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BUILDING LIME

ITS PROPERTIES, USES, AND MANUFACTURE[1]

by

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[1] The views and opinions expressed in this paper are those of the authors and do not necessarily reflect the views of the secretariat of UNIDO. The document is presented as submitted by the authors without re-editing.

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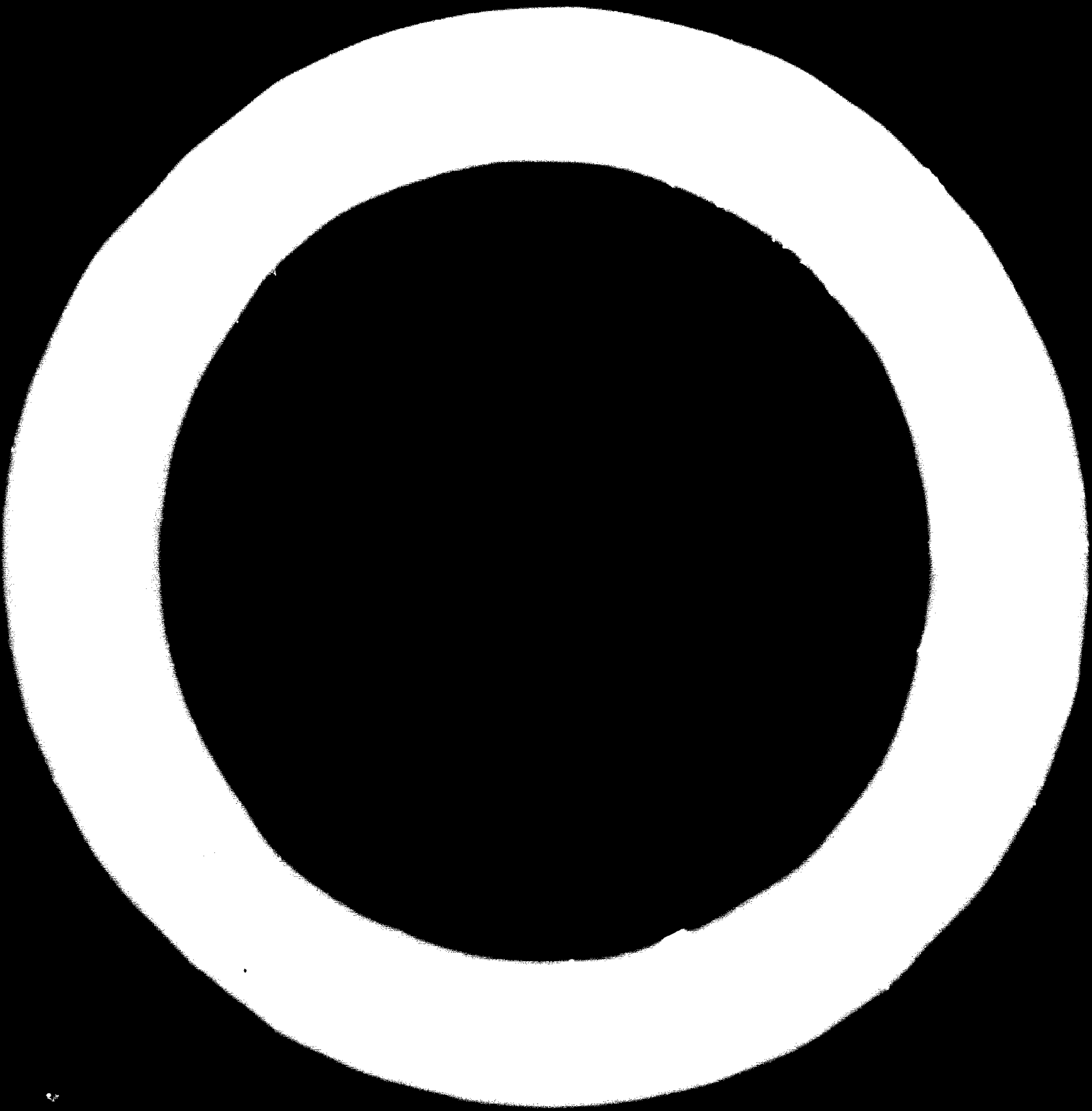

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Foreword

This paper is reproduced in the same terms and form as presented by the authors. As will be observed, the paper deals largely with modern technology evolved in the advanced countries. The introduction of such methods is both feasible as well as timely in several developing countries.

However, there are a few countries in which, it is believed, such mechanized processes will not be suitable. Accordingly, it is proposed to issue a second part of this Paper, dealing more extensively with the simpler, labour-intensive methods of manufacturing building lime.

Part III of this paper will cover The Winning and Beneficiation of Calcareous Materials.

Division of Industrial Technology
United Nations Industrial Development Organisation

PREFACE

This paper deals specifically with building lime - its properties, uses, methods of manufacture, and economic factors, such as costs, involved in its manufacture. It is intended that this information will help overseas countries to develop their own building lime industry. Due to its high plasticity, water retention, and bonding power, building lime offers so many advantages in construction - for mortar, plaster, masonry units, etc., that every country should have adequate supplies available at reasonable cost.

No country, however, should enter the lime business solely to produce building lime. Lime is also a vital chemical and agricultural material, having a multitude of uses. This has to be emphasized at the outset, because the type of plant to be selected will vary, depending on the type of lime to be produced. For example, in the United States of America the majority of building lime is made from high-purity dolomitic limestone, but as the uses for dolomitic lime are not as extensive as high-calcium lime, it may be better to utilise a high calcium-limestone, particularly when calcining and hydrating techniques can be adapted to enhance the lime's plastic properties.

In addition to structural lime, other important potential lime uses which developing nations should consider are: stabilization of clayey soils for low-cost road base construction, agricultural liming and insecticides, water and sewage treatment, smelting of ores, manufacture of sand-lime brick or stabilised earthen brick, whitewash, leather tanning, and sugar refining. Lime can also be used as a major industrial raw material, particularly in manufacturing steel, alkalis, calcium carbide, pulp and paper, and aluminum. For these industrial uses, lime's chemical properties are much more significant than its physical (plastic) properties.

Although throughout this paper the main emphasis will be placed on ways to produce good building lime, the authors will not lose sight of the production of satisfactory lime for the host of other potential uses in the developing nations.

Necessarily, this treatise encompasses only a guideline type of presentation on building lime; it is not a manual on how to build or operate a lime plant. For more detailed information on these aspects, the reader is referred to several valuable books on the subject, as well as to trade journals such as "Pit and Quarry" (Chicago, Illinois), "Rock Products" (Chicago, Illinois), "Cement, Lime and Gravel" (London, England) and "Zement-Kalk-Gips" (Wiesbaden, Germany).

CHAPTER I - INTRODUCTION

What is Lime? The principal raw material for making lime is limestone, a sedimentary rock consisting chiefly of calcium carbonate ($CaCO_3$); it may also be made, however, from dolomitic limestone (which also contains magnesium carbonate), and from chalk, marble and marine shells. After crushing and screening, the clean calcareous material is calcined in kilns at about 2000°F, driving off carbon dioxide (CO_2), forming quicklime (CaO). Following cooling, this product can be used directly as building lime (after slaking on the job) and many other purposes; or it can be hydrated at the plant through the addition of sufficient water to form calcium hydroxide ($Ca(OH)_2$). This second product can also be used for building purposes, as well as for many other uses.

History of Lime - It has been surmised that lime was first discovered during the latter part of the Stone Age, before recorded history. One popular and credible theory is that primitive man, who had previously learned to use stone to construct crude shelters, make tools and weapons, and to confine his fires, "stumbled on" lime by chance. Blocks or slabs of limestone employed in building his crude fireplaces were calcined into lime (at least partially) by the heat from his fires. Later, rain caused the lime to hydrate (slake) into a plastic-like putty, resulting in disintegration of the original limestone. When this plastic putty was used "neat", or crudely mixed with a sandy soil, he found that its adhesive, plastic qualities were useful in bedding units of stone together securely into monolithic-like walls, representing possibly the earliest forms of masonry. Also, he found that when this wet plastic mass was spread over the rough surface of a rock assemblage that, after drying, it adhered well and formed a relatively smooth surface; thus, plastering was probably first conceived. Consequently, lime is one of the oldest inorganic building materials, only antedated by stone and mud.

Its first recorded use was in the construction of the Egyptian pyramids, about 4000 B.C., as a mortar material. Archaeologists have documented other ancient applications of lime in the form of pieces of two-coat lime plaster containing hair, which was used as a backing; the plaster was unearthed from the ruins of the Palace of Knossos in Crete, built about 1500 B.C. From the Cretan civilisation, it spread to the Greek era of Homer and from there to the Romans.

Lime is cited in several passages of the Old Testament, and the Great Wall of China was largely laid with lime mortar. However, it was really the Romans who fully developed and exploited lime's structural uses.

