

J.A.H. Oates

Lime and Limestone

Chemistry and Technology,
Production and Uses

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Preface

The Lime and Limestone Industries are dynamic industries, with new production methods, new products and new uses continually being developed. They are particularly interesting and challenging, because of the wide variety of products made, and the even wider range of applications.

Both industries are being profoundly affected by the general requirement to improve environmental performance. On the one hand, this presents a challenge, which is leading to heavy capital investment, mergers and even closures. On the other hand, it presents new opportunities to supply environmental control products.

Another major development, which affects both producers and customers, is the widespread reduction of manning levels. While this increases productivity and profitability, it places greater pressures on everyone to cope with less technical assistance than in the past. In consequence, there is a need to develop and broaden individual expertise, and to have improved access to up-to-date information.

One of the aims of producing this book is to present an integrated perspective of the Lime and Limestone Industries, and to indicate how they have been, and still are being shaped by customer-led requirements.

- It describes the many complex interactions, relating to product quality, that exist between suppliers and customers, both within and outside the Industries. This should help production personnel in the Industries to appreciate the impact of their actions and decisions on their customers.
- For users of lime and limestone products, it seeks to give an understanding of the factors which affect product quality and the ways in which the products interact with the processes in which they are used. It also indicates how the Lime and Limestone Industries control product quality, and what actions might be taken to tailor quality for a particular application.
- It may also provide a basis for constructive dialogue between suppliers and customers, thereby facilitating the development of new and improved products.

The formation of the European Union is leading to the preparation of a large number of application-specific Standards, specifying both product quality and test methods. Combining the diverse products and practices used in so many countries, each with its own traditions, is proving to be both demanding and stimulating. While many relevant CEN Standards have already been published, many others are still in preparation at the time of going to press.

The structure of the book and of individual chapters has been designed to present the information in a logical way that gives as coherent an account of the Industries as possible. Some chapters, such as quarrying and the processing of limestone, have much in common with other segments of industry. In such cases, the text has been kept relatively short and reference has been made to more specialist publications. In other chapters, such as the production of lime, and its use in building and construction, the subjects are so broad that it is beyond the scope of this publication to do them justice. In such cases, a brief description has been given, supplemented by a relatively large number of references for further reading. Annex 2 contains a list of journals and reference books of interest to the reader wishing to up-date, or broaden his knowledge of a particular subject.

During the past four decades that the author has been involved with both Industries, there have been many profound changes. No doubt the rate of change will accelerate, bringing new challenges and opportunities. If this work can, in some small way, help those involved to meet those challenges and to exploit the opportunities, it will have achieved its objective.

Buxton, Derbyshire, England
March, 1998

J.A.H. Oates

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I particularly welcomed the contributions, help and encouragement from scores of people throughout the world (in the Lime and Limestone Industries, as well as suppliers to and customers of those Industries), who generously shared their knowledge and expertise, and provided diagrams and photographs. I hope that the finished product does justice to their inputs.

With the help of the above-mentioned people, and others who have assisted with producing diagrams, typing and proof-reading, I have endeavoured to produce a text that is as comprehensive, accurate and up-to-date as possible. However, the responsibility for any omissions or errors is mine alone. Finally, I would like to thank the publishers for having the courage to commission me, and faith in my ability to deliver the required product.

Tony Oates

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1 Introduction

1.1 General

- *Limestone* is a naturally occurring mineral that consists principally of calcium carbonate. Part of the calcium carbonate may have been converted to dolomite by replacement with magnesium carbonate as a secondary component (up to 46 % by weight). Many limestones are remarkably pure, with less than 5 % of non-carbonate impurities. Limestone is found in many forms and is classified in terms of its origin, chemical composition, structure, and geological formation. It occurs widely throughout the world, and is an essential raw material for many industries.
- *Quicklime* is produced by the thermal dissociation of limestone. Its principal component is calcium oxide. Its quality depends on many factors including physical properties, reactivity to water and chemical composition. As the most readily available and cost-effective alkali, quicklime plays an essential part in a wide range of industrial processes.
- *Slaked lime* is produced by reacting, or “slaking” quicklime with water, and consists mainly of calcium hydroxide. The term includes *hydrated lime* (dry calcium hydroxide powder), *milk of lime* and *lime putty* (dispersions of calcium hydroxide particles in water). Slaked lime is widely used in aqueous systems as a low-cost alkali.

