soils, but the scab organism does not; an effort is therefore sometimes made to keep the soil acid for scab-free potatoes (the alternative is to grow a variety that resists scab). Ammonium fertilizers are particularly advantageous for potatoes susceptible to scab because of their acidifying effect.

With a few exceptions, such as those noted, farmers in humid regions need to apply lime from

13

Calcium, Magnesium, and Sulfur

Calcium, magnesium, and sulfur are macronutrients in plant nutrition. They are abundant elements and are usually present in soils in large enough amounts to meet the needs of plants. These elements are often called secondary nutrients and usually are not considered as fertilizer elements, though they may be present in fertilizers as components of the materials used to provide desired fertilizer elements. Large amounts of calcium, magnesium, and sulfur are added to the soil in fertilizers and in soil amendments even though they receive much less notice than nitrogen, phosphorus, and potassium.

The use of calcium and magnesium in the form of lime to raise the pH of acid soils was discussed in Chapter 8. The use of sulfur and sulfur compounds to lower pH was also discussed in Chapter 8. The presence of calcium and sulfur in nitrogen, phosphorus, and potassium fertilizers was pointed out in Chapters 10 to 12. These applications of soil amendments and fertilizers that incidentally contain calcium, magnesium, and sulfur undoubtedly eliminate many deficiencies that would otherwise require fertilization with these elements. Deficiencies may become more prevalent in the future because the percentages of calcium and sulfur in fertilizers have declined steadily in recent years, as shown in Figure 13.1. The trend has been to increase the analyses of N, P, and K, and to decrease the amounts of other elements present even if they are also plant nutrients such as Ca and S. Furthermore, efforts to reduce outputs of sulfur dioxide as an atmospheric pollutant may also decrease the sulfur supply and thus increase the future need for sulfur fertilizer.

Calcium

Calcium occurs in soils and plants as the divalent cation Ca^{++}. Some calcium minerals, such as calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$), have very low solubilities. These minerals are leached out of the sola of humid-region soils but remain in the sola of soils in arid regions.

Calcium also occurs in the minerals apatite, plagioclase, and hornblende. Calcium minerals weather slightly faster than the average soil minerals. There is therefore a tendency for the percent calcium in a soil to gradually decline as weathering and leaching progress. The data of Neilsen and Stevenson (1983) plotted in Figure 13.2 show the relative losses of calcium, magnesium, and potassium from a sandy soil in an apple orchard in Canada. The losses varied considerably from one year to another, but they were always in the sequence Ca>Mg>K. Also,

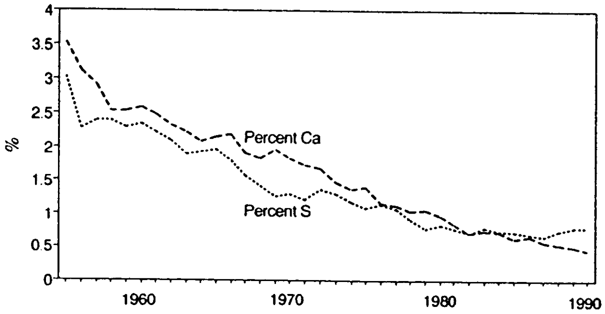

Figure 13.1. Average amounts of calcium and sulfur in ammonium sulfate, potassium sulfate, superphosphate, and triple superphosphate as percentages of the total amount of single-nutrient fertilizers applied in the United States from 1950 to 1990.

there was always more loss if the soil was tilled beneath the trees than if a grass cover was maintained. The overall average annual loss rates in this experiment were 387 kg Ca/ha, 118 kg Mg/ha, and 44 kg K/ha (345, 105, and 39 lb/ac, respectively). These authors considered it likely that these losses would ultimately lead to a magnesium deficiency and a calcium-potassium imbalance for the orchard. The losses of calcium and magnesium from the soils of humid regions would undoubtedly be much more rapid if Ca^{++} and Mg^{++} ions were not strongly attracted to cation-exchange sites.

Calcium in Soils

Calcium may constitute more than 5 percent of the weight of a saline soil in an arid region or as little as 0.01 percent of the weight of a soil in the humid tropics. Most soils of humid temperate regions contain about 1 to 2 percent Ca. This amount is roughly the same as their potassium contents.

Very low calcium contents occur in highly leached soils with low cation-exchange capacities. This includes some tropical soils—those that contain mostly oxide clays. Ritchey, Silva, and Costa (1982) reported that the soil survey in central Brazil located several Oxisols with less than 0.2 meq of exchangeable Ca plus Mg per 100 g of soil. Root growth and crop yields were restricted on these soils, but both were normalized where a calcium fertilizer was added. Such low calcium contents are unlikely to be found in temperate regions except possibly in very acid, sandy soils. The temperate region soils will almost certainly need calcium in the form of lime to raise the soil pH long before they need it as a fertilizer.

Calcium usually represents 75 to 85 percent of the total exchangeable bases present in temperate region soils. Most soils contain between 200 and 10,000 lb/ac (or kg/ha) of exchangeable calcium in the plow layer. The exchangeable calcium is in equilibrium with the few pounds of dissolved calcium present in the soil solution, even though there is likely to be 1,000 times as much exchangeable calcium as dissolved calcium in the soil.

The great concentration of calcium on cation-exchange sites is a result of the comparatively small hydrated size of the Ca^{++} ion relative to its +2 charge. The charge concentration causes a preferential adsorption of Ca^{++} ions over other ions that are likely to be present. Preferential adsorption is strong

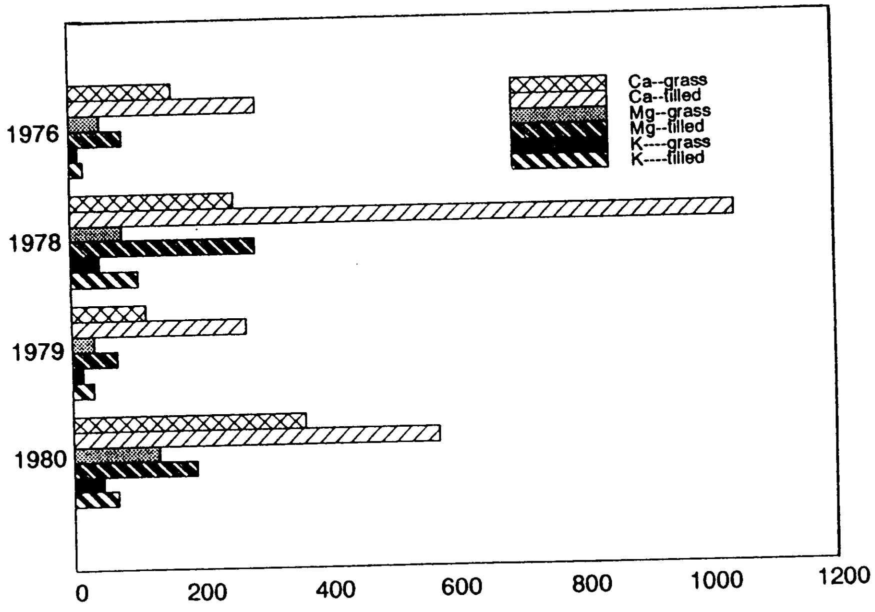

Figure 13.2. A comparison of the amounts of calcium, magnesium, and potassium leached in 4 different years from a sandy soil with and without grass cover in an apple orchard in Canada. (*Neilsen and Stevenson, 1983*)

in clays such as montmorillonite that have high cation-exchange capacities and is less pronounced in clays such as kaolinite that have low cation-exchange capacities. Calcium adsorption is highest in humus (Naylor and Overstreet, 1969) because humus has a high cation-exchange capacity and because some of the Ca^{++} ions may be chelated by organic compounds present in humus (chelates are organic materials that can enclose metallic cations; they will be discussed in Chapter 14).

The exchangeable calcium in a soil has an important relationship to soil pH and to the availability of several nutrient elements. The amounts of calcium and other basic cations present in a soil decline as a soil becomes more acid and increase as it becomes more alkaline. An excess of calcium causes calcium carbonate to precipitate and buffer the pH to a value near 8. Excess calcium usually results in low solubility of phosphorus, iron, manganese, boron, and zinc, and sometimes causes deficiencies of one or more of these essential plant nutrients.

Calcium, like other nutrients, becomes depleted in the zone immediately surrounding growing plant roots, as shown if Figure 13.3. This depletion apparently results from the withdrawal of soil water from the same zone. The concentration of calcium in the soil water remaining near the root actually increases slightly (Brewster and Tinker, 1970). The same is true of magnesium and sodium concentrations in the soil water but is not true for potassium. Plants absorb potassium so rapidly that its concentration in solution near a growing plant root drops to less than half of the original concentration.

One conclusion that can be reached from the above information is that more than one type of transport mechanism is involved in moving ions to plant roots. Potassium ions move to the root much faster than does the soil water; diffusion therefore appears to be the dominant transport mechanism for potassium. Calcium, magnesium, and sodium ions move to the plant roots slightly slower than does the soil water unless the humidity is high enough to slow the rate of transpiration (Elgawhary, Malzer, and Barber, 1972); mass flow therefore appears to be the dominant transport mechanism for them.

Calcium dissolved in the soil solution can move by mass flow and by diffusion, but exchangeable calcium has a very low mobility. Wadleigh (1957) reported that plant roots will not enter soil layers that are devoid of calcium even though other conditions are favorable for growth and calcium is available in other layers. Monovalent ions such as Na^+ and K^+ are more mobile because they are less strongly attracted to cation-exchange sites than are Ca^{++} ions.

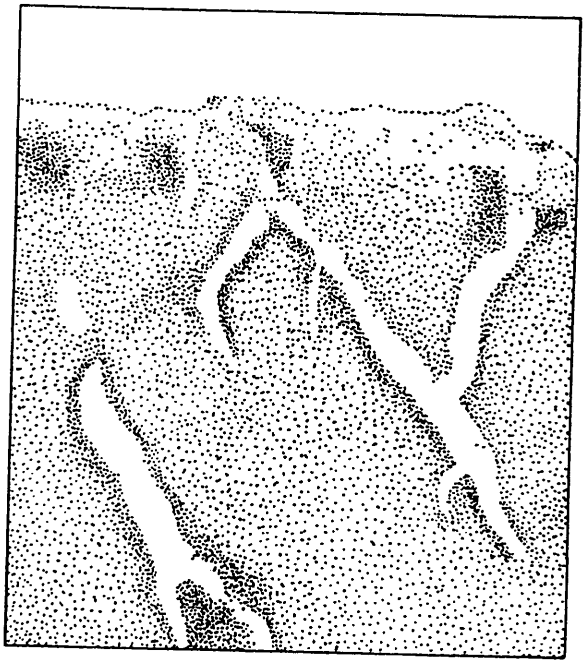

Figure 13.3. Calcium-45 depletion around wheat roots. Dark areas represent calcium-45 in soil or plant. Lighter areas represent regions from which calcium-45 has been depleted by plant growth. *(Based on Wilkinson, Loneragan, and Quick, copyright 1968 by the American Association for the Advancement of Science)*

Calcium in Plants

Calcium is a structural component of cell walls and is therefore vital in the formation of new cells. Furthermore, calcium is so integrated into cell walls that it cannot be removed from old cells to form new cells (Loneragan and Snowball, 1969). Plants deficient in calcium are stunted because they produce fewer and smaller cells. They have weak stems because their cell walls are thinner than normal. Rangnekar (1974) showed that substitution of potassium for all the calcium in the nutrient solution of 24-day-old tomato seedlings began to limit their growth rate after only 4 days and halted growth in about 10 days (Figure 13.4).