Before Christ, a military engineer under Julius Caesar - Vitruvius - wrote specifications on lime quality and its uses for mortar, plaster and road construction. During this period, lime manufacture must have flourished in many parts of Rome, and even in some of its outlying semi-civilized territorial possessions. Proof that the Romans introduced it during their occupation of England is found in some old Roman ruins (100-200 A.D.). However, probably the most significant Roman development with lime was their discovery that a mixture of quicklime, volcanic ash and aggregate would harden under water and develop higher strength than a straight lime-sand mortar. This hydraulic or pozzolanic characteristic, imparted by lime and volcanic ash, led to the development of so-called "Roman cement" or lime-pozzolans (artificial highly hydraulic lime). This earliest form of cement was mixed with coarse and fine aggregates to yield a crude type of concrete for slabs, pavements, piers, jetties, and also (with sand alone) for mortar. Thus, the renowned Appian Way contained lime in three of its four courses (36" total pavement thickness).

With the fall of the Roman Empire, much of this technology was lost to mankind, and construction deteriorated badly in the ensuing Dark Ages. However, a surprising amount of the old Roman edifices that incorporated lime mortar and lime-pozzolan mixtures, and which eluded the ravages of the Hun and Vandal, endured for many centuries, some even up to the 20th century, weather-beaten, but still structurally sound, providing mute testimony to its durability.

With the Middle Ages and Renaissance periods, its use as pure and hydraulic (impure) limes or lime-pozzolan mixtures was revived. In fact, until the latter part of the 19th century, when portland cement was first introduced, these materials comprised the only available cementitious materials, at least for exterior use. Consequently because of this prehistoric heritage, and the fact that limestone, the raw material for lime, occurs at least to some extent in nearly every country in the world, it is not surprising that lime in varying degrees is (and has been) used over the last hundred years for building construction in all developed and most developing countries.

Other Lime Uses - Although lime's first historical applications were for construction, its alkaline nature and certain useful chemical properties gradually led a myriad of other functions, largely identified with the industrial revolution and the 20th century creation of vast chemical process industries. As a result, in the United States, Canada, Japan and the most industrialized European nations, a greater tonnage of lime is currently employed as a chemical alkali (calcium oxide or hydroxide or calcium-magnesium oxide or hydroxide) than as building lime. Its most important chemical applications are for fluxing (purifying) steel in open hearth and oxygen converter furnaces; as a causticization agent in sulfate paper pulp, aluminum, and alkali chemicals manufacture (soda ash and caustic soda), to make calcium carbide (an important source of acetylene), to assist in the beneficiation of non-ferrous ores, and to make the important intermediate, magnesia for magnesium metal manufacture; to purify water by coagulation and sterilization, to soften potable and industrial process water; in beet and cane sugar refining; for neutralization of acids in many chemical processes, for industrial trade waste treatment; to manufacture autoclaved calcium silicate building products (brick, block, and insulation, in which lime reacts with silica to form calcium silicates, strong cementing compounds); de-hairing hides in leather tanning; and many other lesser functions. A large new use in soil stabilization, called "lime stabilization" (in road base and sub-base construction) has been developed in the United States since World War II, and is spreading gradually to other countries throughout the world. There is also extensive use of ground quicklime and hydrated lime for agricultural liming of soils, although the predominant liming material is pulverized limestone.

Types of Lime - Besides comprising quick and hydrated types, lime is also classified according to its chemical composition, particularly with respect to its relative proportion of calcium and magnesium oxides (CaO and MgO). If the quicklime is composed primarily of CaO and contains less than 5% MgO, it is further defined as a high calcium variety; if it contains between 5 and 20% MgO, it is a magnesium type; and if the MgO content is between 20 and 41%, it is a dolomitic lime. Calcined dolomite itself has about 58% CaO and 42% MgO. The same relationship and nomenclature on these basic types of quicklime also apply to hydrated lime.

Table 1 summarizes the above information on lime types, and Table 2 presents typical ranges of chemical analyses, including CaO, MgO, and the major impurities.

Table I

Summary of Limes

Common Name	Main Chemical Ingredient	Chemical Formula
High calcium quicklime	Calcium Oxide	CaO
High calcium hydrated lime	Calcium Hydroxide	$Ca(OH)_2$
Magnesian quicklime	Calcium Oxide	CaO *
Hydrated magnesian lime	Calcium Hydroxide	$Ca(OH)_2$ *
Dolomitic quicklime	Calcium, Magnesium Oxide	$CaO \cdot MgO$
Dolomitic lime monohydrate	Calcium Hydroxide, Magnesium Oxide	$MgO \cdot Ca(OH)_2$ **
Dolomitic hydrated lime	Calcium, Magnesium Hydroxide	$Ca(OH)_2 \cdot Mg(OH)_2$

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* Contains 5 to 20% MgO

** Contains 5 to 10% $Mg(OH)_2$

[Ref.]

Table II

Typical Ranges of Chemical Analyses of Limes

CaO	92.00 - 98.00	76.00 - 92.00	54.00 - 65.00
MgO	0.30 - 3.00	5.00 - 20.00	30.00 - 41.00
SiO_2	0.20 - 2.50	0.25 - 3.00	0.10 - 2.50
Fe_2O_3	0.10 - 0.50	0.10 - 0.50	0.05 - 0.50
Al_2O_3	0.10 - 0.70	0.10 - 1.00	0.10 - 1.00
CO_2	0.50 - 3.00	0.50 - 3.00	0.25 - 2.00
SO_3	0.01 - 0.10	0.01 - 0.10	0.01 - 0.10
P	Trace - 0.05	Trace - 0.05	Trace - 0.05

[Ref.]

Building Lime - As discussed earlier, *building lime* may be either the quick or hydrated type; it may also be high-calcium, magnesian, or dolomitic. However, the use of this term might be restricted locally to the hydrated types in some areas or countries where only hydrated lime is employed for construction purposes. The only possible distinguishing characteristic of building lime is that the putty produced from it has high plasticity and water retentivity, two physical properties that not all limes, even the purest types, always possess. Many building limes (of relatively high lime assay) may also be employed for many or most chemical uses of lime, except where only one type (high calcium or dolomitic, etc.) is specified. Building limes can be freely employed for agricultural liming or road stabilisation. By the same token, many so-called chemical limes will qualify as satisfactory to good building limes. On the other hand, unrefined hydrated limes, like agricultural lime hydrate, or poorly burned quicklimes generally will not develop adequate plasticity for structural use. Consequently, the term building lime is *relative*, dependent largely on the physical properties of the lime, rather than on its chemical properties; and its quality evaluation is established empirically by building artisans rather than by laboratory tests.

The above discourse is definitive for the relatively pure or "fat" limes with at least 92% quicklime and 95% total oxides (non-volatile basis); but it does not include the impure types, called *hydraulic limes* of widely varying degrees of hydraulicity. Unlike the above pure types, hydraulic limes are derived from the calcination of impure calcitic limestones that contain 8 to 23% silica and alumina, largely the former, as impurities. These limes will develop greater strength and set faster than "fat" limes, but generally they do not possess as much plasticity or water retentive qualities. When pure limes are gauged with a small amount of portland cement (20 to 40% of the lime by volume), they will at least equal and usually exceed the strength and rate of set of the hydraulic limes. Also, unlike the pure building limes, the hydraulic types can only be employed for structural purposes; there is virtually no other possible application. As a result, they do not offer as much marketing versatility as the pure limes.

The consensus of opinion is about divided on whether hydraulic lime is a type of building lime or not. In the United States it is not regarded as such, but in some European countries, like France and Germany, it is considered as a segment of the building lime family. Certainly those hydraulic lime manufacturers who blend it with portland cement and/or pozzolans should not be regarded as building lime producers because of the proprietary character of their material. A common classification of hydraulic limes is as follows: weakly hydraulic, moderately hydraulic, and eminently (or highly) hydraulic.

Since the term "building lime" is often not sufficiently definitive, more specific terms are employed for more precise delineation. Many of these terms are repetitious and overlapping. The following are in common use and are described briefly:

Autoclaved lime is a special, premium-priced form of highly hydrated dolomitic lime, largely utilized for structural purposes, that has been hydrated under pressure in an autoclave. It develops plasticity quickly without soaking and can be introduced as a dry powder directly into the mixer with the other mortar ingredients.

Fat lime connotes a pure lime, quick or hydrated, that yields a plastic ("fat") putty or mortar, distinguishing it from an impure or hydraulic type or other limes of inferior plasticity.

Finishing lime is a hydrated lime used expressly for the finish coat in plaster or stucco. It usually is a special, highly refined type of hydrate that commands a premium price. It is adaptable for any structural application.

Lime putty is a form of lime hydrate in a wet, plastic paste form that contains about 20-30% free water.

Lump lime is a physical shape of quicklime, 2½" to 10" in size, that is produced from vertical kilns. It must be slaked into a putty and soaked for 16-24 hours before use.

Mason's lime is a hydrated lime used in mortar for masonry purposes; it may be highly refined or of ordinary quality.

Pressure hydrate is synonymous with autoclaved lime and is the most common variety of ASTM-designated Type S hydrated lime.

Pebble lime is a physical shape of quicklime, ¼" to 2½" in size, that is derived from rotary or special kilns, or by crushing lump lime.

Pulverized lime is a finely comminuted quicklime passing 100% through a No. 20 mesh sieve and 85-95% through a No. 100 mesh screen. It is made by grinding any size of quicklime, slaking it into a putty, and aging it for 12 to 24 hours before use.