The generic term, *lime* includes quicklime and slaked lime, and is synonymous with the term *lime products*. “Lime” is, however, sometimes used incorrectly to describe limestone products (e.g. agricultural lime): *this is a frequent cause of confusion*.

Because the quarrying of limestone and the production of quick- and slaked lime are long-established industries, they have generated many traditional terms. These are explained in the Glossary of Terms (Annex 1).

1.2 Importance of Lime and Limestone

1.2.1 Limestone

Because limestone deposits are widely distributed throughout the world, a high proportion of humanity has ready access to the material. No reliable figures

appear to have been published for the world-wide use of limestone, but the author estimates that it is about 4,500 million tonnes per annum (tpa).

In most countries, the major uses of limestone are as an aggregate in construction and building and as the primary raw material for the production of cement.

The *amount* of limestone used in construction and building varies widely from one locality to another and depends on its availability and cost relative to other aggregates, such as gravel and crushed hard rocks. In the USA, for example, limestone sales amounted to about 800 million tonnes in 1994 — about 72 % of the crushed rock sales.

The *proportion* of limestone quarried that is used in construction and building is also affected by availability and cost. In many countries, the level is around 40 to 50 %, whereas in the USA and the UK, where limestone is widely available and relatively inexpensive, the level is over 70 %.

While limestone is not an essential raw material for the production of cement, it is generally the cheapest source of calcium oxide. On the basis of the global production of cement, the limestone used in its production probably amounts to about 1,500 million tpa, or one third of the total extracted.

Some limestones contain over 95 % CaCO_3 . Such “chemical grade” materials are particularly suitable for lime production, flue gas desulfurisation and a range of other processes. The quantities involved, however, amount at most to a few percent of the total extracted.

Very finely divided limestones (whiting) and precipitated calcium carbonate are used as fillers. While the tonnages involved are minute when compared with the total, they are very high added-value products that play important roles in a wide range of industries.

The main market outlets for limestone products are outlined in chapter 7 and are described in more detail in chapters 8 to 12.

1.2.2 Lime

As mentioned in section 1.1, lime is the least expensive and most widely-used alkali. The global production of lime products is believed to be over 200 million tpa. This amount includes an estimated production in China of about 20 million tpa (although much higher rates for that country have been quoted).

Lime is one of the most heavily used chemicals. In the USA, for example, about 15 million tpa of lime are produced, making it the fifth largest-selling chemical on a tonnage basis (the four chemicals with larger sales are sulphuric acid at 40 million tpa, nitrogen at 36 million tpa, with oxygen and ethylene both at 17 million tpa).

In most industrialised countries, the major uses of lime products are in steel-making, and the construction and building industry. In the European Union, for example, some 38 and 36 %, respectively is used in those industries.

The remaining lime is used in a large number of industries. The main market outlets are outlined in chapter 25 and described in more detail in chapters 26 to 32.

1.3 History [1.1–1.3]

1.3.1 Limestone

Limestone has undoubtedly been used since the Stone Age, although primitive man probably found uses for it before that time. The first records relate to the Egyptian Second Dynasty (some 5,800 years ago), when it was employed in the construction of the Giza Pyramids. Marble, a highly crystalline form of limestone, was used by the Greeks shortly after this period for statues and the decoration of buildings. Limestone was widely used by the Romans for building roads.

Over the centuries, limestone has been used extensively as an aggregate in building and construction. It has been used as aggregate in lime-based concrete since Roman times, and, more recently, in cement-based concrete. Although limestone cannot readily be dressed, it has been used extensively in building in both the rough-hewn form and as cut dimension stone.