A calcium shortage restricts the growth of roots as well as that of stems, leaves, and other parts. The inability of calcium-deficient roots to elongate rapidly handicaps the plant for exploiting new portions of the soil volume to obtain water and nutrients. Miller, Peverly, and Koeppe (1972) found that an increased calcium supply stimulated the uptake of phosphorus by corn roots. Restricted root growth could produce or aggravate other nutrient deficiencies as well.

The amount of calcium required to promote good root growth increases under a variety of adverse conditions. Gerard (1971) found that high soil temperatures increased the calcium needs of pea and cotton roots and that the high osmotic concentrations of saline soils also increased calcium needs. A study of cotton roots showed that salinity reduced the uptake of calcium enough to require 140 h instead of 70 h to form thick cell walls (Gerard and Hinojosa, 1973).

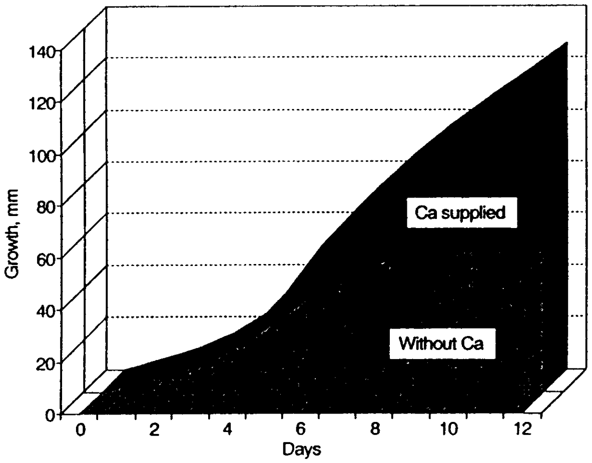

Figure 13.4. The growth rates of tomato seedlings following 24 days of age with half of them deprived of calcium during this growth period. (*Based on data of Rangnekar, 1974*)

Calcium supplies are smaller in acid soils than in alkaline soils. Part of the peril of aluminum toxicity is related to calcium deficiency. The amount of calcium needed to promote good root growth was found by Lund (1970) to depend on the concentration of aluminum in solution.

Calcium is normally abundant in plant leaves. A calcium deficiency prevents the growth and unfolding of new leaves. It also prevents the growth of the margins of existing leaves, which results in curled leaves.

The amount of calcium utilized by plants differs greatly from one plant to another. Table 13.1 shows that legumes use much more calcium and magnesium than do plants of the grass family. Legumes usually respond very favorably to the liming of acid soils.

It was shown in Table 12.6 that legumes utilize nearly equal amounts of calcium and potassium but corn and oats utilize several times as much potassium as calcium. The data indicate that divalent cations (Ca^{++} and Mg^{++}) carry most of the positive charges absorbed by legumes and monovalent cations (K^+ and Na^+) carry most of the positive charges absorbed by other plants. Most of the calcium in fertilizers is associated with phosphorus compounds and is applied for the benefit to be derived from the phosphorus. Apatite and ordinary superphosphate contain over twice as much calcium as phosphorus. Triple superphosphate, however, contains only about two-thirds as much calcium as phosphorus, and the ammonium phosphates contain no calcium at all. An

Table 13.1. Average Amounts of Calcium and Magnesium in Legumes and Nonlegumes (in dry plant materials)

Crop	Calcium (g/1000g)	Magnesium (g/1000g)	Ca:Mg ratio
Legumes			
Alfalfa	13.91	3.55	3.8:1
Red clover	11.42	2.70	4.2:1
Soybeans	12.29	3.88	3.2:1
Nonlegumes			
Corn	2.24	0.86	2.6:1
Oats	1.65	0.98	1.7:1
Wheat	1.45	0.87	1.7:1

Source: Compiled from several sources.

increasing reliance on these latter materials for phosphorus needs has greatly reduced the calcium content of the average fertilizer in the United States (as was shown in Figure 13.1).

Calcium Fertilizers

Lime ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$) are the two materials most likely to be considered if and when specific needs for calcium fertilizer are identified. Ordinary superphosphate could also serve; 70 percent of its calcium is in the form of gypsum. Lime is appropriate if it is advisable to raise the pH. Gypsum can be used if a neutral salt is desired. The neutral effect of gypsum might very well be desired for a tropical soil with a low buffer capacity resulting from a low cation-exchange capacity.

Magnesium

The magnesium ion, Mg^{++}, is chemically similar to the calcium ion, Ca^{++}. Nevertheless, there are important differences in the behavior of these ions in minerals and plants.

The nonhydrated Mg^{++} ion is small enough to fit into octahedral spaces in mineral structures, whereas the Ca^{++} ion requires larger spaces. Magnesium in igneous rocks is closely associated with the iron-containing (ferromagnesium) minerals such as olivene, various inosilicates, and biotite mica. It occurs in sedimentary rocks as a component of the mineral dolomite ($CaCO_3 \cdot MgCO_3$).

None of the magnesium minerals mentioned are as resistant to weathering as are the feldspars, quartz, and hydrous oxides. Soils tend to be depleted of magnesium minerals somewhat sooner than they are depleted of the more resistant potassium, sodium, and calcium minerals. Magnesium's association with iron ends when the iron is oxidized from ferrous (Fe^{++}) to insoluble ferric (Fe^{+++}) compounds and the magnesium is leached away.

Magnesium in Soils

Finer particles contain more magnesium than coarser particles. Mokwunye and Melsted (1973) tested nine temperate and tropical soils and found the following distribution of magnesium in the soil separates: clay, 51 to 70 percent of the total magnesium present; silt, 22 to 42 percent; and sand, 0.1 to 11 percent. They found that severe weathering, soil erosion, and clay eluviation all tend to reduce the magnesium content of surface soil horizons. Magnesium can be released equally well from either the silt or the clay fraction and even the interlayer magnesium and lattice structure magnesium are partly available to plants (Christenson and Doll, 1973).

Exchangeable magnesium is the largest source of available magnesium in soils. Magnesium ions behave more like calcium ions when they are in the soil-solution cation-exchange complex than when they are in minerals or plants. From 12 to 18 percent of the exchangeable bases are normally Mg^{++} ions, an amount that is second only to the 75 to 85 percent represented by Ca^{++} ions. The Mg^{++} ion hydrates to form a larger ion than the Ca^{++} ion, and therefore is adsorbed less strongly by the cation-exchange complex. Other consequences of this hydrated-size relationship are that a soil high in magnesium disperses more readily, is less permeable, and is likely to hold more water than a similar soil that is higher in calcium (Girdhar, Yadav, and Shukla, 1982). Magnesium excess is indicated when exchangeable Mg^{++} represents more than 40 to 60 percent of the cation-exchange capacity; magnesium deficiency is indicated by less than 3 to 8 percent exchangeable Mg^{++} (Martin and Page, 1969). Some highly leached soils are near the deficiency level and require magnesium fertilization. Lombin and Fayemi (1975) anticipate serious magnesium deficiencies in Nigeria in the future. Moore and Patrick (1989) suggest that calcium and magnesium deficiencies for rice production may be occurring in acid sulfate soils in southern United States.

The percentages of Ca^{++} and Mg^{++} ions in the soil solution are much lower than on the cation-exchange sites. Preferential adsorption of the double-charged ions is so strong that their concentrations in solution are reduced to about the same level as the concentrations of K^+ and Na^+ ions. Potassium fertilization on low-magnesium soils, combined with preferential adsorption of Mg^{++} by cation exchange and preferential absorption of K^+ by plants, can

Table 74. Influence of Fungi on Soil Aggregation (from Swaby)

Aggregation	Mean Weight of Aggregates, >1 Mm/50 Gm Soil	Total Number of Strains	Growth on Agar, Number of Strains	
			Woolly	Prostrate
	gm			
Excellent	37–45	21	18	3
Very good	29–37	15	10	5
Good	21–29	11	3	8
Fair	13–21	3	0	3
Totals		50	31	19

Soil Inoculation

It often becomes necessary to introduce into the soil bacteria and certain other microorganisms that may be lacking there. Among these, root-nodule bacteria occupy a pre-eminent place, as brought out previously. At first, soil in which the legume was grown successfully was used for inoculation. Soon after, however, artificial cultures in liquid and solid media were substituted for the soil. In recent years, peat material has been utilized as a carrier for legume bacteria.

Although soils in which legumes have once grown contain for some time the organisms responsible for formation of nodules on the corresponding plants, it was found that these bacteria may deteriorate in the soil, either by loss of vitality or through the effect of antagonistic microorganisms. It may, therefore, become advisable to inoculate a soil frequently for a certain legume. The existence of various strains of bacteria, which vary greatly in activity, the formation of bacteriophages active against the specific bacteria, and the potential effect of antibiotics produced by other microorganisms lead more and more to recognition of the importance of repeated inoculation of soils with vigorous cultures of organisms.

On a much smaller scale, but of potential importance, are the mycorrhiza fungi. These are capable of producing associations with various higher plants, notably certain evergreens, resulting in increased plant growth. It has been found advisable to inoculate nursery beds with a small amount of soil from an old bed in which the corresponding trees have been grown successfully. So far, no pure cultures of fungi have been utilized for this purpose. In certain soils, however, it seems to have been established beyond doubt that the presence of fungi is essential for normal tree development.

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In addition to these two groups of microorganisms—the legume bacteria and mycorrhiza fungi—it has also been found that occasionally inoculation of soils with other organisms may result in increased plant growth. Among these organisms, it is sufficient to mention the nitrifying bacteria, sulfur-oxidizing bacteria, bacteria pathogenic to Japanese beetles or other insects, and nematodes parasitic upon insects or destructive to other injurious nematodes. In some cases the advisability of microbial inoculation of soil is questionable, unless accompanied by certain soil treatments. This is true of the use of certain saprophytic fungi which are believed to act as a check upon the development of pathogenic fungi, of fungi for improving soil structure, and of "all-soil inoculants" (Azotogen).

Fig. 130. Ectotrophic mycorrhiza developing on roots of *Pinus sylvestris* (from Melin).

Enrichment of the soil with organisms not present there originally may lead to development of antagonists, which bring about the destruction of the introduced bacteria.

Modification of Soil Reaction and Microbiological Activities

There is no one particular reaction which is favorable alike to all groups of soil microorganisms. When the soil is acid, especially at a reaction less than pH 6.0, it may become injurious to the growth of many bacteria, notably the nitrifying and the nitrogen-fixing types, and favorable to the development of fungi. This may be because the competition of the bacteria for the available nutrients in the soil is repressed by increased acidity. On the other hand, a less acid or slightly alkaline reaction of the soil may become unfavorable to the development of fungi and have a favorable effect upon many of the soil bacteria. Thus, when conditions are made unfavorable to the development of one group of organisms in the soil, another group may be favored.

Addition of calcium carbonate to an acid soil was found to stimulate greatly the multiplication of bacteria, accompanied by an increase in the decomposition of the soil organic matter. This is shown in Table 75. Addition of excess calcium carbonate and especially of magnesium carbonate, however, may become injurious to many of the soil bacteria.

