Chemistry and Technology of Lime and Limestone

SECOND EDITION

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PREFACE

Whereas many second editions consist of relatively minor changes, a few new developments, and the inevitable updating, this second edition contains such extensive revisions that an estimated 30% of the book has been completely rewritten. It embraces a vast multitude of technological changes and thousands of updated, duly metricated facts. As a result, this effort proved to be about as arduous and intricate to weave together as the first edition. The only aspect of the first edition that remains unaltered is the sequence and organization of the book. Therefore, characterizing this as a second edition could be a misnomer; it approaches being a *new reference text* with the same title and organization.

Postulating on why such drastic changes were necessary since publication of the first edition in January 1966, it would be an oversimplification to allude to the dynamic changes in technology; much more is involved. Foremost is the massive intrusion of governments (almost worldwide), spurred by a social, economic, and political upheaval, into business generally, with the limestone and lime industries seemingly positioned in the center arena. Gradually, since the late 1960s a deluge of statutes and regulations, often conflicting, confusing or ill-conceived, has engulfed industry. In rapid succession lime and limestone have had to contend with a spate of environmental regulations that if fully enforced could cause these industries to collapse. Government mandates insist on virtual eradication of *all* dust from plant and quarry point sources and fugitive dust; zero discharges of waste effluents; severe restrictions on solid waste disposal; compulsory monitoring of and record-keeping on emissions and effluents; crushing penalties for lime spill accidents; zoning ordinances and land conservation constraints that prohibit development of many new quarries and plants; inflexible criteria on rehabilitation of mined-out areas; abatement of noise; intricate safety regulations for workers with punitive fines imposed; and others. Concomitant with the foregoing is a ceaseless "witch-hunt" for toxic materials so that no substance remains above suspicion; even potable water is not sacrosanct. The total impact has been highly inflationary.

The result has been a diminution of industry operations; old, marginal plants have been overwhelmed by the staggering cost and complexity of even attempting to conform. Fifteen lime plants have permanently closed as well as many limestone quarries. Paradoxically, this has occurred during a period of record demand with excess plant capacity shrinking, in spite of some significant expansions in plant capacity. The energy crisis of 1973–1974 further exacerbated the situation. Lime plants are very energy-intensive, more so than limestone and within four years on an average their energy costs more than quadrupled. Just to exist some plants were obliged to install three alternative fuel systems. The resulting inflationary pressure, coupled with regulative overkill, on lime and limestone costs has been unprecedented, causing prices to soar. Lime prices doubled in only four years, and the energy cost factor in a ton of lime in 1978 was about the same as its selling price in 1967–1968. Moreover, there has been increased litigation and more plant strikes of longer duration than ever before.

Unquestionably environmental zealots and liberals with an antibusiness bias have been in command during this recent turbulent decade. There appears to be a growing realization that a rational balance is sorely needed in many of these programs, so hopefully this frustrating situation will be ameliorated in the near future.

Strangely, some of the government's environmental programs are a two-edged sword for limestone and lime. From the billions of dollars spent by government and industry to develop methods for abating pollution, it is evident that lime and limestone are probably the leading antidotes for many of the world's most pressing ecological ills, such as desulfurizing stack gases from burning high-sulfur fossil fuels; clarification of sewage wastewater and stabilization of sewage sludge for safe disposal; neutralization of acid wastewaters from mine discharges and plant effluents; making potable water safer to drink; and so on. But these attractive market growth prospects and the ability to produce these pollution antidotes are ironically menaced by incredible discoordination in government. This is pathetic when only a disputed ½–1% frequently separates industry and government from achieving these laudable goals on a tenable cost-effective basis.

Lime continues to be recognized more for what it is, an indispensable basic chemical, and limestone is moving in this direction. Thus, their stature has been enhanced through education, in which the first edition of this book played a role. Lime uses, which were only 10% chemically oriented in 1910 are 90% chemical and industrial in 1978, representing one of the most dramatic reversals in end use in commercial history. It is the second-place chemical in tonnage in most countries, and limestone ranks second among *all* commodities in total tonnage. These materials are still unglamorous, but they are escaping from their previous humble, mundane and nondescript connotation as a crude rock, mineral dust, cheap construction material or other misconceptions.