The benefits of “liming” soils with marls and soft chalks was known to the Romans in the first century A.D. Pliny reported that the Ubians, north of Mainz, used “white earth” (a calcarious marl) to fertilise their fields.

The high purity of some limestones has been exploited for many centuries by the lime-burning, glass-production, and metals-refining industries. The development of Portland cement in the 19th century caused a major expansion in the demand for limestone, both as a raw material and as an aggregate. This expansion permitted the exploitation of some of the softer and/or less pure deposits such as chalk and marl.

1.3.2 Lime

Some of the earliest evidence for the use of lime dates back some 10,000 years. Excavations in Cajenu in Eastern Turkey, uncovered a Terrazzo floor, which had been laid with lime mortar. That site dated from 7,000 to 14,000 years ago. In some cases, the lime had been used in conjunction with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which raises the question as to whether the lime had been used as a binder in its own right, or had arisen as a result of contamination of the gypsum with calcium carbonate.

Nevertheless, there is firm evidence of the use of lime in the Near East, dating from about 8,000 years ago, and in Lepenski Vir, in the former Yugoslavia, a floor, dated 6,000 B.C., was excavated in the 1960s. That consisted of a type of mortar made from lime, sand, clay and water.

Lime stabilisation of clay was used in Tibet, over 5000 years ago, in the construction of the pyramids of Shersi. It was also used in conjunction with limestone by the Egyptians in the construction of the pyramids and by the Chinese when building the Great Wall.

By about 1,000 B.C., there is evidence of the wide-spread use of quick- and hydrated lime for building by many civilisations, including the Greeks, Egyptians, Romans, Incas, Mayas, Chinese, and Mogul Indians.

Perhaps the earliest excavated lime kiln was at Khafaje in Mesopotamia which was dated at about 2450 B.C. A battery of six lime kilns, excavated at a legionary site at Iversheim, Germany, showed that the Romans produced lime in quantity on military sites. The production of lime in kilns was mentioned by Cato in 184 B.C. Pliny the Elder (ca. 17 A.D.), in his "Chapters on Chemical Subjects" described the production, slaking and uses of lime, and stressed the importance of chemical purity.

The Romans employed hydraulic lime and lime-pozzolan mixtures in many construction projects, including the Appian Way. They developed the technology of lime burning and the use of mortar, cement and concrete, using lime as the binder. They built the first "lime factories", which were operated by legionaries and managed by a "Magister Calcariarum".

Lime was also well known to the Romans as a chemical reagent. In 350 B.C. Xenophon referred to the use of lime for bleaching linen. Almost all of the Mediterranean peoples were familiar with lime as a paint. Lime was used for tanning leather, and was mixed with organic substances to produce putty and glue. The Assyrians described the importance of lime in their recipes for glass. Lime was also used in glazes for pottery. A medical use of lime was recorded by Dioscorides in 75 A.D.

Little is known regarding the condition of the lime industry in medieval times, but a knowledge of its properties and its use for building purposes is reflected in the writings of the day. For example Trevisa (1398) wrote "Whyle lyme is colde in handlyng it conteyneth prevely wythin fyre and grete hete." "Lyme Kilns" and "Lymbrenners" are also mentioned in many ancient church and municipal records.

Quicklime was used in the Middle Ages for offensive purposes in war — there are records that the English hurled it in their enemies' faces at a naval battle in 1217. It was also used by alchemists for "causticising" the alkali metal carbonates in wood ashes and for other purposes, but it was so familiar a material that it was seldom thought to be worth recording. During the 1400s, the use of lime in building spread throughout Europe.

In the 1700s Joseph Black gave the first sound technical explanation of the calcination of limestone including the evolution of carbon dioxide. Lavoisier confirmed and developed Black's explanation. In 1766 De Ramecourt published a detailed account of "the art of the lime burner", which described the design, operation and economic aspects of limestone quarrying and lime burning.