TABLE 75. INFLUENCE OF $CaCO_3$ ON EVOLUTION OF CO_2 FROM SOIL (from König)

$CaCO_3$ Added	CO_2 Evolved per Day
per cent	*mg*
0	181.3
0.04	223.6
0.10	308.4
0.20	416.4
0.40	455.4

EFFECTS OF CULTIVATION AND FERTILIZATION

Cultivation of soil, which results in conservation of the soil moisture, is favorable to the development of various groups of microorganisms. It brings about an increased production of nitrate because of improved soil aeration. By favoring the development of aerobic organisms, cultivation stimulates greater decomposition of the organic matter, leading to increased carbon dioxide evolution and greater liberation of the nitrogen as ammonia. This explains the favorable effect of fallowing upon the activities of the soil microbiological population. The "ripening" of soil in spring is a result of treatments that are favorable to the activities of soil microorganisms.

TABLE 76. INFLUENCE OF TILLAGE UPON ABUNDANCE OF BACTERIA IN SOIL (from Chester)

Numbers in thousands per gram.

Period of Time	Bacteria
At start	2,040
After 7 days	5,495
After 9 days	6,171
After 14 days	11,326
After 24 days	12,600

Fertilization and crop rotation also have an important effect upon the microbiological population. The nature of the fertilizer, the residual effect upon the reaction of the soil, the nature of the crop grown, and the treatment of the crop will influence in one way or another the nature and abundance of microorganisms of the soil. This is true especially of the addition of available energy in the plant residues, the excretion by plants of substances favorable to microbial development, the increase in soil nutrients, and the improvement in the buffering capacity and physical condition of the soil.

MICROORGANISMS AND PLANT GROWTH

Plants and microorganisms exert numerous effects upon one another. Plants supply to the microorganisms most of the energy and nutrients in the form of the numerous residues in the roots and stubble. They also secrete soluble substances which affect in various ways the growth of microorganisms. Plants control the chemical composition of the soil solution, thus modifying the nature of the medium in which most of the activities of microorganisms take place. By removing some of the nutrients from the soil, plants may exert an injurious effect upon the growth of microorganisms, or may actually compete with them for some of these nutrients. Plant roots influence the structure of the soil and bring about an improvement in soil aeration, thus affecting greatly the growth of microorganisms.

Microorganisms, in their turn, exert numerous influences upon the growth of higher plants. By decomposing the plant and animal residues in the soil, thus bringing about their mineralization, microorganisms liberate the nutrients required for plant growth, especially the carbon dioxide, nitrate, phosphate, and sulfate. The symbiotic nitrogen-fixing bacteria, through their association with the roots of leguminous plants, effect the fixation of large quantities of nitrogen. Plants and microorganisms form a variety of other symbiotic associations, designated as mycorrhiza (roots and fungi) and bacteriorrhiza (roots and bacteria). Although the importance of mycorrhiza in plant development has been definitely established, the effect of the bacteriorrhiza formations is still under discussion.

Various microorganisms are believed to produce plant-growth-stimulating substances, including vitamins and hormones. Although this is still open to debate, the fact remains that plants may benefit considerably from addition of certain hormones and vitamins to the soil. To what extent bacteria and other organisms are responsible for the production of such substances has not been established as yet. There is no doubt, however, that addition of organic matter, especially stable manures, to the soil results in favorable effects upon plant growth, which cannot be ascribed to the mere inorganic fertilizer constituents of the manure. The favorable action, resulting from decomposition of the organic residues, upon plant growth must be definitely ascribed to the activities of microorganisms.

TABLE 77. INFLUENCE OF PLANT DEVELOPMENT UPON THE ABUNDANCE OF MICROBES AND THEIR ACTIVITY IN SOILS AT DIFFERENT DISTANCES FROM THE PLANT ROOTS *
(from Starkey)

Plant	Region of Sampling	Bacteria *millions*	Actinomycetes *millions*	Fungi *thousands*	CO_2 Formed *mg*
Bean	15 inches from main roots	18.6	7.6	24.6	9.7
Bean	9 inches from main roots	32.8	10.0	21.6	12.0
Bean	3 inches from main roots	36.2	8.0	20.0	12.0
Bean	Close to main roots	55.4	6.2	19.2	15.1
Bean	Superficial layer of the roots	199.4	12.6	55.2	
Beet	15 inches from main root	18.6	10.0	25.8	11.2
Beet	9 inches from main root	27.0	11.4	25.0	13.6
Beet	3 inches from main root	33.4	10.4	25.8	14.9
Beet	Close to main root	57.4	6.8	30.0	18.2
Beet	Superficial layer of the roots	427.4	10.6	156.0	
Corn	15 inches from main root	22.8	8.4	29.6	10.3
Corn	9 inches from main root	26.2	11.8	23.2	15.2
Corn	3 inches from main root	44.8	8.8	29.6	15.2
Corn	Close to main root	93.2	10.2	49.6	25.0
Corn	Superficial layer of the roots	653.4	8.6	278.0	

* Age of plants, 113 days.

The effect of antibiotics produced by microorganisms upon plants is another debatable question. Certain compounds, like actinomycin and clavacin, are formed in artificial media by soil-inhabiting microorganisms. These compounds have a toxic effect upon plant growth, resulting in a type of wilting. The question remains, however, to what extent these substances are produced in the soil itself and how their activities are modified by the inorganic and organic soil colloids.

SOIL POPULATION AS A WHOLE

The numerous interrelationships existing in the soil between plants and microorganisms, on the one hand, and between soils and microorganisms, on the other, demonstrate the manifold activities of the extensive microbiological population inhabiting the soil. These microorganisms are responsible for numerous chemical reactions taking place in the soil. The organisms do not exist and multiply in the soil in a fixed manner. Their growth and activities are constantly modified, depending upon the nature of the soil, its treatment, the crop grown, and various changes in environmental conditions. The microbiological population of any soil, at a given moment, may be in a state of equilibrium. Any modification of this equilibrium will bring about a marked change, both in qualitative composition and in quantitative interrelations, among the constituent members of this population.

Under natural conditions, modifications of this equilibrium take place constantly. The freezing of soil in winter, the melting of snow and the thawing of ice in spring, the frequent wetting and drying of soil in summer and in fall, the addition of leaves, roots, and other plant stubble from the growing vegetation, will continuously modify the soil population by changing the conditions of the soil. The nature of the crop and the treatment of the soil, especially cultivation and fertilization, further influence in many ways the nature and composition of the soil microbiological population.

Aside from those modifications, man has learned to influence the soil population through various specific treatments, such as addition of lime or of acid-reacting fertilizers, air-drying or steam-sterilization, or treatment with various antiseptics. This is true particularly of greenhouse soils and of nursery beds. All these treatments bring about marked changes in the composition of the microbiological population.

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Untersuchungen zur Prufung der Reaktionsgeschwindigkeit und Kalkwirkung von Flugaschen aus Braunkohlegruben-Kraftwerken

Source

Kongressband 1992 Gottingen. Vortrage zum Generalthema des 104. VDLUFA-Kongresses vom 14.-19.9.1992 in Gottingen: Okologische Aspekte extensiver Landbewirtschaftung. VDLUFA-Verlag, Darmstadt, Germany: 1992. 341-344. 2 ref.

Abstract

Fly ash and other liming materials were applied to various acid soils in container and field experiments. Data are presented on barley and sugarbeet yields after application of fly ash, burnt lime and CaCO<sub(3)> each at rates of 1, 2, and 5 t/ha on soils with pH values of 4 and 5.5. The influence of pH value and hydrolytic acidity and deactivation of toxic Mn were also assessed.

Citation 5.

Accession Number

881921169

✓ **Author**

Gutser, R. Amberger, A.

Title

The Ca and Mg efficiency of different liming materials. [German]

Original Title

Kalk- und Mg-Wirkung verschiedener Kalkdunger

Source

Bayerisches Landwirtschaftliches Jahrbuch. 1987. 64: 3, 375-384. 7 ref.

Abstract

The efficiency of Ca and Mg of differently processed "natural" liming materials was studied in model and pot experiments. Calcium carbonate, raw dolomite, burnt lime with or without Mg, and Mg-silicate were tested by measuring the pH changes of an acid loess soil over a period of ten weeks. The results showed that their efficiency decreased with increasing Mg content. Silicates, especially Mg-silicate were less efficient than carbonates or oxides. The efficiency of calcium carbonates increased with fineness of grinding. Data are tabulated and discussed and the results from pot experiments with oats and maize are briefly considered.

Citation 6.

Accession Number

721900074

Author

Kaurichev, I. S. Ganzhara, N. F.

Title

Role of humus substances in processes occurring during soil stabilization with lime. [Russian]

Source

Izvestoya Timiryazevskoi Sel'skokhozyaistvennoi Akademii. 1972. No.5, 97-103.

Abstract

In laboratory experiments, the effects of 1-5% CaO added as burnt lime to the humus horizons of a moderately loamy derno-podzolic soil and of a chernozem, and to a mantle loam on gas exchange between the mixture and the atmosphere, on the microbial population of the humus horizons and on the group composition of the humus, and on the group composition of the humus in mantle loam to which humic acids had been added showed that the lime hydrolysed humus substances, decreasing the humic-acid content and increasing the fulvic-acid content.[117.1:222.11].

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Copyright Information

TITLE

Long-term effects of successive Ca(OH)2 and CaCO3 treatments on the water quality of two eutrophic hardwater lakes

PERSONAL AUTHOR

Prepas,-Ellie-E; Babin,-Jay; Murphy,-Tom-P

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ABSTRACT

1. Whole-lake experiments were conducted in two hardwater lakes (Halfmoon and Figure Eight) in Alberta, Canada, to investigate the effectiveness of repeated lime (slaked lime: Ca(OH)2 and / or calcite: CaCO3) treatments (5-78 mg L-1) for up to 7 years. 2. Randomized intervention analysis of intersystem differences between the experimental and three reference lakes demonstrated a decline in euphotic total phosphorus and chlorophyll a concentrations in the experimental lakes after repeated lime treatments. 3. After the second lime application to Halfmoon Lake, mean winter total phosphorus release rates (TPRR) decreased to < 1 mg m-2 day-1 compared with 3.6 mg m-2 day-1 during the winter after initial treatment. In the final year of lime application, mean summer TPRR decreased to 4.5 mg m-2 day-1 compared with 7.6 mg m-2 day-1 in the pretreatment year. 4. Mean macrophyte biomass declined and species composition was altered at 1 and 2 m depths in Figure Eight Lake during lime application. Over the first 6 years of treatment, macrophyte biomass at 2 m declined by 95% compared with concentrations recorded during the initial treatment year. In the last year of the study, macrophyte biomass at 2 m reached initial treatment concentrations, which coincided with the greatest water transparency. Over the treatment period, macrophyte species shifted from floating to rooted plants. 5. Multiple lime applications can improve water quality in eutrophic hardwater lakes for periods of up to 7 years. Reprinted by permission of the publisher.