This edition, as was its predecessor, is aimed primarily toward the industrial world and secondarily for academic use. Both aims are important because of the continuing need for education. But in addition to providing a balanced comprehension of these materials, an earnest attempt has been made to provide the reader with a "feel" for the industry and its products. Naturally this book could have been written in greater detail, but that would require several volumes. The selected bibliographies will facilitate further probing by those who desire it. I have endeavored to distill the facts and present a current or composite picture rather than the many existing discordant, controversial theories and data. Disagreement with some conclusions is inevitable, but all opinions are based on sincere conviction. Worldwide technology and data are reported in more detail than in the first edition; the development of an International Lime Association has facilitated this.

I have been intimately associated with this industry for over 32 years, including considerable study and travel abroad, and am indebted to a few hundred knowledgeable technical and executive leaders, both in the United States and abroad, for much of the information and background that made this book possible. However, private and proprietary information, relayed to me in confidence by many industry friends, is respected and not divulged.

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Chincoteague, Virginia

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CHAPTER ONE

Introduction

There are a few absolutely indispensable forms of matter, like air and water, that are generally taken for granted by mankind but without which life simply would cease. There are also other almost equally basic materials without which life would be greatly diminished (and possibly not sustainable) and modern commerce and industry could not exist. Among these ancient, prosaic, unglamorous, and low-cost materials are lime and limestone. Literally any object that exists in man's home, his office (or virtually any manufactured product) has required lime or limestone in some phase of its manufacture, directly or indirectly, either as a prime or incidental processing material, as Chapter 5 and 11, on the interminable uses of these materials, testify. In fact, lime and limestone's basic essentiality has been likened to one leg of a six-legged stool on which industry revolves, the other essential legs being iron ore, salt, sulfur, petroleum, and coal. Stated another way, these are the six essential building blocks of commerce and industry. Of these, limestone is the greatest in physical volume, surpassing coal for the first time in 1962. The strategic importance of these materials is frequently overlooked or erroneously minimized in favor of other scarcer, more costly, and more dramatic products that are essential for a few important purposes but not for industry as a whole.

Limestone's abundance is evidenced by the fact that an estimated 3.5–4% of the elements in the earth's crust contain calcium and 2% contain magnesium. Of all elements calcium ranks fifth in abundance, exceeded only by oxygen, silicon, aluminum, and iron. Of course, as with most elements, there are strata of limestone laminated between layers of shale and sandstone that are so deep in the earth's crust as to be inaccessible. In varying amounts calcium is also present in all soils, most water, and all plant and animal life. Human and animal assimilation of it through food is vital to life; inadequate amount cause poor health and bone deformities like rickets in babies. In fact, 99% of all bones and teeth are composed of calcium and phosphorus, with calcium predominant. There are a great many different forms and types of limestone, varying in color, chemical composition, mineralogy, crystallinity, texture, and hardness. There are also other important calcium- and magnesium-bearing rocks and minerals, like gypsum, phosphate rock, serpentine, and fluorspar, that should not be confused with limestone since they are not carbonate rocks, an essential characteristic of limestone, but none of these natural resources are as basic. Next to sand and gravel, limestone, including all of its carbonate forms, is the second greatest tonnage material produced in the United States. But coal should surpass limestone in 1978–1980, spurred by the urgent national objective to use coal in place of scarce oil and gas.

BASIC DEFINITIONS

Lime and limestone are much-abused terms. Often users, and even some sellers, refer to some form of limestone as lime and, less often, to lime as limestone.