Ready-mixed lime mortar is a factory-proportioned mixture of lime, sand, and water in mortar form, ready for use in construction, and is generally produced at central mixing plants, similar to ready-mixed concrete operations.

Roman lime is generally synonymous with highly hydraulic hydrated lime, but it can also refer to a lime-pozzolan, an artifically compounded mixture.

Slaked lime is a hydrated form of lime, either a dry powder or putty.

Type N hydrated lime (also called "normal" hydrate) is an ASTM designation, meeting certain specified provisions for structural uses.

Type S hydrated lime (also called "special" hydrate) is another ASTM designation for a specification lime for all structural purposes. It constitutes the highest general quality for structural hydrated limes. All autoclaved or pressure hydrated limes are Type S, but some non-autoclaved hydrates also qualify.

Unslaked lime is any form of quicklime.

Forms of Building Lime - Lime may be supplied to the building trades in quite a number of diverse forms and manners, which are outlined as follows:

Lump or pebble quicklime may be slaked at the job site in pits excavated in the earth or in large metal drums or tanks. After slaking, the putty is cured or aged for one day to a week before use, since some aging is necessary to attain the desired high plasticity. With some limes the longer the curing period of up to a week or two, the higher the plasticity. The putty may be used even after aging for months, providing that it is covered (to impede recarbonation) and water is added to maintain the desired consistency. For best construction results, the putty should be screened through at least a No. 10 mesh screen (preferably No. 30 mesh) to remove coarse particles, such as core (uncalcined carbonate forms of lime) and impurities, primarily silica.

Pulverized quicklime is also job-slaked and cured in much the same manner as above; but because of its fine particle size, slaking is much more rapid and simpler, and the necessary curing period can usually be shortened.

Type N (normal) hydrated lime is soaked overnight or up to 24 hours in order to yield a plastic putty. With certain limes a longer duration of soaking may be required to obtain the desired plasticity. After soaking, the putty is then blended into the mortar mixer with sand and other mortar ingredients as necessary.

Type S (special) hydrated lime attains high plasticity quickly, in 15-30 minutes, so that prolonged soaking to form a putty is unnecessary. Consequently, it is fed dry into the mortar mixer.

Ready-mixed putty and mortar are provided by commercial central-mixing plants that purchase bulk quicklime or hydrate, usually the former; and after proper slaking and aging, the putty is delivered to the job-site in drums or tank trucks. Alternatively, it may be mixed with sand at the plant and delivered as a sanded lime mortar, ready for use; then, on the job, the mortar is usually gauged with portland cement. Similarly, the putty may be used for finish coat plaster, but is usually mixed with other proportioned ingredients on the job.

Proprietary or patent mortars often contain varying amounts of lime blended with portland or natural cements and/or pozzolans that are ball milled at a lime, cement, or independent plant in dry form. Almost invariably such plants use bulk commercial hydrated lime, rather than quicklime, since it is a dry process in which the prepared mortar is packaged in paper bags for delivery to the job-site. Quicklime may be employed, but it must be hydrated into a dry powder instead of a putty, and this processing step entails more control and more elaborate equipment.

Construction Applications - It was cited earlier that in industrialized countries, building lime has been surpassed by chemical lime in tonnage. Yet lime's utility as a structural material has continued over the years, in spite of countless architectural vogues, introduction of many newer building materials, and changing economics - and doubtless always will. Its building applications are described briefly as follows:

Unit Masonry - Lime is employed as an ingredient in mortar for laying masonry units - clay brick and tile, concrete brick and block, sand-lime brick, large cellular concrete blocks and slabs, stone, including decorative cut facing stone, and even glass block. This use encompasses all types of exterior and interior walls as mortar for facing units and/or back-up in brick veneer, curtain, load-bearing, or partition walls. The original and simplest mortar is a mixture of lime and sand in a volumetric proportion of one part lime to three to four parts well-graded sand. Greater ultimate mortar strength and a much faster setting time is obtained by substituting portland cement for a portion of the lime. Such lime-cement mortars are employed in a wide range of proportions, depending upon temperature, job conditions and load requirements, of 1:4:15 to 4:1:12 (cement, lime, sand, respectively, by volume). However, probably the two most frequently used proportions on an international basis are 1:1:6 and 1:2:9.

Slight increases in compressive and tensile strength of the mortar and in its setting time are achieved by the addition of such proven pozzolans (siliceous materials) as volcanic ash, diatomaceous earth, tripoli, silica flour, pulverized blast-furnace slag, fly ash, ground burnt clay (also called surkhi), and certain types of finely pulverized shale. These additives are employed usually in lieu of portland cement in such volumetric ratios as 2:1 to 1:2 lime, pozzolan, respectively The degree of reactivity of these pozzolans with lime and the optimum proportions to be used can be determined empirically or by tests.

The greatest value of lime in mortar is the high degree of plasticity that it imparts. The other mortar materials contribute little or nothing to plasticity. When a mortar is very plastic, the mason's productivity is increased, as the mortar is more workable and spreads more easily, thus facilitating the embedding of the blocks. Moreover, the watertightness of the masonry is markedly improved. Mortar joints are much more completely filled than with harsh-working mortars, and a more intimate extent of bond is achieved at the mortar-block interface, thus rendering the walls impervious to driving rains. The bond strength is further enhanced by the adhesiveness of lime in contact with the blocks and its high water retentive property, that resists the moisture suction of the masonry blocks. Lime contributes a modest amount of strength to mortar by carbonating through absorption of carbon dioxide from the atmosphere. When pozzolans are used, further strength is gained by lime reacting with the available silica present, forming complex calcium silicates. However, for most masonry purposes and except for special circumstances, such as abnormally heavy loads or below-grade construction, high strength in mortar is unnecessary, and sometimes even undesirable. The low to modest compressive strengths, characteristic of high-lime mortars, are generally completely adequate; and the mortars exhibit a slight degree of resilience, in contrast to the very hard and rigid, but brittle mortars of high portland cement content that are prone to part (break bond) at the mortar-block interface.

<u>Plaster</u> - Closely related to the use of lime in masonry is established usage as an important component for interior and exterior plaster. Again, the lime is generally employed in a wet, plastic sanded mortar, either in proportions similar to the masonry mortars previously described or with other modifications. All plaster is applied in at least two coats and usually in three coats, known as the scratch, brown, and finish coats.

For interior plastering 1:3 to 1:4 (lime and sand) mortars are employed in which hair or fiber is added for extra reinforcement. Such plaster sets extremely slowly, and to accelerate the set, carbon dioxide is introduced into the atmosphere from salamanders or oil burners to hasten the carbonation of the lime. In gypsum-sanded plaster it may be admixed with the gypsum to improve plasticity of the base-coat (scratch and brown coats), but it is more commonly used in recent years as the finish coat, neat or with sand, in which varying amounts of gypsum, gauging plaster or keene's cement are often added to accelerate the set of the finish coat. Other countries employ standard lime-cement mortars, such as 1:1:6 and 1:2:9 for interior plastering. There is a good deal of variation throughout the world in plaster composition and practices and in the type of plaster backing that is employed. In some countries all walls are lathed and often furred out from the wall; in others the plaster is applied directly to the masonry wall, providing the wall possesses adequate porosity and is cored or contains enough irregularities to develop a strong keying action. Laths employed are wood, metal (of different gauge), and gypsum "rock" lath (wallboard type).

For exterior plastering (which is also called stucco or rendering in some countries), the composition of materials is limited to sanded mixtures of lime and cement in varying proportions. Gypsum cannot be employed. The mortar proportions are very similar to those used in masonry, except that they tend to contain slightly more sand, e.g. a ratio of one part lime and cement to four to five parts sand or lightweight aggregate. Both two- and three-coats are employed, but generally the coats are slightly thicker than for interior use. Such plaster is applied with a smooth surface or with various types of textured, mottled or roughened finish coats, often achieved by the addition of coarse aggregate to the final finish coat (pebble-dash finish).

<u>Concrete</u> - There has been a small, sporadic use of pure lime hydrate as a 5 to 10% additive to the portland cement content of concrete. Its virtues for concrete are claimed to be improved workability, increased density (because of its micron size particles), and reduction of segregation (honeycombing). In lean concrete mixes or where high strength concrete is not necessary, it has served as a cement saver, with or without pozzolan additives, or as a means of producing so-called "Roman Cement".

Building products - Lime can be used to make three types of masonry units: autoclaved concrete blocks, calcium silicate (sand-lime) brick and block, and crude adobe-like brick. The calcium silicate products are made with 7-8% lime, graded sand, and fine silica.

The adobe-type units are made in small primitive plants or even at the job site. Generally, 5-6% of dry hydrated lime is admixed thoroughly with certain pulverized plastic clays or loams that are devoid of organic matter. Water is added up to the optimum moisture content and mixed in intimately. The mixture is fed into molds and compacted by ramming or tamping. The "green bricks" thus formed are permitted to cure for two to three weeks, during which time they gain considerable strength (magnitude of 150-300 p.s.i. compressive strength, which is five to ten times greater than ordinary sun-dried clay brick). Admittedly, such units are definitely inferior in quality to specification-controlled factory-produced burnt clay brick, concrete block, or calcium silicate units, but may prove to be adequate in dry, warm climates for low-cost construction where economy is the keynote.