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TITLE

The effects of lime addition on aquatic macrophytes in hard water: in situ and microcosm experiments

PERSONAL AUTHOR

Chambers, Patricia A; Prepas, Ellie E; Ferguson, Mary E

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ABSTRACT

1. Aquatic macrophytes are abundant in ponds and canals that are constructed in semiarid regions for water storage and conveyance, as well as in lakes that are culturally enriched. 2. Addition of Ca(OH)2 to two hardwater ponds at 250 or 275 mg L-1 caused an immediate eradication of submersed aquatic plants. Although these ponds are well-buffered (alkalinity: 2.57-3.94 mequiv L-1; pH: 8.1-9.0), lime addition caused an immediate increase in pH of 0.2-3 units. 3. Application of 135 mg L-1 Ca(OH)2 for 24 h or 210 mg L-1 Ca(OH)2 for 65 h to two irrigation canals had no effect on macrophyte biomass at the lower concentration and duration, but resulted in the elimination of aquatic macrophytes 1 month after the higher concentration, longer duration treatment. 4. Unlike the macrophyte control achieved following application of 210-275 mg L-1 Ca(OH)2 to ponds or canals, microcosm experiments in which lime formulation [slaked lime (Ca(OH)2), calcite (CaCO3), or a 1 : 1 mixture] and concentrations (up to 1500 mg L-1) were manipulated failed to elicit a consistent change in macrophyte biomass. Macrophytes in microcosms treated for the short-term (23-33 days) with [greater or equal] 200 mg L-1 Ca(OH)2 or a mixed Ca(OH)2/CaCO3 formulation always lost pigmentation, but biomass was not consistently reduced. 5. Declines in macrophyte biomass

following treatment of ponds and canals may have been triggered by a short-term rise in pH which, in these relatively warm (22-23 [degree]C) alkaline (2.28-3.94 mequiv L-1) systems, would have resulted in low concentrations of free CO2 and bicarbonate for photosynthesis. Reprinted by permission of the publisher.

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Citation 1.

Accession Number
IND20599735.

✓ **Author**
Oguntoyinbo, F.I. Aduayi, E.A. Sobulo, R.A.

Institution
Federal College of Agriculture, Ibadan, Nigeria.

Title
Effectiveness of some local liming materials in Nigeria as ameliorants of soil acidity.

Source
Journal of Plant Nutrition. [Monticello, N.Y. : Marcel Dekker Inc] 1996. v. 19 (7) p. 999-1016.

Abstract
The effectiveness of three local liming materials: basic slag (a byproduct of iron and steel industry), cement flue dust (a waste product of cement factory), and ground limestone was compared with that of imported hydrated lime in a greenhouse study using acid soils from two sites in Southern Nigeria. The soils were taken from Onne, near Port Harcourt in Rivers State and Epe near Lagos in Lagos State. The soils were classified as Typic paleudult and Typic udipsamment, respectively. The results show that the four liming materials were capable of neutralizing soil acidity. Their relative effectiveness was in the order: hydrated lime > basic slag > cement flue dust > ground limestone. Uptake of phosphorus (P), potassium (K), and calcium (Ca), and dry matter yield increased with increasing lime rates up to 500 and 1,000 mg Ca/kg soil for Epe and Onne soils, respectively. The lime requirements of the two soils are in the order of the aluminum (Al) saturation of the effective cation exchange capacity (ECEC) and are equivalent to exchangeable Al multiplied by 1.74 and 1.50, respectively. While differences among lime rates were significant for nutrient uptake and dry matter yield, there were no significant differences among the lime sources.

Citation 2.

Accession Number
IND20538425.

Author
Odland, T.E. Allbritten, H.G.

Title
Soil reaction and calcium supply as factors influencing the yield of potatoes and the occurrence of scab.

Source
Agronomy Journal. [Madison, Wis. : American Society of Agronomy, [1949-] June 1950. v. 42 (6) p. 269-275.

Abstract

The results are reported from two experiments on the influence of soil reaction and additions of calcium with the fertilizer on yield of potatoes and the occurrence of scab. The soil reaction was regulated by the use of hydrated lime or sulfur. Supplemental calcium was added with the fertilizer either in the form of limestone or as gypsum. The rates used were 100 and 200 pounds per acre of CaO equivalent. The amount and grade of fertilizer was varied in order to determine what effect it might have. In the first experiment, during 1937-1941, an area was used that had been planted to corn continuously for more than 40 years. The basic fertilizer application on this area, Series I, was 1 ton per acre of a 4-8-8 grade. No significant yield increase occurred when the application was 2,400 or 2,800 pounds per acre. A small increase in yield resulted when this grade was changed to a 5-8-8. No greater yield was obtained when the potash was increased to make a 4-8-10 grade. A half-ton per acre of an 8-16-16 grade was as effective as 1 ton of a 4-8-8 grade. Except for one highly limed plot in 1941 and a subsequent crop on the same plot in 1942, practically no scab occurred on any of the treatments or pH levels on this area. By starting with an apparently scab-free soil and treating the seed each year, the crop was kept relatively scab-free over the 5-year period. The supplemental calcium added with the fertilizer had no effect on crop yield or incidence of scab. In the second experiment, covering the period 1942-1946, the plots were located on an area, Series II, where various crops including potatoes had been grown previously. Increasing the amount of a 5-10-10 grade fertilizer from 2,000 to 2,500 pounds per acre. resulted in a significantly greater yield. The average soil reaction levels in the second experiment were pH 4.8, 5.5, and 6.1. No significant yield differences were obtained for these pH levels although there was a definite tendency toward a lower yield on the higher soil reaction. The average yields were 308, 305, and 281 bushels per acre for these three levels, respectively. On the plots where an average pH of 4.8 was obtained through sulfur applications, only small and lessening amounts of scab occurred. At pH 5.5 the scab occurring each year (10%-21%) was enough to be detrimental. At the 6.1 pH level, scab became increasingly serious. In 1945 and 1946 more than 90 of the tubers were scabby. On this second series of plots, no differences in crop yield or scab infestation resulted when small amounts of calcium were added with the fertilizer either as limestone or as gypsum. Considering both experiments, it can be concluded that under the conditions of these tests the potato yield was little influenced by soil reactions between 4.8 and 6.1. When soil reactions went below 4.8 or above 6.1 there was a definite tendency toward reduced yields. Keeping the reaction at or below 5.0 controlled scab. A soil reaction of 5.5 or higher tended to induce scab. The addition of small amounts of calcium with the fertilizer either in limestone or in gypsum had little influence on the yields of potatoes or the occurrence of scab. A soil reaction between pH 5.0 and 5.5 seems advisable in order to obtain the best yields of potatoes with the least scab.

Citation 3.

Accession Number

IND93035820.

Author

Metzger, W.H.

Institution

Kansas State College, Manhattan, KS.

Title

The rates of reaction with acid soils of finely divided soil liming materials.

Source

Journal of the American Society of Agronomy. [Madison, Wis. : American Society of Agronomy] June 1933. v. 25 (6) p. 377-383.

Abstract

The study reported pertains to the reaction rates of four finely divided liming materials with two acid soils. The materials included were hydrated lime, pulverized high calcium limestone, pulverized dolomitic limestone, and a by-product precipitated calcium carbonate known commercially as "Plant Lime". All materials were employed at three rates of application and in chemically equivalent amounts. Change in pH, decrease in Jones lime requirement, and decrease in total carbonates were used as criteria of rate of reaction. The incubation periods varied from 1 week to 1 year. Both pH change and decrease in lime requirement proved unreliable indicators of rate of reaction. The former remained approximately constant after 1 week. Lime requirement reached a minimum in 1 or 2 weeks and thereafter showed a material increase. Based upon the disappearance of carbonates, hydrated lime and the precipitated carbonate were about equally rapid in reaction. The precipitated carbonate reacted faster than the high calcium limestone. The difference can probably be accounted for by the somewhat greater fineness of the former. The dolomitic limestone was measurably less active than the high calcium limestone, the difference largely disappearing after 2 months incubation. It is doubtful whether any practical significance may be attributed to the differences in rates of reaction among the materials studied.

Citation 4.

Accession Number

IND93033232.

Author

Walker, R.H. Brown, P.E.

Institution

Iowa State University, Ames, IA.

Title

Nitrification in the grundy silt loam as influenced by liming.

Source

Journal of the American Society of Agronomy. [Madison, Wis. : American Society of Agronomy] May 1935. v. 27 (5) p. 356-363.

Abstract

1. Plats of Grundy silt loam were treated with different amounts of quarry-run limestone, with limestones of different degrees of fineness, and with hydrated lime. The soil of these plats was sampled frequently over a period of 5 years and its nitrifying power was determined. 2. The limestones and hydrated lime exerted an appreciable effect on the pH and also the nitrifying power of the soil. The changes in nitrifying power appeared to be associated directly with the changes in hydrogen-ion concentration, these changes being, to a certain extent, a function of the amount of limestone, or of the degree of fineness of the limestone applied. 3. The data were analyzed statistically to determine the significance of the differences in nitrifying power of the variously treated soils. This analysis shows that where limestone was applied in amounts less than the lime requirement of the soil or slightly above, the mean increases in nitrifying power induced by 1-ton additional applications of limestone were comparatively large and rather consistent, but they ere not quite large enough to be significant. 4. Two-ton increases in amounts of limestone applied, induced such large increases in nitrifying power that they were significant or highly significant in each case. 5. Where limestone was applied n amounts beyond the lime requirement of the soil, the increase in nitrifying power induced per unit of limestone was reduced somewhat, and larger additional amounts were found necessary to bring about significant increases in nitrifying power. 6. The 5-year means of the nitrifying power of soils treated with equal amounts of quarry-run, 20-mesh, 40-mesh, and 100-mesh limestones were comparatively uniform, and all except that for the 40-mesh limestone

were significantly lower than that for the hydrated lime. The mean difference in nitrifying power between the 40-mesh and hydrated lime treated soils lacked only a very small amount of being significant statistically.

Citation 5.

Accession Number
IND92067908.

Author
MacIntire, W.H. Shaw, W.M. Sanders, K.B.

Institution
Tennessee Agricultural Experiment Station, Knoxville, TX.

Title
The influence of liming on the availability of soil potash.

Source
Journal of the American Society of Agronomy. [Madison, Wis. : American Society of Agronomy] June 1927. v. 19 (6) p. 483-505.