Limestone is a general term embracing carbonate rocks or fossils; it is composed primarily of calcium carbonate or combinations of calcium and magnesium carbonate with varying amounts of impurities, the most common of which are silica and alumina. In contrast, *lime*, which is invariably derived from limestone, is always a calcined or burned form of limestone, popularly known as *quicklime* or *hydrated lime*. The calcination process expels the carbon dioxide from the stone, forming calcium oxide (quicklime), and when water is added, calcium hydroxide (hydrated or slaked lime) is created. Although all three of these products have some similarities, using the correct term is important, since there are many pronounced differences. Webster recognizes the above distinction in defining both of these materials.

An analogy to the close relationship of limestone and lime is provided by sulfur and sulfuric acid. The former are the native ores, which in spite of processing are still used in their original chemical composition; the latter are their primary manufactured products, basic chemicals, of different chemical composition. The limestone group consists of the most basic alkalies; sulfur is at the other end of the pH scale—the most basic acid. The uses of these two sets of materials are at the same time totally diverse, complementary, and often interchangeable. There are a sufficient number of overlapping uses for lime to regard limestone as its principal competition. However, from a tonnage standpoint the main competition for limestone is other aggregates, such as sand and gravel, granite, basalt, and so on.

HISTORY

Unquestionably the use of lime and limestone is prehistoric; they are among the oldest materials used by mankind. During the Stone Age, primitive man utilized limestone and other forms of rock to confine fires, construct stone shelters, and make crude tools and weapons. It is conjectured that lime was discovered later in the same age. One intriguing theory on its discovery is that primitive man probably found his slabs of limestone, used for fireplaces, disintegrating into a white, pastelike putty following a hard rain. The stone had been calcined by the heat from his fires, and the resulting quicklime was simply hydrated by the rainwater. The pyramids of the Egyptians, however, are the first recorded use for limestone and employ huge nummulitic limestone blocks and lime along with alabaster (gypsum) for mortar and plaster between 4000 and 2000 B.C. Marble statuary and luxurious wall construction was initiated shortly after this period. Although lime was originally used for construction, it was employed by the Greek and early Roman empires also as a chemical reagent. Xenophon in 350 B.C. records how a ship carrying a cargo of linen and lime "for its bleaching" was wrecked near Marseilles. Cato mentioned the burning of lime in kilns in 184 B.C. The medical use of saturated solutions of limewater was cited by the Roman, Dioscorides, in 75 A.D. The first great highway builders, the Romans, used both limestone and lime extensively. There was even some application and recognition of the virtues of agricultural liming at the time of Christ.

One of the early forms of chemical warfare was the reported gruesome practice of the English of throwing quicklime in the faces of the French, their enemy in a war in A.D. 1217. Shakespeare and earlier English writers, like Layamon, frequently mentioned lime in their writings, prose and plays. European alchemists in the Middle Ages are known to have causticized the potassium carbonate present in wood ashes with lime to produce a crude form of lye as a base for soapmaking.

The first sound technical explanation of lime calcination, including its expulsion of CO_2 gas, was by the British chemist Joseph Black in the eighteenth century. Lavoisier, the French scientist, a few years later confirmed Black's theory and elucidated further on it. Other renowned French scientists—Vicat, Debray, and Le Châtelier—in the nineteenth century are credited with measuring most of the earliest fundamental data, such as the dissociation temperature and pressure incident to calcination as well as evaluating structural limes and mortars for construction.

In the New World lime was one of the earliest manufactured products. After the Spanish settled St. Augustine, Florida, they made lime by burning coquina, a thin shell that abounds in shallow coastal water. Lime plus unburned bits of coquina and sand were used for mortar and plaster in the construction of the first buildings. Later, in the first part of the seventeenth century at Jamestown, Virginia, the English obtained lime by burning oystershells, dredged by hand from the James River estuary. The site of a lime kiln is clearly marked in the restoration of colonial Jamestown. No occurrence of hard limestone existed in these coastal areas. Probably the first settlement to obtain lime from limestone was in Rhode Island, followed by the Quakers in settling Philadelphia and Dutch settlers of the Hudson River valley. Cargoes of lime were shipped by boat from Rockport, Maine, to Boston and later New York City in the early 1800s.