Soil Stabilization - There are currently many burgeoning applications for lime in stabilization of clayey soils for base construction. Its efficacy has been clearly proven in the United States, having been used in the construction of every conceivable type of highway, including about 1000 miles of interstate construction in fifteen states and involving a wide variety of climates and soil types. Off-highway uses are also developing, including airport runways and taxiways, parking lots, hard stands for heavy military and construction equipment, temporary access or construction roads, stabilized foundations for building construction, and railroad subgrades. Generally, 3 to 5% of hydrated lime by weight, with water added to reach at least the optimum moisture content, is mixed into the soils with mechanical equipment, ranging from disc harrows to rotary mixers. This lime addition corresponds to 15-25 lbs. of lime per square yard per 6 in. of depth, or about 100-150 tons per mile of road. After curing a few days, the lime-soil mixture is mechanically compacted to maximum practical or specified density, such as 90 to 100% Proctor density.1/ After further moist curing for one to five days, depending on job conditions, a successive layer, such as base course material or paving surface, is applied.

1/ 100% Proctor density is the maximum compaction possible with that material.

The lime reacts slowly with the available silica in the soil, forming calcium silicates that exert a binding or cementing action. Only clays, loams and most silts that contain less than 5% organic matter will react with lime in this manner. Sandy soils are unreactive unless a pozzolanic additive is also introduced. The lime greatly reduces the plasticity index of the soil by increasing its plastic limit and decreasing its liquid limit. Through a base exchange mechanism the calcium ions from the lime displace the sodium, potassium, or hydrogen ions in the soil and alter the physical character of the soil by agglomerating the fine clay particles into silt and sand sizes. As a result, the lime-treated soil possesses little or no swell or shrinkage tendencies. Construction is greatly expedited during or after grading, since lime will quickly dry up a saturated sub-grade, and after compaction the lime-treated sub-grade is relatively impervious to subsequent downpours, permitting construction to proceed with minimum delay.

CHAPTER II - PROPERTIES OF LIME

To give a clear understanding of building lime, the raw material from which it is derived, its method of manufacture, and its utilization, it is desirable to re-state the principal chemical and physical properties of lime.

Chemical Properties - Both quick and hydrated lime are reasonably stable compounds. Up to almost any commonly-attainable temperature, quicklime is completely stable, but hydrated lime will decompose and revert back to quicklime at about 540°C (or about 490°C for dolomitic hydrate). Quicklime's main vulnerability is water; even moisture in the air causes destabilization by slaking the oxide to its hydroxide form. Highly reactive quicklimes will hydrate with explosive violence. Consequently, quicklime is a desiccant. In a sense, however, hydrated lime is more stable than quicklime, since water does not affect its chemical constitution. Yet, lime hydrate is most vulnerable to carbon dioxide, and will usually carbonate rapidly by absorption of CO_2 from the atmosphere, thus reconverting the hydrate back to the chemical composition of its limestone antecedent. This largely explains its hardening action in mortar; even the 0.03% CO_2 in the atmosphere is readily absorbed.

Both quicklime and hydrated lime behave as reactive chemicals when in contact with acids, effecting neutralisation that yields calcium (and magnesium) salts. In this role they are strong alkalis. They will absorb and neutralise most acid gases and will react chemically with silica and alumina under certain moist conditions, with temperature, pressure, and compaction acting as accelerators. It will readily convert other carbonates into hydroxides. Minute amounts added to water will increase the pH of the water sharply up to 12.5, thus providing sterilisation action against bacteria.

Physical Properties - Quicklime is generally white in colour in varying degrees of intensity, depending upon its purity. Invariably, the purest types are the whitest; less pure or improperly calcined types may possess an ash gray, buff or yellowish colour. Quicklime is generally much whiter than its limestone antecedent. Similarly, hydrated lime is characterized by a high degree of whiteness and is also invariably whiter than its quicklime parent. Impure types will possess a faint gray cast. Minute dark flecks that occur in the "snow" white hydrate are usually silica. For building lime, usually a high degree of whiteness is desirable and aesthetically essential for finish coat plaster work.

Both quicklime and the hydrate possess a faint, but distinctive, musty or "earthy" odor that is difficult to define but is inoffensive.

Both of these forms of lime are crystalline. With some limes the crystals are so minute that the lime appears to be amorphous, but high-powered microscopy reveals them to be cryptocrystalline. In other limes the crystals are visually relatively coarse. Quicklime crystals are cubic, whereas hydrated limes are in the hexagonal system.

The porosity of quicklime varies between 5 and 40% depending upon the crystallinity of its parent limestone and the calcination conditions.

The specific gravity of a pure high-calcium quicklime is 3.34, but such a value presupposes zero porosity, a condition that is unattainable in manufacture. Impurities will affect this theoretical value slightly; dolomitic values will range slightly higher - up to 3.5 to 3.6. The apparent specific gravity of quicklimes ranges between 1.6 and 2.8. Values for chalk limes are less. True specific gravities for commercial hydrated limes will range as follows:

High-calcium	2.3 to 2.4
Highly-hydrated dolomitic	2.4 to 2.6
Normal-hydrated dolomitic	2.7 to 2.9

The high value for the normal dolomitic hydrate is attributable to its high percentage of unhydrated oxide.

The bulk density of quicklimes varies between 48 and 70 lb./cu.ft., partially dependent upon the physical size of the particles. Similarly, values for hydrates vary between 25 and 40 lb./cu.ft., largely dependent upon the degree of entrapped air that these fluffy materials contain. Values for dolomitic grades average 3 to 5% higher than for high-calcium types.

In hardness quicklime lies between 2 and 3 on the Moh's scale; dolomitic lime is generally slightly harder than high-calcium lime. Values for lime hydrate are similar.

The melting points of pure CaO and MgO are 2570°C and 2800°C, respectively.

The specific heats of limes are shown in Fig. 1 and range as follows, depending upon temperature:

High calcium	0.17 to 0.32
Dolomitic	0.185 to 0.319
MgO	0.195 to 0.316

The angle of repose varies considerably, particularly with hydrates, because of their propensity for absorbing an electrostatic charge; however, 50° to 55° for pebble quicklime is an average value, and for lime hydrate it averages about 70°.

The heats of hydration of pure forms of calcium and magnesium hydroxide are:

$Ca(OH)_2$	15,300 cal./g. mol. or 27,500 B.T.U./lb. mol.
$Mg(OH)_2$	8000 to 10,000 cal./g. mol. or 14,400 to 18,000 B.T.U./lb. mol.

Heat of solution for high calcium hydrates approximates 2790 cal./mol. at 18°C; the values for dolomitic hydrates are 30 to 40% lower.

The solubility of 100% calcium hydrate is 1.33 g. CaO/1 (0.133%) of saturated solution at 10°C so that it might be characterized as slightly soluble. This value decreases steadily and sharply with increase in temperature, as Fig. 2 depicts. The presence of most extraneous soluble salts, down to fractional percentages, increases the solubility of lime in varying amounts. However, the presence of even traces of alkalis depresses its solubility markedly. Such soluble organics as sugar increase its solubility many-fold. Dolomitic hydrate is usually slightly less soluble than high calcium; $Mg(OH)_2$ is almost insoluble, about 100 times less soluble than $Ca(OH)_2$.

Plasticity - However, the most significant property of lime for structural purposes is its rheology, specifically its degree of plasticity when mixed with water into a moldable putty or a sanded mortar. All producers of building lime continually strive for uniform and maximum plasticity, regardless of whether they sell quicklime or hydrated lime to the building trades, since limes of poor or inconsistent plasticity are not as saleable. Actually, nearly all limes possess some degree of plasticity, but its usefulness to the building mason can be greatly enhanced by even seemingly modest improvements in plasticity. In fact, many builders will pay 10 to 20% more for a highly plastic lime than for one of moderate plasticity.