Abstract

It is pointed out that the results of laboratory interchange studies have served as the basis for unjustified assumptions that potassium will be liberated by calcium in the practice of liming. Evidence is cited to show that a neutral salt of calcium may liberate potassium to the leachings from an acid soil, but that the reverse effect results when supplementary additions of CaO or MgO are made. Studies were made of the present availability of the potash of three soils which had been subject to the influence of liming in plat studies extending over respective periods of 7, 17, and 21 years. Distilled and carbonated water, HCl (1.115), and 0.2 N HCl digestion and leachings to equilibrium with 0.05 N HCl and with N/I NH4Cl were used to measure the present availability of native and added potash as influenced by liming. In general the two dilute acid and NH4Cl procedures gave comparable results without consistently showing a definite effect from liming, although indicating increase in potash reserve supplies where potash had been added. The two aqueous extraction procedures did indicate a definite decrease in availability of native and added potash as the result of liming. No indication of potassium liberation was adduced in any case. The extraction studies were in line with the yields from those plats as given by Mooers. From a four-year supplementary lysimeter study upon the influence of surface and subsurface incorporations of Ca(OH)2 at four rates, high-magnesic lime, and five limestone and five dolomite constants upon native potash it was demonstrated that: (a) The surface-zone incorporations gave consistently greater yields, whereas the subsurface incorporations gave consistently lower yields, of leachable potash than were given by the untreated soil; (b) neutral calcium salts exerted no liberative effect in the zone of alkali-earth incorporation; (c) calcium salt leachings effected a potash liberation in the lower untreated acid zone; (d) progressive decreases in annual outgo were found; and (e) high-magnesic limes caused diminished potash outgo, irrespective of zone of incorporation. From a second supplementary lysimeter study relative to the influence of hydrated lime, that of ground limestone and that of dolomite (all equivalent to 1 ton of CaO), upon the fate of water-soluble potash added through clover cuttings, where all additions were mixed throughout the full depth of soil, it was found that: (a) Each unsupplemented alkali-earth addition resulted in a potash outgo less than that from the control; (b) the several incorporations so "fixed" the 70-pound potash increment from 2 tons of clover as to give an average outgo less than that from the no-clover soil; and (c) the 99-pound increase in potash outgo from the unsupplemented 8-ton clover incorporation, which supplied 280 pounds of K2O, was reduced to an outgo of only 72 pounds as an average from the five lime treatments. It is pointed out that, when pH values indicate excess of H-ions, potash liberation is

BIO-NEWS
4 (1) Winter 1999

Effects of Common Calcium Sources on Soil Microbial Activity

By Dr. Bill Zimmer D.V.M.

During the summer of 1998, Midwestern Bio-Ag tested several common sources of calcium used in the upper Midwest for their effects, negative or positive, on soil microbes. This experiment was designed to address the concern among some organic certification organizations that Bio-Cal may harm soil microbes, similar to effects seen with burnt and hydrated limes, which are prohibited for organic use by most organizations.

Bio-Cal, burnt lime (calcium oxide), hydrated lime (calcium hydroxide), finely ground limestone (calcium carbonate flour), pelletized limestone (calcium carbonate), and pelletized gypsum (calcium sulfate) were applied to small plots at the rate of 2 tons per acre (4000 pounds / acre). This rate was chosen to represent the typical rates of ag lime recommended in our area. The rate is higher than typical for other sources, but was used to make all treatments the same. For example, for Bio-Cal, the rate is four to eight times greater than typically recommended rates.

Cotton strips were placed into each treatment plot. These strips represent plant residue, and the rate at which these strips were degraded represents the microbial activity present in the soil.

The experiment was conducted at three locations in Wisconsin, representing medium textured, neutral to alkaline soils (C.E.C. ~ 14 to 16, pH ~ 7 to 8) with moderate to high biological activity present.

Compared to the negative control plot (received no additions), Bio-Cal, limestone and hydrated lime similarly increased the microbial activity (about 10%). Gypsum increased microbial activity only slightly in this experiment. Burnt lime decreased microbial activity as measured by the disappearance rate of cotton strips.

Of interest, was the fact that burnt lime increased soil alkalinity by ten fold and hydrated lime by four fold. None of the other treatments had any significant effect on soil pH. Sudden drastic changes in pH are known to decrease microbial activity. This may be one factor by which burnt lime negatively affects soil life. In this experiment, hydrated lime increased microbial activity overall despite also changing the pH significantly. One of the locations showed a large increase in microbial activity for hydrated lime, while another location showed a large decrease.

Also of interest in this experiment, was the effect in the positive control treatment plot. In this plot, microbial/root stimulant (BioRoot) was applied at the rate of 200 pounds per acre. Microbial activity increased by over 20% in this plot!

High soil calcium levels have been shown beneficial in numerous experiments conducted by Dr. William Albrecht and others. Bio-Cal, burnt and hydrated lime are used as highly available sources of soluble calcium for soil application. Midwestern Bio-Ag has tauted the positive effects of soluble calcium from Bio-Cal for years. Bio-Cal did not negatively affect soil microbial activity as commonly seen with burnt lime, and in this experiment actually increased microbial activity in the soil significantly, even at much higher application rates than typically recommended.

This is just one experiment, with a few replications. More experimentation is needed to better estimate the actual amount by which soil microbial activity is raised or lowered by these typical calcium sources. For now, it can generally be said that Bio-Cal is a beneficial addition for soil microbiology.

You should also note that the limestone sources used in this study are not typical field grade lime, but rather powder fine products. Fine powder sources are significantly higher in calcium availability than typical field grade lime so the effects seen in this experiment may not be seen with similar applications of your field grade limestone. ~

(Note: Our thanks to Bart Hall for his hard work in completing this valuable experiment.)

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Volume 34, Issue 5
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Control of microorganisms in vitro by calcium hydroxide ▸ pastes

Estrela, C; Bammann, L L; Pimenta, F C; Pécora, J D

Department of Endodontics, Federal University of Goiás, Goiânia

Abstract

AIM: The aim of this study was to determine the influence of vehicles on the antimicrobial efficiency of ◂**calcium hydroxide.**▸ METHODOLOGY: A total of 588 size 50 sterile absorbent paper points, were immersed in various microbial suspensions for 3 min. The points were then placed on Petri dishes and covered with intracanal dressings containing ◂**calcium hydroxide:**▸ Ca(OH)2 + saline; Ca(OH)2 + camphorated paramonochlorophenol; Ca(OH)2 + 1% chlorhexidine solution: Ca(OH)2 + 3% sodium lauryl sulphate; Ca(OH)2 + Otosporin. After 1 min, 48 and 72 h and 7 days, 147 absorbent paper cones were removed from contact with the intracanal dressings and individually transported and immersed in 5 mL of Letheen Broth, followed by incubation at 37 degrees C for 48 h. Microbial growth was evaluated by turbidity of the culture medium. A 0.1-mL inoculum obtained from the Letheen Broth was transferred to 5 mL of BHI, and incubated at 37 degrees C for 48 h. Bacterial growth was again evaluated by turbidity of the culture medium. Positive BHI tubes were selected and inocula were spread on the surface of BHI agar and incubated at 37 degrees C for 48 h. Gram staining of the BHI growth and from colonies growing on BHI agar was carried out. RESULTS: An antimicrobial effect occurred after 48 h on the cultures of S. mutans, E. faecalis, S. aureus, P aeruginosa, B. subtilis, C. albicans and a mixed culture, irrespective of the intracanal dressing. CONCLUSIONS: Under the conditions of this study, the various vehicles associated with ◂**calcium hydroxide**▸ pastes did not influence the time required for microbial inactivation. [Journal Article; In English; England]

CAS Registry Numbers: Anti-Infective Agents, Local; Root Canal Irrigants; Vehicles; 1305-62-0, ◂**Calcium Hydroxide**▸

Citation Subset Indicators: Dentistry journal

MeSH Terms: Anti-Infective Agents, Local - * pharmacology (PD); Bacillus subtilis - drug effects (DE); ◂**Calcium Hydroxide**▸ - * pharmacology (PD); Candida albicans - drug effects (DE); Enterococcus faecalis - drug effects (DE); Microbial Sensitivity Tests; Pseudomonas aeruginosa - drug effects (DE); Root Canal Irrigants - * pharmacology (PD); Staphylococcus aureus - drug effects (DE); Streptococcus mutans - drug effects (DE); Vehicles

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Mechanism of action of calcium and hydroxyl ions of calcium hydroxide▸ on tissue and bacteria

Estrela, C; Sydney, G B; Bammann, L L; Felippe Júnior, O

Faculdade de Odontologia, Universidade Federal de Goiás, Goiânia, GO,Brasil

Abstract

The biological and bacteriological action of calcium hydroxide confer to its current success as an intracanal dressing. For this reason the mechanism of action of calcium and hydroxyl ions on tissue and bacteria deserves further study. The objective of the present paper is to analyze and discuss the mechanism of action of calcium and hydroxyl ions on anaerobic bacteria, starting from the isolated study of the influence of pH on these bacteria , as well as the mechanism of action of calcium hydroxide on tissue. [Journal Article, Review, Review, Tutorial; 20 Refs; In English; Brazil]

CAS Registry Numbers: Ions; Root Canal Irrigants; 1305-62-0, Calcium Hydroxide; 3352-57-6, Hydroxyl Radical; 7440-70-2, Calcium

Citation Subset Indicators: Dentistry journal

MeSH Terms: Bacteria, Anaerobic - * drug effects (DE), enzymology (EN), ultrastructure (UL); Calcium - pharmacology (PD); Calcium Hydroxide - metabolism (ME), * pharmacology (PD); Cell Membrane - enzymology (EN); Dental Pulp Cavity - * drug effects (DE), metabolism (ME); Human; Hydrogen-Ion Concentration; Hydroxyl Radical - metabolism (ME), * pharmacology (PD); Ions; Root Canal Irrigants - * pharmacology (PD)

Brazilian Dental Journal
Volume 6, Issue 2
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Efficacy of chemical treatments in eliminating Salmonella and Escherichia coli O157:H7 on scarified and polished alfalfa seeds

Holliday, S L; Scouten, A J; Beuchat, L R

Center for Food Safety and Department of Food Science and Technology, University of Georgia, Griffin, 0223-1797, USA

Abstract

Alfalfa seeds are sometimes subjected to a scarification treatment to enhance water uptake, which results in more rapid and uniform germination during sprout production. It has been hypothesized that this mechanical abrasion treatment diminishes the efficacy of chemical treatments used to kill or remove pathogenic bacteria from seeds. A study was done to compare the effectiveness of chlorine (20,000 ppm), H2O, (8%), Ca(OH)2 (1%), Ca(OH)2 (1%) plus Tween 80 (1%), and Ca(OH)2 (1%) plus Span 20 (1%) treatments in killing Salmonella and Escherichia coli O157:H7 inoculated onto control, scarified, and polished alfalfa seeds obtained from two suppliers. The influence of the presence of organic material in the inoculum carrier on the efficacy of sanitizers was investigated. Overall, treatment with 1% Ca(OH)2 was the most effective in reducing populations of the pathogens. Reduction in populations of pathogens on seeds obtained from supplier 1 indicate that chemical treatments are less efficacious in eliminating the pathogens on scarified seeds compared to control seeds. However, the effectiveness of chemical treatment in removing Salmonella and E. coli O157:H7 from seeds obtained from supplier 2 was not markedly affected by scarification or polishing. The presence of organic material in the inoculum carrier did not have a marked influence on the efficacy of chemicals in reducing populations of test pathogens. Additional lots of control, scarified, and polished alfalfa seeds of additional varieties need to be tested before conclusions can be drawn concerning the impact of mechanical abrasion on the efficacy of chemical treatment in removing or killing Salmonella and E. coli O157:H7. [Journal Article; In English; United States]

CAS Registry Numbers: Disinfectants; 1305-62-0, **Calcium Hydroxide**▸

Citation Subset Indicators: Index Medicus

MeSH Terms: Alfalfa - * microbiology (MI); ◂**Calcium Hydroxide**▸ - pharmacology (PD); Comparative Study; Disinfectants - * pharmacology (PD); Escherichia coli O157 - * drug effects (DE), growth & development (GD); Food Handling - * methods (MT); Food Microbiology; Germination; Salmonella - * drug effects (DE), growth & development (GD); Seeds; Treatment Outcome