Debray, in 1867, carried out the first measurements of the dissociation pressure of calcium carbonate. He heated Iceland Spar in a tube to the temperature of boiling mercury, sulphur, cadmium and zinc (357, 445, 767, 907 °C respectively). He found no decomposition at the first two, but measurable pressures at the boiling points of cadmium and zinc. The first exact measurements of the dissociation pressure were made by Le Chatelier in 1886.

In 1935 Searle [1.2] described some 40 designs of lime kiln. Since then, a large number of designs have been developed. A great variety of designs are still operated, but only a limited number continue to be commercially viable. The more important of these are described in chapter 16.

1.4 References

- [1.1] R.S. Boynton, "Chemistry and Technology of Lime and Limestone", John Wiley & Sons, 1980.
- [1.2] A.B. Searle, "Limestone and its Products", Ernest Benn, 1935.
- [1.3] N.V.S. Knibbs, "Lime and Magnesia", Ernest Benn, 1924.

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Part 1 Production of Limestone

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2 Formation, Classification and Occurrence of Limestone

2.1 Formation of Limestone

2.1.1 Origins of Calcium Carbonate

The chemical components of calcium carbonate — dissolved calcium ions and carbon dioxide — are widely distributed. Calcium is the fifth most common element in the earth's crust (after oxygen, silicon, aluminium and iron). It was extracted from early igneous rocks by the combined effects of erosion by the weather and corrosion by acidic gases (oxides of sulfur, oxides of nitrogen and carbon dioxide dissolved in rain water). Carbon dioxide makes up about 0.03 % by volume of the earth's atmosphere and is dissolved in both fresh and sea water. Combination of dissolved calcium ions and carbon dioxide resulted in the sedimentary deposition of calcium carbonate, which was subsequently converted into limestone rock. Early limestones (Precambrian — Table 2.1) are believed to have been deposited as precipitates of CaCO_3 , and/or as a result of the biochemical activity of very simple organisms, such as bacteria.

Table 2.1. Table of geological periods

Era	Period	Maximum age 10^6 years
Cenozoic	Quaternary	1
	Tertiary	75
Mesozoic	Cretaceous	135
	Jurassic	180
	Triassic	225
Palaeozoic	Permian	270
	Carboniferous	350
	Devonian	400
	Silurian	440
	Ordovician	500
	Cambrian	600
Precambrian	—	> 600

2.1.2 Carbonate Sedimentation

The sedimentation of calcium carbonate occurs by two mechanisms — *organic* and *inorganic*. The *organic* route involves a wide variety of organisms, which build

shells, skeletons or secrete carbonate. The *inorganic* route involves the direct precipitation (or crystallisation) of carbonate.

Most commercially viable deposits of carbonate were formed by the *organic route*. Carbonate-secreting organisms (e.g., bivalves, gastropods, brachiopods, corals, sponges, bryozoans, echinoderms, ostracods, foraminifera and various algae) have existed in all of the world's seas. The factors which controlled the rate of carbonate production (calcium, magnesium and carbon dioxide concentrations, temperature, salinity, water depth and turbidity) resulted in most of the thick deposits being produced in shallow seas (i.e., in the photic zone) between 30° north and south of the equator. Such deposits may now be outside that band as a result of continental drift.

At least eight mechanisms can cause the surface layers of the sea to become super-saturated with respect to aragonite, calcite and dolomite [2.1]. The rate of formation of dolomite, however, is very much slower than those of calcite and aragonite. As a result, while some organic species produce aragonite structures and others make calcite, none produce dolomite directly. The aragonite structures are generally very low in magnesium (typically less than 0.5 % MgCO_3). Depending on the organism and on the chemistry of the water (principally the ratio of calcium to magnesium), calcite structures are generally either low in magnesium with less than 4 % MgCO_3 , or high with, typically, 11 to 19 % MgCO_3 .