Figure 1

Specific heats for calcium oxide, magnesium oxide and Dolomitic quicklime

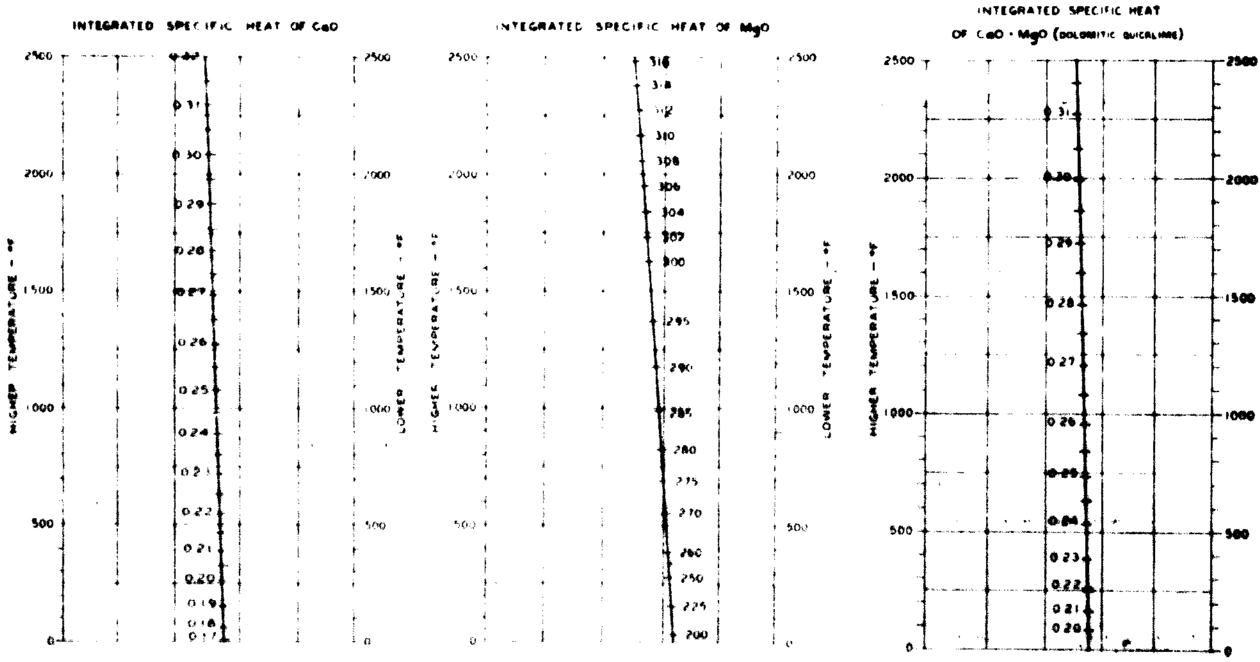
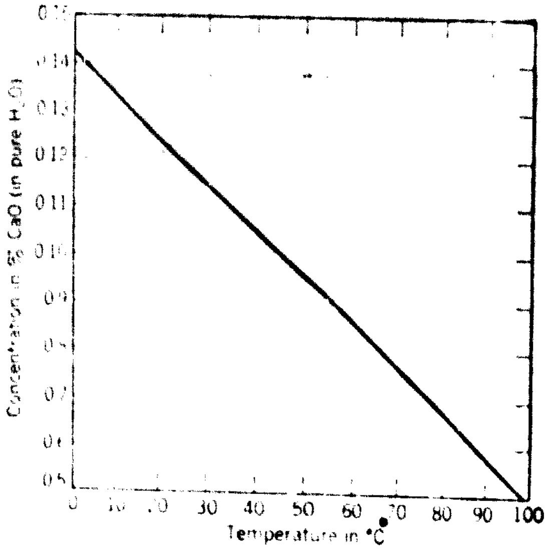


Figure 2

Solubility of pure calcium oxide at various temperatures



So there is a definite profit stimulus in striving for high plasticity, since such limes can be produced at little or no additional cost. A general observation here is that the use of lime in construction frequently declines when only limes of indifferent plasticity are procurable; builders will simply switch to other construction methods and materials that do not require lime.

The major obstacle confronting the manufacturer in quality control of plasticity is the lack of a universally accepted, foolproof, and reproducible method for measuring plasticity. In the United States and Canada, the Emley Plasticimeter test, described in ASTM specification C 110, is generally employed and accepted, although it possesses some limitations, because of questionable reproducibility and its intricate, time-consuming nature. This test simulates the application of lime putty plaster finish coat to an absorptive base. Yet even critics of this test will (although reluctantly) use and accept it as being the most realistic test yet propounded. This test is rarely employed in Europe and other countries, and is never used as a specification requirement. But in North America, the United States Government and the American Society for Testing and Materials will require a minimum plasticity-index value of 200 by the prescribed Emley test in some of their structural lime materials specifications.

In the United States, Emley plasticity values of over 500 have been reported, but generally a lime hydrate or quicklime putty that possesses a value of 200 is considered quite satisfactorily plastic for all structural purposes. Values as low as 80 to 90 for hydrates have been reported, but such limes would possess no saleability in North America. Generally, European hydrated limes have less plasticity than American hydrates. In spite of this, in some countries (for example, Germany, Austria and certain East European countries), there is proportionately a much greater consumption of lime <u>per capita</u> than in the United States. Plasticity index values of 100 to 150 generally prevail, which would be regarded in quality as unsaleable or submarginal in the United States. This anomaly can only be explained by the greater promotional effort of the lime industries of these countries, and either a shortage of other building materials or weak sales effort by the competing building material producers. The quicklime putty used in most countries, if adequately cured, will possess higher average plasticity than the dry hydrates, soaked or unsoaked, and will attain plasticity values of 200 or more. Hydrates derived from some quicklimes appear to be inherently of inferior plasticity, yet the slaked and aged putties from these same quicklimes will often be of superior plasticity. Thus, a lime manufacturer has two opportunities for producing a saleable building lime - as quicklime slaked at the job-site, or as a dry hydrated lime. Ideally he should strive to produce quality products of both types.

Another laboratory method for measuring plasticity is the non-absorbent flow table method that is used in the United Kingdom. A truncated cone of putty of standard prescribed consistency is placed on the flow table. The table is bumped, and these impacts of the table gradually flatten the cone of mortar. The number of bumps is recorded when the cone is flattened to three times its original diameter. In this test the British will require a minimum of 10 and 13 for hydrated lime and quicklime putty, respectively, values that would be regarded as substandard in the United States. A highly plastic lime should be able to undergo 16 to 24 bumps.

. A very simple indicative test (but of questionable reproducibility and accuracy) is the so-called blotter test. A glob of putty of standard consistency is placed on a specified thickness of filter paper or blotter and is spread evenly over the surface with a spatula. The number of strokes required before the putty loses its moisture and "balls up" under the spatula is a very approximate measure of plasticity.

An indirect measurement of plasticity of excellent reproducibility is the water retentivity test (described in ASTM C 110). This method measures the ability of a mortar of specific consistency to retain its moisture against artificially imposed moisture suction. The extent to which a lime mortar resists this absorptive force and retains its moisture is measured as its percentage of water retentivity. An almost invariable characteristic of a highly plastic lime is a correspondingly high water-retentive property. It is still controversial whether these values can be correlated in a precise direct proportional manner, but a high water retentivity value definitely indicates a high degree of plasticity. Values as high as 94% have been reported. Certainly 85% or higher would be regarded as satisfactorily plastic. But some lime mortars will test as low as 75%; a cement mortar will measure only about 60%, so in lime-cement mortars, as the cement proportion is increased, the water retentivity value decreases.

Another indirect indication of plasticity is the Voss extrusion energy test. Actually this test measures quantitatively the amount of sand by volume that a given volume of lime can "carry" without becoming oversanded (or the sand-carrying capacity of a mortar). Since it has been empirically established for centuries that the higher the plasticity of lime, the greater is its sand-carrying capacity, a value on the volumetric ratio of lime to sand is revealing as to its degree of plasticity, as a standard Ottawa sand is employed. An extrusion energy machine, called a plastometer, is employed which measures the pressure exerted in extruding a cylinder of mortar under confined conditions. If the mortar extrudes easily and quickly with little pressure, it is adjudged plastic and workable; if it is harsh and of low plasticity, it stiffens in the machine and considerable pressure and time are necessary for complete extrusion. As much as 200 psi pressure has been recorded for mortars of poor plasticity, whereas one of high plasticity requires only 3 to 10 psi. Thus, by a process of trial-and-error, the optimum amount of sand can be determined for a given lime, or the plastometer can be used to compare two limes using the same sand.

Soundness - A structural lime should be sound and not subject to disruptive volume change (shrinkage or expansion) or the disfiguring effect on a plaster surface caused by pitting and popping. Under certain circumstances in construction, some limes have caused plaster, particularly the finish coat, to expand and bulge, with failure, resulting in the form of a spalling plaster coat. This is due to the expansive force of delayed hydration; such hydrated lime is not completely hydrated, and contains an appreciable amount of oxides. However, most of these failures can be attributed to such extenuating circumstances as faulty construction design and workmanship, since this expansive force is of a low order of magnitude. An incompletely hydrated lime is not as foolproof or as trouble-free as one that is fully hydrated, and consequently a manufacturer should strive to produce a commercial hydrate that contains no more than 8% unhydrated oxides. This limit is contained in most American specifications. This problem only applies to dolomitic and magnesian limes, since it is the MgO component, not the CaO, that resists hydration under atmospheric conditions. Methods for complete or substantial hydration of dolomitic and magnesian limes are discussed in the chapter on hydration. A proposed American test to determine the expansion of a lime consists of subjecting a lime-cement bar to 295 psi pressure in an autoclave for one hour, and then measuring the linear expansion. If the expansion exceeds 1%, then the lime would be adjudged unsound. This accelerated test is regarded as unreasonably harsh, unrealistic, and not easily reproducible; it has not been adopted, except for research purposes.

The other form of unsoundness characterized by pitting and popping is now of little consequence, due to improved milling practices that yield hydrates of more uniform and finer particle size. Efficient air separation of the hydrate that removes most of the No. 200 mesh particles is nearly a guarantee against popping and pitting, assuming reasonable workmanship and the absence of deleterious foreign matter in the mixing water and sand. A tedious laboratory test of questionable value for pitting and popping is contained in ASTM specification C 110. This test is now rarely employed. Instead, a gradation limit of no more than 0.5% retained on the No. 30 mesh sieve and no more than 15% retained on the No. 200 mesh sieve is considered an effective safeguard against pitting and popping. With quicklime putty, somewhat the same end result is obtained by requiring the user to screen off the coarse fractions from the putty.