Strangely, many of the ancient civilizations appear *independently* to have discovered lime and perfected their own uses. Some civilizations undoubtedly learned from each other, like the Greeks from the Egyptians and the Romans from the Greeks. But who educated (at that time) such isolated civilizations as the Incas, Mayas, Chinese, and the Mogul Indians? Their ancient applications of lime have been repeatedly confirmed by archaeologists through the artifacts they unearthed. Somehow they all "stumbled" onto it by primitive ingenuity or happenstance. Fragmentary decipherings of their scarce records reveal some barbarous methods of making lime mortar, such as slaking quicklime in barley water, mixing blood from animals into the lime and sand, and so on. Yet some of their edifices stood for 2000–3000 yr, dissheveled from the erosion of time but still intact and often structurally sound. Restoration societies have rescued many of these old structures from desuetude and have remortared their eroded joints with modern cementing materials. Ironically often these modern, scientifically prepared mortars disintegrate in 5–20 yr, requiring repeated expensive maintenance, in contrast to the thousands of years that the ancients' bizarre mortars have endured. Possibly modern civilization has not advanced in some respects as much as we think.

CHAPTER TWO

Formation and Properties of Limestone

ORIGIN

In defining and describing limestone and its properties more emphasis is placed here on its physical and chemical than on its geological characteristics.

This most important and abundant of all *sedimentary* rocks that are employed commercially is usually of organic origin.[1] Fossiliferous, marine sediments in oceans and fresh bodies of water, consisting of shells and skeletons of plants and animals, were gradually accumulated through deposition, layer on layer, to form in some instances massive beds of limestone. Some of this sediment was deposited by natural chemical reactions, namely, the infinitesimally slow dissolution of calcium carbonate fossils through the solvent action of carbon dioxide, forming calcium bicarbonate, which was subsequently reprecipitated in carbonate form. Sometimes this precipitation was indirect, with plant and animal organisms acting as the intermediary. Direct precipitation of the carbonate through a saturated solution was caused either by an increase in temperature, which reduces the solubility of the calcium carbonate, or evaporation. Originally the fossils were formed by gradual assimilation of the carbonate as a bicarbonate from the seawater, inducing a very slow but inexorable buildup of the shell or skeletal structure. On the demise of the organism its shell, of almost pure calcium carbonate, remained as a nucleus to perpetuate the preceding phenomenon. It is a true reversible reaction, with dissolution and precipitation in approximate equilibrium.

Huge coral reefs are gradually accumulated in this manner over thousands of years, and in the millions of years of geologic ages that have reshaped the geography of the world, they have formed mountains in the interior of continents. Many mountains in Europe and North America are coralline in origin. Pressure and heat have supplemented chemical precipitation in consolidating the minute carbonate particles into these imposing compact masses.

In a similar manner, inland streams and rivers are carriers of soluble calcium bicarbonate through the leaching effect of rainwater percolation through soils in watersheds and the gradual dissolution of carbonate rocks