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Oral Surgery, Oral Medicine, and Oral Pathology
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The comparative antimicrobial effect of calcium hydroxide▸

Stuart, K G; Miller, C H; Brown, C E Jr; Newton, C W

Indiana University School of Dentistry, Indianapolis

Abstract

The antimicrobial effectiveness of calcium hydroxide, camphorated paramonochlorophenol, and formocresol in root canals of extracted human teeth was compared. Canals in single-rooted teeth were enlarged and inoculated with Streptococcus mutans, Actinomyces viscosus, and Bacteroides gingivalis or Bacteroides fragilis. After treatment with a test agent and sealing and incubation for 1 hour, the canal contents were analyzed for the number of viable test bacteria and compared with that of inoculated teeth not treated with test agents. All test agents exhibited antimicrobial activity against all bacteria, with percent reductions in viable bacteria ranging from 64.3% to 100%. The combined data for Pulpdent paste and calcium hydroxide showed significantly higher antimicrobial activity than the combined data for camphorated paramonochlorophenol and formocresol for S. mutans and B. gingivalis or B. fragilis but showed no difference for A. viscosus. [Journal Article; In English; United States]

CAS Registry Numbers: Anti-Infective Agents, Local; Chlorophenols; Drug Combinations; Formocresols; 1305-62-0, Calcium Hydroxide; 37203-87-5, formocresol; 39393-11-8, Pulpdent; 76-22-2, Camphor; 8003-18-7, camphorated parachlorophenol

Citation Subset Indicators: Dentistry journal; Index Medicus

MeSH Terms: Actinomyces - * drug effects (DE); Adult; Anti-Infective Agents, Local - * pharmacology (PD); Bacteroides - * drug effects (DE); Calcium Hydroxide - * pharmacology (PD); Camphor - * pharmacology (PD); Chlorophenols - * pharmacology (PD); Colony Count, Microbial; Comparative Study; Dental Pulp Capping; Dental Pulp Cavity - microbiology (MI); Drug Combinations; Formocresols - * pharmacology (PD); Human; Materials Testing; Streptococcus mutans - * drug effects (DE)

Oral Surgery, Oral Medicine, and Oral Pathology
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In vitro determination of direct antimicrobial effect of calcium hydroxide▸

Estrela, C; Pimenta, F C; Ito, I Y; Bammann, L L

Federal University of Goiás, Goiânia, Brazil

Abstract

The objective of this study was to determine in vitro the time required for calcium hydroxide in direct contact with microorganisms to express its antimicrobial effect. The microorganisms used were: Micrococcus luteus (ATCC-9341), Staphylococcus aureus (ATCC-6538), Fusobacterium nucleatum (ATCC-25586), Pseudomonas aeruginosa (ATCC-27853), Escherichia coli, and Streptococcus sp. The strains were cultivated in Brain Heart Infusion (BHI), with the exception of F. nucleatum (BHI-PRAS). Pure and mixed suspensions of the microorganisms were prepared. Paper cones immersed in these substances were covered with calcium hydroxide paste, and after 0, 1, 2, 6, 12, 24, 48, and 72 h and 7 days they were transferred to an appropriate medium to observe the growth and multiplication of the microorganisms. Incubation was conducted at 37 degrees C for 48 h, according to the requirements of oxygen of each microorganism. The antimicrobial effect of calcium hydroxide was shown to occur after 12 h on M. luteus and F. nucleatum, 24 h on Streptococcus sp, 48 h on E. coli, and 72 h on S. aureus and P. aeruginosa. Mixture II (M. luteus + Streptococcus sp + S. aureus) was sensitive to calcium hydroxide antimicrobial potential after 48 h, whereas mixture I (M. luteus + E. coli + P. aeruginosa), mixture III (E. coli + P. aeruginosa), and mixture IV (S. aureus + P. aeruginosa) were inactivated after 72 h of exposure. [Journal Article; In English; United States]

CAS Registry Numbers: Anti-Infective Agents; Root Canal Irrigants; 1305-62-0, Calcium Hydroxide

Citation Subset Indicators: Dentistry journal

MeSH Terms: Anti-Infective Agents - * pharmacology (PD); Bacteria - * drug effects (DE); Calcium Hydroxide - * pharmacology (PD); Microbial Sensitivity Tests - statistics & numerical data (SN); Root Canal Irrigants - * pharmacology (PD); Time Factors

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Antimicrobial evaluation of calcium hydroxide in infected dentinal tubules

Estrela, C; Pimenta, F C; Ito, I Y; Bammann, L L

Federal University of Goiás, Goiânia, Brazil

Abstract

The objective of this study was to evaluate the antimicrobial activity of calcium hydroxide in infected dentinal tubules. Four microorganisms, strains of ATCC (Streptococcus faecalis (ATCC-29212), Staphylococcus aureus (ATCC-6538), Bacillus subtilis (ATCC-6633), and Pseudomonas aeruginosa (ATCC-27853)) and one mixture of these were used. These strains were inoculated in brain heart infusion (BHI) and incubated at 37 degrees C for 24 h. Sixty-three human maxillary central incisors were prepared and sterilized by autoclaving. Five groups of 12 teeth each were contaminated for 28 days using new 24-h cultures every 72 h, prepared and adjusted to tube 2 of the MacFarland scale (6 x 10(8) cells/ml). Root canals were then irrigated with 5 ml of saline, dried, and completely filled with calcium hydroxide paste. At intervals of 0, 48, and 72 h, and 7 days, dressings were removed and teeth were immersed in 5 ml of BHI and incubated at 37 degrees C for 48 h to observe the growth and multiplication of the microorganisms. Three uninoculated teeth were maintained in a humid environment as an aseptic control. These teeth were immersed in BHI and maintained at 37 degrees C for 7 days to determine microbial growth. Bacterial growth was shown by turbidity of the culture medium and confirmed by seeding these broths on BHI agar at 37 degrees C for 24 h. The positive BHI tubes were selected, and inoculum was spread on the surface of BHI agar, followed by the same incubation conditions. Gram stain was conducted from BHI growth and from colonies growing on solid medium. Calcium hydroxide in infected dentinal tubules showed no antimicrobial effect on S. faecalis, S. aureus, B. subtilis, P. aeruginosa, or on the bacterial mixture used throughout the experiment. [Journal Article; In English; United States]

CAS Registry Numbers: Root Canal Irrigants; 1305-62-0, Calcium Hydroxide

Citation Subset Indicators: Dentistry journal

MeSH Terms: Bacillus subtilis - drug effects (DE); Calcium Hydroxide - * pharmacology (PD); Dentin - * microbiology (MI), ultrastructure (UL); Enterococcus faecalis - drug effects (DE); Human; Incisor; Microbial Sensitivity Tests; Pseudomonas aeruginosa - drug effects (DE); Root Canal Irrigants - * pharmacology (PD); Staphylococcus aureus - drug effects (DE)

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The antimicrobial effect of calcium hydroxide in root canals pretreated with 5% iodine potassium iodide

Molander, A; Reit, C; Dahlén, G

Department of Endodontology/Oral Diagnosis, Faculty of Odontology, Göteborg University, Gothenburg, Sweden

Abstract

Calcium hydroxide (CH) is often used as a routine interappointment dressing during the endodontic treatment of teeth with apical periodontitis. However, it fails to consistently produce sterile root canals. The present study was set up to find out whether an antimicrobial strategy including the use of CH could be made more effective if: 1) canals were pretreated with 5% iodine potassium iodide (IPI), and 2) the dressing period was extended up to 2 months. Fifty human teeth, with radiographically verified apical periodontitis, were microbiologically sampled. After chemomechanical preparation the canals were pretreated with IPI for 3-7 days. Teeth where microorganisms persisted were then treated with CH for 2 months. Following instrumentation and dressing with IPI, 43 bacterial strains were recovered in 22 of the teeth. Samples obtained after the CH dressing period disclosed growth of 13 facultative and two strict anaerobic strains in 10 teeth. Enterococcus faecalis was identified in two specimens. In conclusion, the present study gave no evidence for an increased antimicrobial effect of CH if it was left for longer periods in the root canal. Although pretreatment with IPI from a quantitative point of view did not seem to add antimicrobial power, it might reduce the frequency of persisting strains of E. faecalis. [Journal Article; In English; Denmark]

CAS Registry Numbers: Anti-Infective Agents, Local; Iodides; Root Canal Irrigants; 12298-68-9, Lugol's solution; 1305-62-0, Calcium Hydroxide; 7681-11-0, Potassium Iodide

Citation Subset Indicators: Dentistry journal

MeSH Terms: Adult; Aged; Anti-Infective Agents, Local - * pharmacology (PD); Bacteria, Anaerobic - drug effects (DE); Calcium Hydroxide - administration & dosage (AD), * pharmacology (PD); Colony Count, Microbial; Dental Pulp Cavity - * microbiology (MI); Dose-Response Relationship, Drug; Enterococcus faecalis - drug effects (DE); Human; Iodides - pharmacology (PD); Middle Age; Periapical Periodontitis - * microbiology (MI); Potassium Iodide - * pharmacology (PD); Root Canal Irrigants - administration & dosage (AD), * pharmacology (PD); Root Canal Therapy; Time Factors

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Material Safety Data Sheet
for
Cement Kiln Dust

Section I - Identity

Manufacturer's name and address: Ash Grove Cement Company
8900 Indian Creek Parkway
P. O. Box 25900
Overland Park, KS 66225
Emergency Telephone Number: (913) 451-8900
Information Telephone Number: (913) 451-8900
Chemical Name and Synonyms: Cement Kiln Dust; CKD

Chemical Name and Synonyms: A mixture of sulfates, chlorides, carbonates, and oxides of sodium, potassium and calcium; quartz (CAS No. 01-4808-60-7), limestone (CAS No. 1317-65-3), fly ash, dolomite, feldspars, and iron oxides; glasses of silicon dioxide, aluminum oxide and iron oxide; and cement compounds (CAS No. 65997-15-1). Cement kiln dust (CKD) is a partially calcined mineral mixture collected by or in electrostatic precipitators (ESPs) or by other air pollution control devices (APCDs), and deposited in ESP collection bins.

When waste-derived fuels comprise a part of the fuel source, CKD may contain 200-2000 ppm lead and traces of other heavy metals, including, but not limited to, arsenic, chromium, cadmium, antimony, barium, beryllium, silver, mercury, thallium, selenium and nickel.

Calcium oxide may also be present in freshly generated CKD. If CKD is mixed with water, the calcium oxide will hydrate to form calcium hydroxide.

Revision Date: August, 2000

Section II - Hazardous Ingredients

	OSHA PEL	ACGIH TLV	Carcinogen Status
Inert or Nuisance Dust Respirable Fraction Total Dust	 5 mg/m^3 15 mg/m^3	 3 mg/m^3 10 mg/m^3	Not Applicable
Calcium oxide, Quicklime, CaO	5 mg/m^3	2 mg/m^3	Not Applicable
Hydrated Lime, $Ca(OH)_2$:Total: Respirable:	15 mg/m^3 5 mg/m3	5 mg/m^3 (Total)	Not Applicable
Respirable Quartz, Free Silica, SiO_2	$\frac{10 \text{ mg/m}^3}{\% SiO_2 + 2}$	0.05 mg/m^3	NTP - Yes IARC - Yes OSHA - No
Total Quartz, Free Silica, SiO_2	$\frac{30 \text{ mg/m}^3}{\% SiO_2 + 2}$	Not Applicable	NTP - Yes IARC - Yes OSHA - No

CKD contains greater than 0.1% crystalline silica.