Purity - As a control on the purity of building limes in North America, materials specifications require that hydrate contains at least 95% total oxide content (CaO+MgO) on a non-volatile basis and that the carbon dioxide content shall not exceed 5%, when tested at point of manufacture, or 7% when tested at other locations. Most European structural hydrate specifications are more liberal in varying degrees, such as a minimum of 90% total oxide content and 8 and 10% CO_2 content, respectively. This is probably due to the fact that most European limestone deposits are not as pure as in North America; but it also reflects poorer milling techniques, since modern air separation, when efficiently applied, effects the removal of much of the impurities in the form of coarse particles, thereby elevating the total oxide content of the hydrate.

With respect to the purity of quicklime for structural purposes as a slaked putty, the American standard also requires a total minimum oxide content of 95%, with maxima of 5% for total silica, alumina, and iron oxide and 3% of CO_2, if sampled at point of manufacture. If sampling occurs at any other place, the maximum allowable CO_2 content is 10%. Again, European standards are much more liberal, permitting a minimum of 90% total oxides (in some cases 85% total oxides are even tolerated).

As a generalization, however, the degree of plasticity (fatness) and particle fineness are frequently in direct proportion to the chemical purity of the lime, as reflected in its total oxide content. Some American hydrates will assay over 98% total oxides, non-volatile basis.

CHAPTER III - MANUFACTURE OF BUILDING LIME

To produce a good building lime having satisfactory plasticity, water retention, soundness, etc., the manufacturer must pay close attention to all phases of production, starting with quarrying and going on through to the milling of the hydrate. Although there is some disagreement on the exact processing requirements and the desired physical properties of the resultant lime to achieve this end, preponderant opinion adheres to the following criteria:

1. Quality of stone. Some limestones are most difficult to calcine uniformly and completely; it decrepitates into small pieces in the kiln during calcining. Other stone is too impure; the impurities, primarily silica, alumina, and iron, are chemically combined with the lime during calcination through a fluxing action. Consequently, limestone of certain physical and chemical properties is a necessary requisite for high plasticity. Further elucidation on the quality of limestone needed is contained in chapter IV.

2. Rate and severity of calcination. The limestone should be soft-burned and of high chemical reactivity -- not hard-burned or over-burned, with sluggish reactivity. The degree of reactivity is easily observed by measuring the rate of slaking with water. Close control over calcination temperature and its duration must be exercised for optimum quality. Further elaboration of this requisite is contained in chapter V.

3. Hydrating (slaking) of the quicklime. When quicklime is employed, the responsibility for obtaining a plastic lime is transferred to the user. However, the manufacturer can assist the user greatly by recommending the optimum amount of water for slaking and how it should be applied. The exact amount of water for maximum plasticity can only be established empirically by tests, and the method of application frequently varies with different limes. If too little water is added, the lime can be "burned"; if too much water is added, "drowning" of the lime can result. In both cases complete hydration is impeded and a poor quality of putty results, that may contain coarse, rounded and agglomerated particles.

In case of commercial hydration by the lime manufacturer, the amount of water to be added is just as critical, and should be carefully controlled. Slaking temperatures are also critical for optimum hydrate quality.

In both of the above methods, the hydrate produced immediately after slaking should be cooled as rapidly as is economically possible. This practice will assist in yielding hydrate particles of great fineness and high surface area that are invariably found in all highly plastic limes.

4. Milling of the hydrate. Immediately following hydration, the dry hydrate should be milled further, preferably with an air separator, which will remove coarse particles, including almost all + No.30 mesh material and some of the + No.200 mesh particles. The coarse fractions separated are largely core (uncalcined limestone) and impurities that are free or combined with the lime. Other supplemental milling practices that enhance plasticity include various grinding and agglomerating techniques which tend to flatten the particles into laminar shapes.

Fig. 3 contains a schematic flow chart of an integrated lime operation, comprising the above four essentials. Fig. 4 shows a more specific flow sheet of a modern medium-sized rotary kiln lime plant. Reference to both charts is suggested in the following three chapters on limestone preparation, calcination, and hydration.

Figure 3

Simplified flowsheet for lime and limestone products

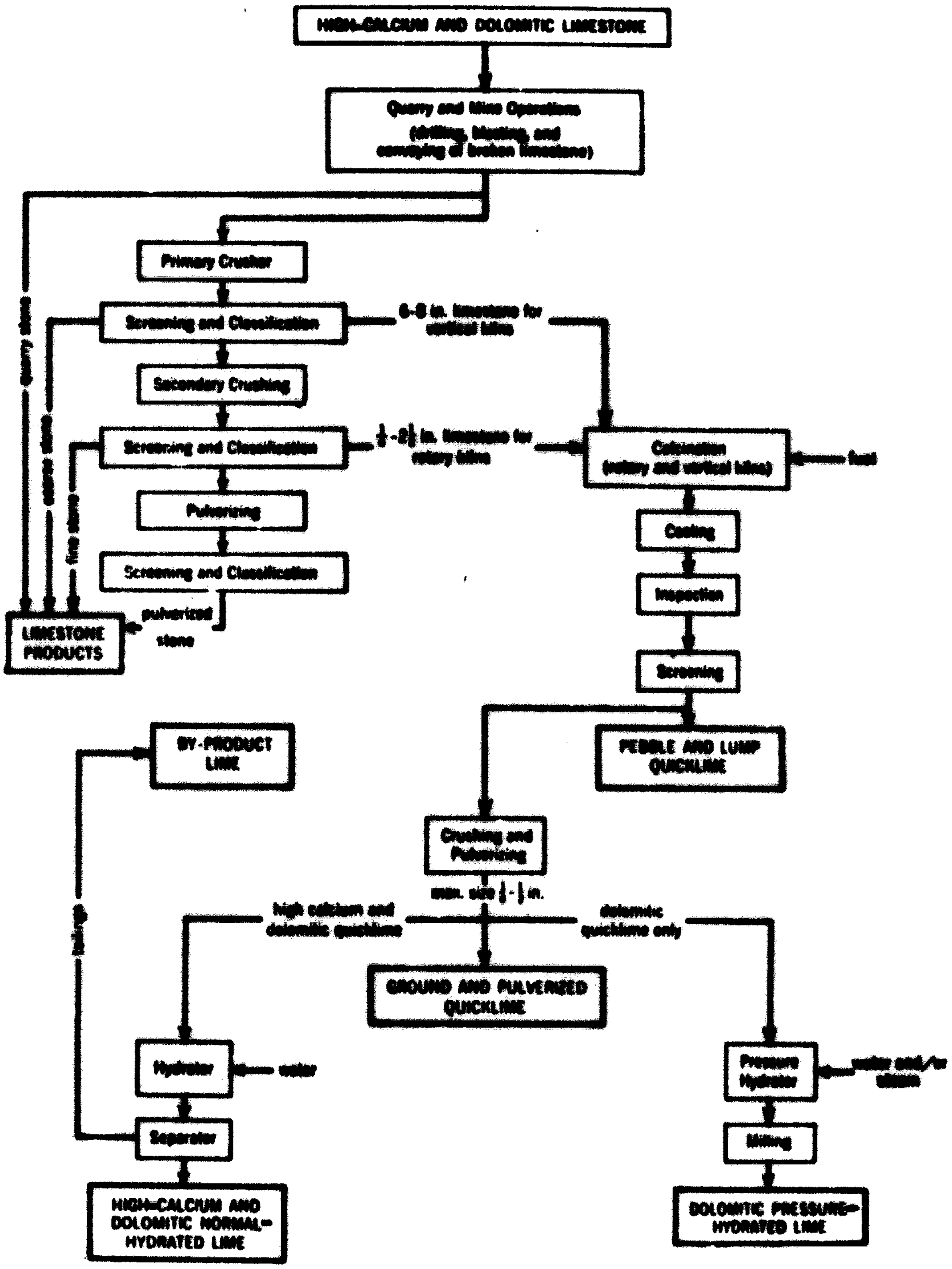
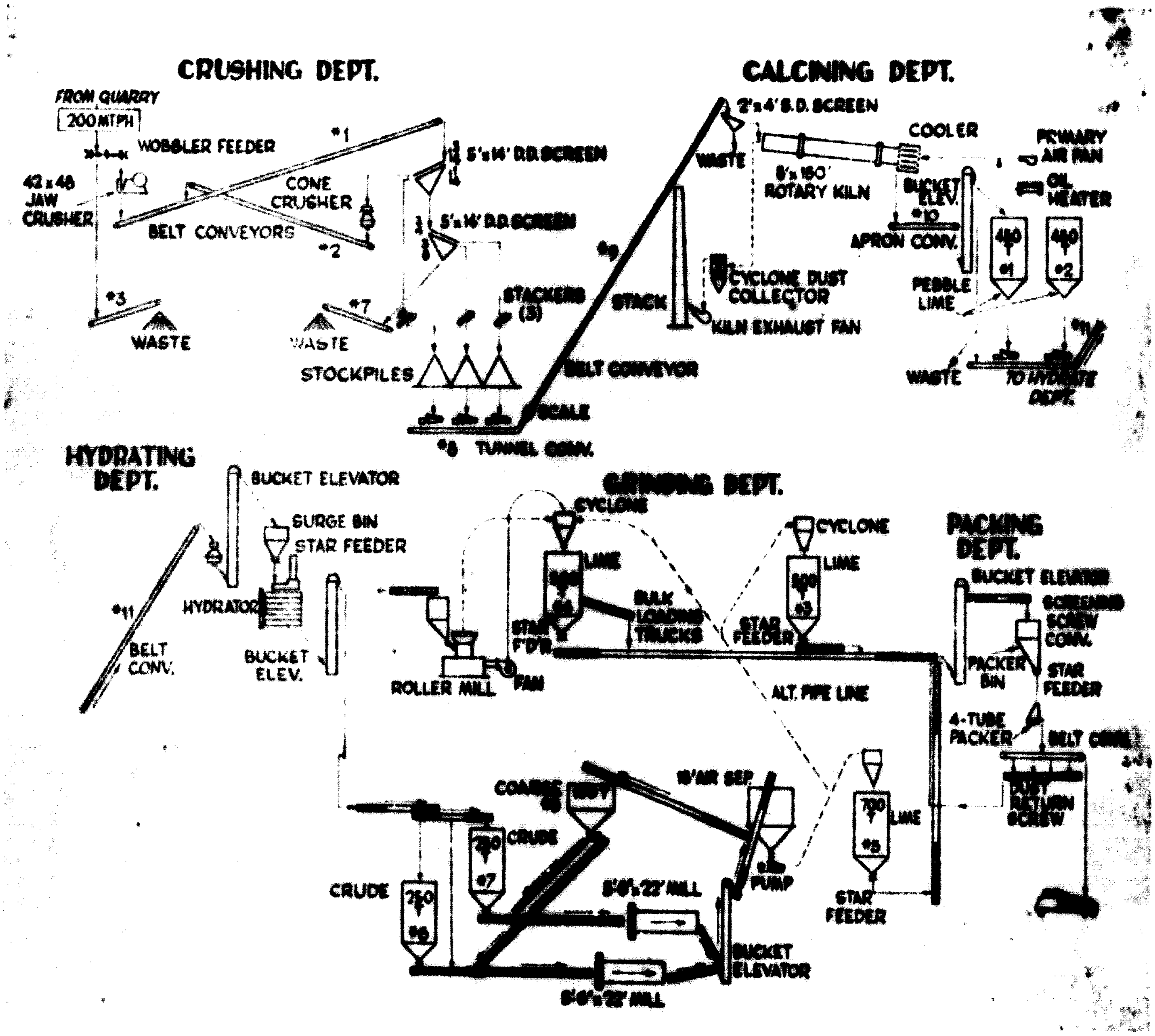