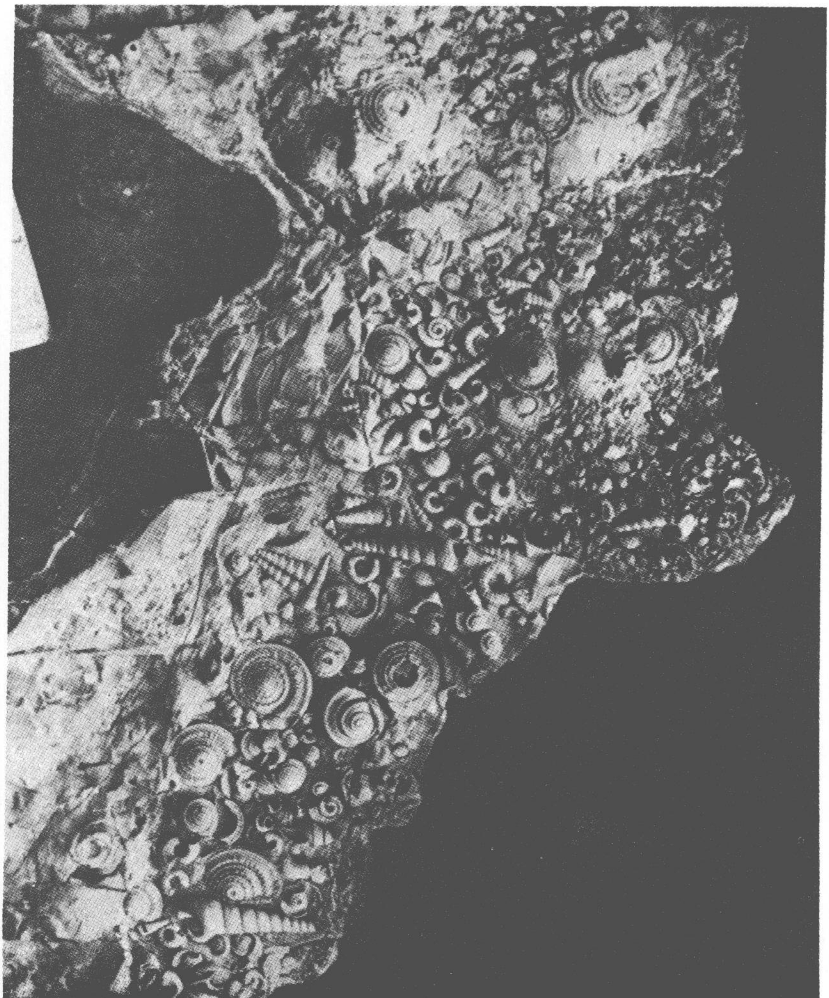

Fig. 2-1. Lower Ordovician limestone from Missouri displaying wide assortment of fossils in unusual clarity: gastropods, crinoids, brachipods, pelecypods, and other prehistoric shell and vertebrae of marine organisms. (Courtesy, U.S. National Museum Collections.)

as the streams cascade over them. The coreactant, carbon dioxide, must be present to effect this phenomenon. Most soils contain at least traces of calcium and magnesium; some are highly calcareous. Such soluble calcium is the most common type of mineral hardness that exists in varying amounts in freshwater bodies.

The texture and crystalline form of the limestone depends on the size and shape of the calcareous particles or grains that are deposited. Usually this deposition is contaminated with varying amounts of impurities, like silica, that through time become an intimate part of the stone, seemingly cemented to the carbonate particles. Generally the purest limestone formations occur more often in the thickest masses or beds of up to several hundred feet thick. However, frequently these thick beds contain strata of relatively impure stone. Contamination of the stone with soil usually occurred at the commencement of deposition, but in some instances impurities were absorbed through pores and interstices during deposition. These impurities occur both vertically and laterally in the bed, but usually a change in purity is much more gradual laterally than vertically.

The calcareous sediment may remain relatively soft, like chalk or marl, or it may be metamorphosed through high temperature and fused into a highly crystalline form, such as marble. Examples of limestone that are not of organic origin include stalactites and stalagmites in caves and some oolitic limestone, travertine, and calcareous tufa. However, the presence of fossils in varying degrees is apparent in most commercial limestone, and this enables the geologist to determine from which geologic age it was derived. Often the prehistoric fossils are found intact in the stone in an almost perfect state of preservation (Fig. 2-1).

The other common constituent of limestone, magnesium carbonate, is formed in a related manner, but it is also theorized that much of it was created by chemical displacement of calcium with magnesium salts that abound in seawater.[3,4] Decomposition of serpentine (hydrous magnesium silicate) is another possible origin.

MINERALOGY

All geological authorities are in agreement that limestone may be composed of four minerals,[5,6] exclusive of impurities, having the following physical characteristics:

CALCITE. $CaCO_3$; rhombohedral; molecular weight—100.1; specific gravity—2.72; molecular volume—36.8; hardness—3; may be colorless, but often variously tinted by impurities.