Section II - Hazardous Ingredients (Continued)

Metals - Representative Exposure Limits			
	OSHA PEL	ACGIH - TLV	Carcinogen Status
Arsenic	0.01 mg/m^3	0.01 mg/m^3	OSHA - Yes IARC - Yes NTP - Yes
Chromium	1.0 mg/m^3	0.50 mg/m^3	OSHA - No IARC - Yes NTP - Yes
Cadmium	0.005 mg/m^3	0.01 mg/m^3	OSHA - Yes IARC - Yes NTP - Yes
Lead	0.05 mg/m^3	0.05 mg/m^3	OSHA - No IARC - Yes NTP - No
Antimony	0.50 mg/m^3	0.50 mg/m3	OSHA - No IARC - No NTP - No
Barium	0.50 mg/m^3	0.50 mg/m^3	OSHA - No IARC - No NTP - No
Beryllium	2 Φg/m^3	0.002 mg/m^3	OSHA - No IARC - Yes NTP - Yes
Silver	0.01 mg/m^3	0.01 mg/m^3	OSHA - No IARC - No NTP - No
Mercury	C* = 0.1 mg/m^3	0.025 mg/m^3 SKIN **	OSHA - No IARC - Yes NTP - No
Thallium	0.1 mg/m^3	0.1 mg/m^3, SKIN**	OSHA - No IARC - No NTP - No
Selenium	0.20 mg/m^3	0.20 mg/m^3	OSHA - No IARC - Yes NTP - Yes

Nickel	1 mg/m^3	0.1 mg/m^3	OSHA - No IARC - Yes NTP - Yes

*C = Ceiling

** SKIN = can be absorbed through skin

Section III - Physical/Chemical Characteristics

Chemical Family: Inorganic Base with mixed inorganic oxides and salts
Specific Gravity: 2.82
Vapor Pressure(mm Hg): N/A
Vapor Density: (Air=1) N/A
Evaporation Rate: NA
Solubility in Water: 1.0 to 12%
Appearance and Odor: Buff colored powder; odorless
Melting Point: N/A

Section IV - Fire and Explosion Hazard Data

Flash Point (method used): N/A; Cement Kiln Dust is non-combustible and not explosive.
Flammable or Explosive Limits: LEL: NA **UEL:** NA
Extinguishing Media: N/A
Special Fire Fighting Procedures: Cement Kiln Dust is incombustible
Firefighting Media: N/A

CAUTION: Saturated water solutions of cement kiln dust can have pH of 12-12.5. See Section VII for appropriate precautions.

Unusual Fire and Explosion Hazards: None

Section V - Health Hazard Data

Emergency Overview:
Cement Kiln Dust is a light gray powder that poses little immediate hazard. A single short exposure to the dry powder is not likely to cause serious harm. However, exposure of sufficient duration to wet cement kiln dust can cause serious, potentially irreversible tissue (skin or eye) destruction in the form of chemical (caustic) burns, including third degree burns. The same type of tissue destruction can occur if wet or moist areas of the body are exposed for sufficient duration to dry cement kiln dust.

Route(s) of Entry of cement kiln dust: Inhalation; skin; eyes; ingestion

1. **Inhalation:**
    a. **Acute exposure:** Freshly generated CKD may be corrosive to damp moist skin if calcium oxide and calcium hydroxide are present. Inhalation of this dust may cause sore throat, coughing, choking, and dyspnea.
    b. **Chronic exposure:** Bronchial irritation with chronic cough may occur. CKD can contain crystalline silica in the respirable size range of particulate. Chronic long term exposure to respirable crystalline silica without the use of a respirator can cause silicosis, a serious and progressive pneumoconiosis which can be disabling and in extreme instances lead to death. Symptoms may appear at any time, even years after exposure has ceased. These symptoms may include shortness of breath, difficulty breathing, coughing, diminished work capacity, reduction of lung volume and right

heart enlargement and/or failure. The only reliable method of detecting silicosis is through a chest x-ray. Silicosis may aggravate other chronic pulmonary conditions and may increase the risk of pulmonary tuberculosis infection. Smoking aggravates the effects of silica exposure. NTP and IARC list respirable quartz crystalline silica as a carcinogen; OSHA does not.

2. **Skin contact:**
   a. **Acute exposure:** Freshly generated CKD may be corrosive in contact with unprotected skin, due to the content of calcium oxide and calcium hydroxide (lime). Solutions of lime can penetrate the skin slowly, producing soft, necrotic, deeply penetrating areas on contact; these are potentially serious burns. **NOTE: CKD may also be shipped hot (approximately 200^0 F) and could cause thermal burns to unprotected skin.**
   b. **Chronic exposure:** A chronic dermatitis may follow repeated contact.
   c. **First aid:** Remove contaminated clothing and shoes immediately. Wash affected area with soap or mild detergent and large amounts of water until no evidence of CKD remains (approximately 15-20 minutes). In the case of chemical burns, due to the lime content of CKD, cover the affected areas with sterile, dry dressing. Bandage securely, but not too tightly. Get medical attention.
3. **Eye contact: Freshly generated CKD may be corrosive to moist tissue around the eyes**
   a. **Acute exposure:** Direct contact with the freshly generated solid or aqueous solutions may cause conjunctival edema and/or corneal damage; can lead to and cause blindness.
   b. **Chronic exposure:** Prolonged contact may cause conjunctivitis.
   c. **First aid:** Wash eyes immediately with large amounts of water, occasionally lifting the upper and lower lids, until no evidence of CKD remains (approximately 15-20 minutes). Get medical attention immediately. Qualified medical personnel should perform administration of drugs to the eyes.
4. **Ingestion:** corrosive. If ingested, consult a physician immediately. Do not induce vomiting.

Hazard Information About Trace Metals in CKD:

Arsenic – Routes of entry: inhalation, absorption, skin and/or eye contact, ingestion. Ulceration of nasal septum, dermatitis, gastrointestinal disturbances, peripheral neuritis, respiratory system irritation; hyperpigmentation of skin. Target organs are liver, kidneys, skin, lungs and lymphatic system. Arsenic is associated with lung and lymphatic cancer.

Chromium – Routes of entry: inhalation, ingestion, skin and/or eye contact. Chromium compounds are associated with eye irritation, allergic contact dermatitis and in some cases lung fibrosis. Target organs are the eyes, skin, and respiratory system.

Cadmium – Routes of entry: inhalation and ingestion. Cadmium dust may cause pulmonary edema and shortness of breath. Can result in cough, chest tightness, substernal pain, headache, chills, muscle aches, nausea, vomiting, diarrhea, loss of the sense of smell, emphysma, proteinuria and mild anemia. The target organs are the respiratory system, kidneys, prostate and blood. Cadmium is associated with prostatic and lung cancer.

Lead – Routes of entry: inhalation, ingestion, skin and/or eye contact. Lead is associated with weakness, fatigue, insomnia, facial pallor, anorexia, low weight, constipation, abdominal pain, anemia, lead line on gums, tremors, wrist paralysis, brain alterations, kidney disease, eye irritation and hypotension. The target organs are the GI tract, CNS, kidneys, blood and gingival tissue.

Antimony – Routes of entry: inhalation, ingestion, skin and/or eye contact. Causes irritation of eyes, skin, nose, throat and mouth; dizziness;headache; nausea; vomiting; diarrhea; stomach cramps; insomnia; anorexia; unable to smell properly. The target organs are the eyes, skin, respiratory system and CVS.

Barium – Routes of entry: inhalation, ingestion. Barium compounds can cause severe eye burns and skin irritation. It can cause muscle stimulation followed by paralysis with symptoms including nausea, vomiting,

Beryllium – Routes of entry: inhalation and skin and/or eye contact. Chronic exposure causes berylliosis: anorexia, low weight, weakness, chest pain, cough, clubbing of fingers, cyanosis, and pulmonary insufficiency; also causes eye irritation and dermatitis. The target organs are the eyes, respiratory system, and skin. Beryllium is associated with lung cancer.

Silver – Routes of entry: inhalation, ingestion, skin and/or eye contact. Can cause blue-gray discoloration of skin, eyes and mucous membranes; may cause irritation and ulceration of skin and GI tract disturbances. Target organs are nasal septum, skin and eyes.

Mercury – Routes of entry: inhalation, absorption, ingestion, skin and/or eye contact. Causes skin and eye irritation; cough, chest pain, shortness of breath, bronchial pneumonitis; tremors, insomnia, irritability, indecision, headache, fatigue, weakness, inflammation of the mouth, salivation, GI tract disturbances, anorexia, weight loss and protein in the urine.

Thallium – Routes of entry: inhalation, absorption, ingestion, skin and/or eye contact. Causes nausea and vomiting, diarrhea and abdominal pain; eyelid drooping, loss of binocular vision, peripheral neuritis, tremors; retrosternal tightness, chest pain, pulmonary edema; seizures, involuntary body movements, psychosis; liver and kidney damage; hair loss, tingling in the legs. Target organs are eyes, respiratory system, CNS, liver, kidneys, GI tract, body hair.

Selenium – Routes of entry: inhalation, ingestion, skin and/or eye contact. Causes eye, skin, nose and throat irritation; visual disturbances; headache; chills, fever; shortness of breath, bronchitis; metallic taste, garlic breath, GI tract disturbances; dermatitis; eye and skin burns. In animals causes: anemia; liver necrosis and cirrhosis; kidney and spleen damage. Target organs are the eyes, skin, respiratory system, liver, kidneys, blood, spleen.

Nickel – Roues of entry: inhalation, ingestion, skin and/or eye contact. Causes allergic dermatitis, allergic asthma, pneumonitis. Target organs are nasal cavities, lungs, skin. Nickel is associated with lung and nasal cancer.

Section VI - Reactivity Data

Stability: Calcium oxide and calcium hydroxide, if present in CKD, will gradually absorb carbon dioxide when exposed to air, forming calcium carbonate. Cement kiln dust consolidates when mixed with water. The resulting dry material sets loosely, preventing the material from becoming airborne. With excess water, calcium oxide and calcium hydroxide which may be present in freshly generated CKD can form a corrosive solution, pH 12-12.5.

Incompatibility (Materials to avoid): Contact with mineral acids will cause evolution of carbon dioxide with production of heat.

Hazardous Polymerization: Will not occur.

Conditions to Avoid: Handling, conveying, or releasing CKD as a dry dusty solid. Wetting CKD prior to all handling will prevent the substance from becoming airborne.

Section VII - Precautions for Safe Handling and Use

Handling: Use protective equipment as described in Section VIII.

Storing: CKD should be wet by water spray when discharging from ESP bins to avoid generation of dust when conveying and depositing in landfill. No other precautions needed.

Section VIII - Control Measures

Respiratory Protection: A NIOSH approved (under 42 CFR 84) respirator must be used to control exposure below PELs and TLVs. Respirator must be effective in preventing exposure to respirable particulate composed of crystalline silica, lime and heavy metals at trace concentrations.

Firefighting: Self-contained breathing apparatus with a full facepiece operated in pressure-demand or positive-pressure mode.