Figure 4

Schematic flowsheet for medium-sized rotary kiln plant, from limestone quarrying through lime bagging



CHAPTER IV - LIMESTONE PREPARATION

Several types of carbonate material may be used to produce lime, but limestone (including dolomitic limestone) is the most important. Other calcareous raw materials used are marble, chalk, oyster and clam shells, and coral.

Limestone occurs in abundance throughout the world, and practically every country has deposits. Yet, not all countries have depostis that are economically available -- some are covered with thick overburden, some are not extensive enough, or too badly deformed, to exploit, some are located in remote areas, etc. Furthermore, not all limestones can be burned into satisfactory lime, and not all of these stones can be made into good building lime. Consequently, the starting point for developing lime industry is to find a suitable limestone with adequate reserves for supporting an economically sound venture. The suitability should be determined by a thorough exploration program and with extensive calcining tests being made.

What properties should be sought in the limestone? First, the stone should be exceptionally pure, containing 95% or more carbonate content (calcium and magnesium). It is true that the more impure limestones can be made into hydraulic lime, but these invariably lack the plasticity of the "fat' lime. Furthermore, a high purity lime will lend itself to innumerable chemical and industrial uses, giving the lime industry a much broader base for development.

Secondly, for building purposes, a high purity dolomitic stone may offer some advantages over high calcium. In the U.S.A., over 75% of the building limes are dolomitic.

Thirdly, the stone should be dense, finely crystalline, and sufficiently hard (not friable) so that it will not break down readily during intraplant transfer, or decrepitate during calcining. This is particularly true with shaft kilns, which normally burn stone in a size range of 4" - 10". If fines are generated during transfer to the kiln and during calcining, the even flow of gases in the kiln is impeded, and improper burning and low fuel efficiency result. A further requirement with shaft kilns is that the stone particles should be roughly cubical in shape, and not elongated, in order to produce uniform quicklime; this precludes the use of thin-bedded limestones.

If only moderately soft stone is available, however, making the production of shaft kiln feed difficult, then two principal alternatives are available: use of rotary kilns, which normally burn [illegible] - 2 in. size stone, or one of the newer types of shaft kilns which are specially designed to burn small stone, e.g., the double-incline (German) kiln and the multiple-shafted (Austrian) kiln.

If only soft limestone is available, or if the stone decrepitates during burning, the Fluo-Solids kiln could be used for producing lime. A second possibility is a new process developed recently in New Zealand, using a mixed feed of pulverized limestone and coal. The materials are interground to a fine powder, then pelletized, before burning in a special vertical kiln. American experience gained with the Fluo-Solids units, involving marble, indicates that an excellent building lime can be made.

Limestone Characteristics - Limestone is a consolidated sedimentary rock, primarily of marine origin, consisting of calcium and magnesium carbonates and impurities such as silica, alumina, iron oxide, etc. The principal carbonate minerals in limestone are calcite ($CaCO_3$) and dolomite (the double carbonate $CaMg(CO_3)_2$). A third carbonate mineral, aragonite, is found only in geologically recent limestones, particularly those in arid areas.

If the limestone contains over 95% $CaCO_3$, it is termed high-calcium. It is a high purity dolomite if it contains over 95% of the mineral dolomite (approximately 41-45% $MgCO_3$). A range of intermediate magnesian limestones occur in between, but in the U.S.A. only high-calcium or high-purity dolomitic limestones are used for making lime. In other countries, however, intermediate types are also burned, some of which are used for building lime.

Limestones are classified by geologists into three groups, namely:

1. Autochthonous (or accretionary) limestones, those chemical biochemical precipitates which grew in place.
2. Allochthonous (or detrital) limestones which were mechanically transported and redeposited.
3. Metasomatic limestones, which were profoundly modified by various postdepositional changes (such as replacement by dolomite, silica, phosphate, etc.) so that the original characters are obscured.

The first group are formed by direct extraction of calcium and magnesium carbonate from sea water by either organic or inorganic means, and include such rock types as conquina and chalk. Also included are calcareous tufa and travertine, which are localized chemical precipitates from supersaturated solutions formed in springs, lakes, and caves. The second group, the detrital limestones, are composed primarily of broken pieces of reefrock, and fragmented and worn shell and other fossil debris, which may also contain varying amounts of chemical and biochemical precipitates. All these materials are current-sorted and deposited and have the textures and structures of normal clastic rocks like sandstone and shale. Typical examples are oolitic limestone, lithographic limestone, and some types of coquina. After deposition, these calcareous materials are gradually consolidated into rock by compaction, crystallization, and cementation.

As with all sedimentary rocks, impurities like silica, clay, phosphate, iron oxide, carbonaceous matter, etc. were often deposited with the calcareous material, or were introduced later through secondary replacement. Accordingly, there are siliceous, cherty, argillaceous, phosphatic, ferrugious, and asphaltic stones, to name a few. During calcining, these impurities generally combine with the calcium, thereby reducing the available lime content, but during hydrating and milling operations, the impurities are largely separated out and discarded.

Since calcite and dolomite are the key minerals in limestone, here are their principal physical characteristics.

Calcite: rhombohedral form; molecular weight, 100.1; bulk specific gravity, 2.72; hardness, 3.0 generally white

Dolomitic: rhombohedral form; molecular weight, 184.4; bulk specific gravity, 2.83; hardness, 3.5 - 4.0; generally white, but often tinted pink or tan.

The above characteristics are reflected in the limestone, although the presence of some impurities may have a marked effect, particularly on color. Whereas most limestones are generally white, slight traces of carbonaceous matter produce a gray or even blackish appearance; the presence of iron oxide produces a tan or buff color, occasionally brown or even red; and dolomite gives a pinkish cast to the stone.

Textures vary from coarsely crystalline down to microcrystalline or aphanitic. Bulk density varies from 140-175 lb./cu. ft., with dolomitic stone being about 2.5% higher than high-calcium. A noted exception to this is chalk, a soft, friable, porous limestone consisting of microskeletons of plant and animal organisms, which has a bulk density of 90-125 lbs./cu.ft.

Field Tests - To distinguish limestone from other similar appearing crystalline rocks, the hardness test is very simple and practical. Limestone, with a hardness of 3, will scratch gypsum (H= 2), but not quartz (H=7). For making comparisons, a knife blade has a hardness of 6, a coin 3, and the thumb nail, 2.5. Consequently, a knife blade will scratch limestone, but a coin or thumb nail will not. To determine the presence of calcite or dolomite in a carbonate rock, a simple field test with dilute hydrochloric acid is used. Calcite will effervesce strongly in the acid, whereas dolomite will effervesce only if the acid is heated. A. Hogberg (Sweden) has also developed a staining test to distinguish the two minerals, involving a 30% solution of $Al(NO_3)_3$; calcite will become etched and stained blue, while dolomite will not be effected.