The above process, coupled with the fact that most carbonate-secreting organisms only thrive in clear waters — remote from rivers carrying significant amounts of solids washed from the land — accounts for the remarkably high purities of many carbonate deposits, which often exceed 98 % of calcium plus magnesium carbonates.

Carbonate sediments are also produced in a similar way by organisms in inland waters, but the resulting deposits are generally not as extensive, nor as commercially important as those produced in the marine environment.

Inorganic precipitation of calcium carbonate occurs from both sea and inland waters (as used by geologists, “precipitation” refers to the relatively slow process of crystal growth on surfaces). This route has resulted in some commercially significant deposits, the most common of which are oolitic limestone and travertine (see section 2.2.1). Some minor dolomite sediments have been formed by direct precipitation from sea and lake waters.

2.1.3 Sedimentary Environments

Most carbonate sediments were formed in situ, in shallow water, accumulating where the grains were formed, or were subjected to limited transport, for example down a gently-sloping sub-tidal shelf. Descriptions of depositional environments can be found in the literature [2.1, 2.2]. The major environments are illustrated in Figure 2.1.

The variety of environments (which includes beaches, tidal and sub-tidal flats, lagoons, reefs, shelves, slopes and deep basins) gave rise to many types of deposit, whose characteristics are related to the particular environment in which they were formed [2.1–2.4].

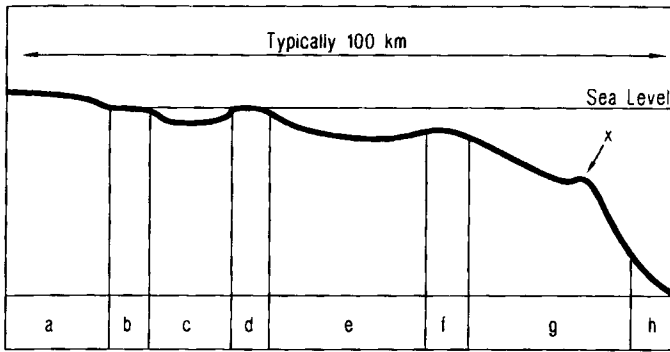


Figure 2.1. Composite diagram of major carbonate depositional environments (a) sub-aerial karst; (b) tidal flat; (c) lagoon; (d) barrier reef; (e) shelf; (f) shelf-margin reef; (g) slope with reef mound (x); (h) deep basin

2.1.4 Diagenesis

Diagenesis is the conversion of sediments into rock by organic, physical and chemical processes. Six main processes have been identified for limestone [2.3] – microbial micritization, cementation, neomorphism, dissolution, compaction and dolomitization.

- **Microbial micritization.** Many organisms bore into carbonate deposits. The most important one is cyanobacteria, but others include cliona sponges, bivalves, polychaetes and fungi. The bore-holes become filled with a calcium carbonate structure called micrite, which typically forms an envelope around the skeletal grains.
- **Cementation** results from the passage of water, super-saturated with respect to calcite, through porous limestone deposits, leading to the growth of calcite crystals in the pores, thereby binding together the components of the deposit. The most common cement in medium- to coarse-grained limestones is *sparite*, or calcite spar (which fills interstitial spaces in fine-grained limestones). Silica, in the form of quartz crystals, also acts as a cement in some limestones.
- **Neomorphism** involves recrystallisation. As aragonite has a higher solubility in water than calcite, it progressively recrystallises over time to produce a very low-magnesium calcite. Calcite recrystallises into larger crystallites – in doing so, under many conditions, the magnesium in high-magnesium calcites slowly dissolves, leaving low-magnesium deposits (but see dolomitisation below).
- **Dissolution** generally occurs when unsaturated ground waters flow through deposits. On the surface it causes typical karst scenery. At greater depths, it produces caves, as well as secondary porosity. The latter increases the capacity of a deposit to act as a reservoir for oil, water, or gas.