Protective Gloves: Gauntlet type work gloves; if handling cement kiln dust in combination with water, chemical resistant gloves must be worn.

Eye Protection: When engaged in activities where cement kiln dust or wet cement kiln dust or concrete could contact the eye, wear safety glasses with side shields or goggles. In extremely dusty environments and unpredictable environments, wear unvented or indirectly vented goggles to avoid eye irritation or injury. Contact lenses should not be worn when working with wet cement kiln dust or fresh cement products.

Other Protective Equipment: Wear impervious clothing with long sleeves and pants to eliminate skin contact. If walking or working in dry or wet cement kiln dust, wear impervious boots taped at the top to the pant legs to keep dust or liquid from entering the boot. If clothing becomes saturated with wet CKD, it should be removed and replaced with clean dry clothing.

Work/Hygienic Practices: Immediately after working with cement kiln dust, workers should shower with soap and water.

This product neither contains nor is directly manufactured with any controlled ozone depleting substances, Class I and II.

TECHNICAL PAPERS

Reprint courtesy of Rock Products 1990

NEW WAY TO BURN HAZARDOUS WASTE

by Eric R. Hansen

Ash Grow Cement Co. has developed an environmentally sound energy recovery system from solid hazardous wastederived fuel that could ignite a revolution in the cement industry

Introducing hazardous waste fuel directly into the middle of a long kiln, where gas temperatures are sufficiently high to assure complete destruction and utilization of such solid waste fuel, could lower energy costs for cement companies while helping solve the nation's waste-disposal dilemma.

Cement kilns have received considerable attention lately as an environmentally sound solution to the problem of what to do with combustible industrial and municipal hazardous waste. High temperatures in the kilns, long residence times, and the ability to absorb inorganic residue allow complete destruction of combustible hazardous waste while recovering the energy they contain in an environmentally sound manner.

As a result of pressure from an environmentally aware society, there are increasing government regulations requiring more industrial and manufacturing waste to be managed as "hazardous waste" because of its flammable or toxic character. Severe limitations are being placed on the landfilling of this industrial waste. Municipal hazardous waste as well is being placed under increasing regulations to minimize its impact on the environment. The only viable means of safe permanent disposal of this combustible waste is by thermal treatment. Cement kilns are not only ideally suited for the safe disposal of this material, but they also can recover the energy from this type of waste.

Although combustible hazardous waste solids represent a potential source of inexpensive energy for the cement industry, concerns about handling the hazardous waste, plant engineering, product quality, and emission control have deterred kiln operators from taking advantage of this inexpensive source of energy. Extensive energy recovery already is being done with liquid hazardous waste-derived fuel.

Liquid hazardous wastes are easily blended with each other and with conventional fuel to provide uniform fuel that can be burned at the firing end of the kiln with little or no modification of the kiln burner configuration. The use of solid hazardous waste has been limited by the extent to which it can be suspended or dispersed into the flame zone of the kiln. If hazardous waste solids are charged into the sintering zone of the kiln without adequate dispersion and rapid combustion, they will come into contact with the clinker bed. The localized reducing conditions created by fuel falling into the clinker will affect clinker quality and cement color. This problem limits the quantity of fuel utilized by this technique.

Low British Thermal Unit (BTU)-content fuel introduced into the flame adversely affects the flame temperature and therefore reduces the thermal efficiency of the process. If the solid hazardous waste-derived fuel could be introduced at a point in the kiln hot enough to assure complete destruction of the fuel components, yet have sufficient residence time to burn out before sintering begins, the clinker quality would not be adversely affected. Therefore, the addition rate of the fuel would be limited only by the ability of the process to utilize the energy generated by the fuel. Also, the inorganic residues would have sufficient time to completely react with the active cement minerals in the sintering zone.

Ash Grove and Cadence Chemical Co. have jointly developed and received a patent' on their new method for introducing solid hazardous waste-derived fuel directly into the middle of a long wet or dry kiln,

The development of the precalciner was a technological revolution for the cement industry. The major benefits of precalcining include:

- Much improved operational stability;

- Reduction of thermal loading in the sintering zone;

- Increased production for a given kiln size;

- The ability to use low-quality fuel;

The addition of a significant portion (25%) of the process fuel directly into the middle of a long kiln also yielded many of the benefits of precalcining.

Ash Grove's experience in adding 15% to 25% of fuel into the middle of a 12 ft x 450-ft wet process kiln. The kiln is continuously monitored for carbon monoxide and total hydrocarbons, as well as nitrous oxide) is shown in a temperature profile.

Upon adding the 30 x 106 BTU/ hr of fuel to the middle of the kiln, the burner firing rate is reduced from a normal 6.5 tph of coal to 5.25 tph. With the lower firing rate and increased oxygen in the burning zone, the primary flame tightens up and becomes intense. The high excess air and high flame temperature improve clinker nodularity and promote a heavy, durable coating in the burning zone; the coating zone is shortened by about 10 ft.

Frequent firing profile changes would be expected to cause refractory problems in the transition zone. The new spinel-based bricks are performing well in this zone. The reduced thermal loading in the burning zone and resulting improved coating are expected to increase refractory life in the burning zone.

It is expected that wet kilns whose capacity is limited by thermal loading and resulting refractory life may take advantage of the secondary firing by increasing productivity and not changing the burner-firing rate.

The biggest advantage is that low-quality, low-cost fuel can be substituted for expensive fossil fuel. The primary burner must receive reasonably high-BTU fuel (greater than 10,000 BTU/lb, preferably greater than 12,000 BTU/ lb) in order to maintain high flame temperatures. Low-BTU fuel adversely affects the flame, and this results in increased energy consumption.

The calcining zone does not require high flame temperatures, as exemplified with precalciners where the fuel is dispersed with the meal to achieve flameless combustion, Some precalciners already take advantage of firing a lower- quality fuel than can be fired in the primary kiln burner. Likewise, the heating value of the fuel to be fed to the middle of a long kiln can be quite low, yet full advantage can be taken of the heating value of the fuel. There is even speculation that the energy from the fuel added to the middle of the kiln is more effectively utilized than if it was added at the burner2.

It was of great importance for Ash Grove to demonstrate that the addition of fuel to the middle of a long kiln did not adversely affect the kiln emissions. The system was engineered so that the fuel would be introduced at a point in the kiln where the temperature is above 950°C. The literature3,4 supports that at temperatures above 950°C, complete destruction of the organic constituents of the fuel is obtained. Studies on municipal hazardous waste incinerators indicate that introduction of the fuel below 950°C can result in dioxin and furan formation.

To demonstrate the use of solid fuel by this method, a study was done on solid fuel spiked with trichlorobenzene. Trichlorobenzene was selected because it contains the most difficult to destroy chlorinated hydrocarbons as found in both laboratory studies and field testing by Dellinger5. No trichlorobenzene was detected in the test, and a greater than 99.9999% destruction and removal efficiency was demonstrated.

To prove that the process is continuously sound environmentally, Ash Grove installed a total hydrocarbon monitor. Compliance with a 20-ppm total hydrocarbon maximum is maintained while hazardous waste fuel is being fired.

Older cement kilns now have an opportunity to compete energy costwise with newer technology while providing society with a solution to its waste problems. As with any new technology, it is always difficult to build the first operating unit. Now that there are operating examples of long kilns with secondary firing, there should be a rapid application of this technology.

TECHNICAL PAPERS

Reprint courtesy of Rock Products 1992

TIRE POWER IS FIRE POWER

by Eric R. Hansen

A new technology utilizing whole rubber tires is opening the door to a vast, low-cost source for kiln energy

A proven technology is available that allows a significant portion greater than 25%-of the energy for long kilns to come from whole tires.

Using tires for fuel is recognized practice in preheater kilns, it never has been considered an option for long kilns- until the emergence of this new technology.

Essentially the process is simple: whole tires are bundled and introduced into the calcining zone of the kiln. However, critical elements such as point of entry, combustion control, and secondary fuel volume must remain in balance for it to work.

Point of Entry

A point in the calcining zone where temperatures typically are between 2,000°F to 2,100°F is the ideal entry point for whole tires. At this point, the kiln is hot enough to assure complete destruction of the tire, including the metal bead, while offering sufficient residence time to completely consume the tire before sintering begins. This location, which is typically 50% to 60% of the length of the kiln from the feed end, is sufficiently downhill so that all the energy is utilized, yet not so far downhill that the life of the drop tube is unacceptable.

Combustion Control

Controlled combustion is the second vital component of the technology. Showing control over the completeness of combustion also is important. The primary reason Ash Grove has been successful with regulators and the general public is our willingness to implement continuous combustion monitoring. Our continuous monitoring program made both groups aware of, and comfortable with, what we were doing. In addition, the information gained from monitoring the combustion process has helped us to improve it.

We have found that controlling combustion is made easier as whole tires, or whole tire bundles, are fed to the kiln. Because of the surface area to volume ratio, their combustion rate is moderated. Tests have shown that, once they enter the kiln, whole tires burn for approximately 15 to 20 min. When two or three tires are added per revolution, as many as 50 to 60 tires can be in the kiln at one time in various stages of consumption. This fuel mass provides a stable and predictable burn rate even if individual tires vary in size and weight. Because they burn slowly, most of the energy from the tires is released in the heart of the calcining zone where it does the most good.

The use of large pieces of secondary fuel applies to other forms of organic waste material as well as tires. In the future, municipal waste processed into bales will most likely be another important energy source for cement kilns.

Surface area to volume ratio is a critical factor. Whole tires perform well as a fuel supplement because of their surface area to volume ratio. Thus combustion is moderated and the fuel releases its energy downhill from the point of entry. This also has the positive effect of thermal load averaging, allowing fuel-addition once or twice per revolution.

Fuel Volume

A 40% substitution rate seems to be the technological barrier for feeding whole, unprocessed tires to the kiln. Inserting whole tires at a greater rate would cool the main frame dramatically and unbalance the process. In the average kiln, a 40% substitution rate would approximate three tires entering the kiln per revolution. Careful attention to the burner design and excess air control may allow higher substitution rates. It all works together in a delicate balance.

For an almost insignificant investment, older cement kilns now will be able to compete head-to-head with newer kilns on a national and international basis. The billions of discarded tires stockpiled throughout the country will give long cement kilns new fire power for the future. 0

Advantages Of Burning Whole Tires In A Kiln

More than 2 billion waste tires currently are stockpiled in the United States. The energy value of these tires is equivalent to 20 million tons of coal. Another 280 million tires-equal to 2.8 million tons of coal- are being discarded each year, When these whole tires are used to supplement a traditional fuel supply, producers can take advantage of some substantial benefits:

- At a 40% substitution rate, a typical kiln producing a quarter million tons a year of clinker has the potential to save $1 million in fuel costs annually;

- Tires burn cleaner than coal. Using tires as fuel reduces nitrogen oxides and does not adversely affect other kiln air emissions;

- Burning whole tires can lessen a kiln's thermal load in the sintering zone, resulting in a better coating and a longer refractory life;

- Because there is a disposal fee built into the price of every tire, tires are delivered to a kiln at no cost or better;

- Improved clinker nodularity, cooler performance, and a better quality end product can result from burning whole tires.

ERIC HANSEN GROUP

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Cadence Park Plaza • Michigan City, IN 46360
219.873.3275 • ehansengvi@earthlink.net • www.erichansengroup.com