Other Carbonate Sources for Lime - Marble, a metamorphic rock produced by the recrystallization of limestone at elevated pressures and temperatures, is also used as a source for lime. The stone closely resembles limestone, although it is nearly always coarsely crystalline and usually contains colored streaks due to the presence of such impurities as graphite, quartz, tremolite, etc. Fossils are virtually non-existent, having been destroyed during metamorphism; bedding planes are also usually contorted.

Oyster shells and clam shells are also used as a minor source for lime. The shells are usually washed and sized before being burned in rotary kilns. Generally, shells are not as suitable for producing building lime as limestone, although historically they were used in colonial America for building purposes.

Occurrence of Limestone - Limestone is one of the most common rock types, occurring throughout most of the world. Deposits were originally formed on the ocean floor, during each of the five geologic eras, from Pre-Cambrian to the present; and now, due to uplift, the limestone strata underlay much of the land masses, even occurring on mountain tops. Some of the limestones have changed little since deposition -- the strata are still horizontal, of high chemical purity, etc. Other limestones, conversely have been altered greatly since deposition -- some through recrystallization to form marble, through postdepositional replacement by silica, dolomite, etc., or by extensive folding and faulting during periods of mountain-building.

The Pre-Cambrian and Cenozoic eras generally have low potential for limestones, even though limestones were formed during those geologic times. In the Pre-Cambrian, for example, the majority of rocks, are of the complex, crystalline igneous and metamorphic types (granite, schist, slate, etc.), with a paucity of limestone. Generally, the limestones that were formed have been marblelized, contain impurities, and are greatly folded and faulted, making quarrying difficult. Most continents incorporate so-called Pre-Cambrian shield areas, which would represent negative areas for limestone.

The Cenozoic limestones tend to be soft and friable, due largely to their younger geologic age. In addition, they are generally not as pure as the older Paleozoic formations.

<u>Exploration</u> - The first and perhaps most important step in developing a mineral operation, and lime is no exception, is the proving of the deposit. This means determining both the <u>quality</u> and <u>quantity</u> of the limestone present when substantial production is the aim, as both are of equal importance in the economics and feasibility of the plant. No short cuts in exploration are advisable, since even a small, modern integrated plant involves too large an investment to be jeopardized by an inadequate exploration study.

A preliminary study should be made first of all geological maps and reports available, which will delineate the best potential areas to begin the exploration. Preferably a qualified geologist should be in charge of the project. For accurate analysis it is desirable to employ core or churn drills for obtaining stone samples; these should then be analyzed chemically, physically, and mineralogically, if possible.

In determining the <u>quantity</u> of the deposit, the following information is needed: thickness and lateral extent of deposit, attitude of beds (horizontal, steeply dipping, folded) and presence of faulting. This may necessitate the development of an accurate geologic map of the deposit, if long-term planning is the goal.

In determining <u>quality</u>, a sufficient number of samples should be obtained, both laterally and vertically, with particular attention being paid to the occurrence of interbedded shale, sandstone, impure limestone, and chert beds; of clay seams, fissures, and pockets; and also of the possibility of high-calcium strata grading laterally into dolomite or other sedimentary rock. The spacing of drill holes will vary with the degree of uniformity of the deposit. Naturally, more holes will be needed where the geology is complex.

A third important consideration is the economic availability of the deposit. Here the amount of overburden is critical, also the remoteness of the location, particularly with respect to haulage of the raw material and finished product; and, of course, the degree of complexity of the deposit. Regarding the latter, if the limestone is interbedded with impure strata of shale, etc., selective quarrying or beneficiation may be required; this may prove to be too costly. On the other hand, where labor is cheap, hand picking or cobbing may be a practical solution. If the deposit is contaminated with clay, extensive washing may be required, which also may be costly; in desert areas it may be impractical. If the overburden is exceptionally thick, underground or sidehill mining may be required, which, of course, means higher stone costs.

Following the geological investigation, the quantity of limestone reserves can be determined mathematically. Since large stone and lime plant facilities represent a big capital investment, the reserves should be ample for at least a 25 year operation.

Besides carrying out an extensive exploration program, the prospective lime manufacturer would be well advised to conduct a study of the burning behavior of the limestone involved. This could be done with differential thermal analysis, as well as with special laboratory kilns and furnaces. In addition, most kiln manufacturers are prepared to perform more elaborate pilot plant tests, and some even actual field tests. Shipment of a carload of the crushed stone to another lime manufacturer for calcination in a commercial kiln would be most revealing, if this can be arranged. Not only would information be gleaned on the stone's thermal characteristics but also on whether the particular type of kiln utilized would be suitable for the stone in question.

CHAPTER V - LIME CALCINATION

Theory of Calcination - An essential prerequisite to successful lime manufacture is a practical comprehension of the theory of calcination. Although this is one of the simplest and most fundamental of all chemical reactions, in practice lime burning can be surprisingly complex; and often numerous empirical modifications are necessary for efficient performance. Stated chemically with molecular weights, this reversible reaction is diagrammed below for both high calcium and a true dolomitic lime.

$$\overset{100}{\mathrm{CaCO_3}}\ \text{(high calcium limestone)} + \text{heat} \rightleftarrows \overset{56}{\mathrm{CaO}}\ \text{(h.c. quicklime)} + \overset{44}{\mathrm{CO_2}}$$

$$\overset{100}{\mathrm{CaCO_3}}\cdot\overset{84}{\mathrm{MgCO_3}}\ \text{(dolomitic limestone)} + \text{heat} \rightleftarrows \overset{56}{\mathrm{CaO}}\cdot\overset{40}{\mathrm{MgO}}\ \text{(dol.quicklime)} + \overset{88}{\mathrm{2CO_2}}$$

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 practically a higher temperature) must be maintained for a certain duration.

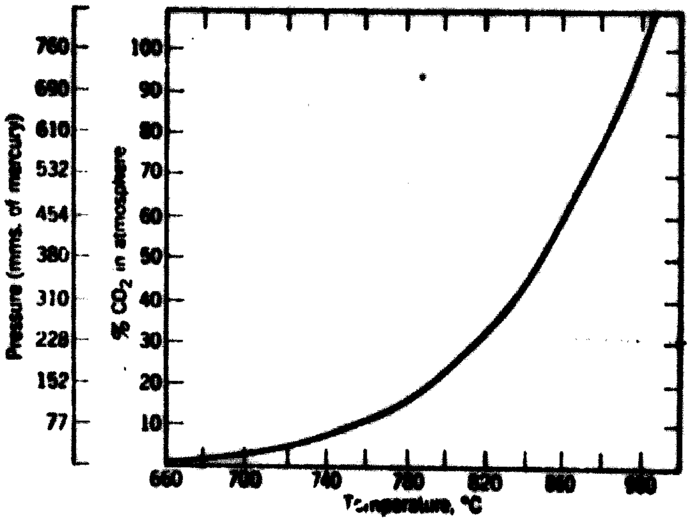
3. The carbon dioxide gas that is evolved must be rapidly removed.

Thermal Decomposition - The dissociation temperature of pure calcitic limestone is well established — 898°C (1648°F) for 760 mm. Hg. pressure (1 atm.) for a 100% CO_2 concentration. With dolomitic and magnesian limestone, however, there i is no general agreement on the exact values. Their $MgCO_3$ component dissociates at a much lower temperature than $CaCO_3$, but values reported range between 500 to 750°C, contingent upon the crystal size in the stone, the coarse crystalline types requiring the higher range of temperature and the dense, fine-grained the least. Complicating this value further is the widely varying percentages of $MgCO_3$ that occur in the stone - from 5 to 45%. A good average value for a dolomitic stone would be 725°C at one atm. pressure, but initial surface dissociation will usually commence at about 100°C less than this. Of course, the $CaCO_3$ component of these stones does not dissociate until the above higher dissociation point is reached. Thus, dissociation of these stones is a two-stage phenomenon.

Fig. 5 illustrates how changes in pressure and CO_2 concentration will alter the above dissociation point for $CaCO_3$. At fractional atmospheric pressures, the dissociation point is less, and at pressures greater than one atmosphere, it is

Figure 5

Relation between dissociation temperature of CaCO$_2$, CO_2 concentration and pressure



more. This same proportionate relationship applies to those limestones containing $MgCO_3$. If the temperature and CO_2 pressure are in equilibrium, regardless of their values, dissociation is static. But if there is a minute change in one of these variables, such as a decrease in CO_2 pressure and concentration or an increase in temperature, dissociation immediately proceeds with the evolution of CO_2 gas and the simultaneous formation of oxides.

It is obvious from the above that calcination of dolomitic and magnesian stone is more complicated than with the high-calcium type. With the former types, in order to calcine the $CaCO_3$, the $MgCO_3$ is necessarily hard-burned. The objective is to minimize this hard-burning by discharging and cooling the lime as quickly as possible after the $CaCO_3$ constituent calcines.

At calcination temperatures of 1700 to 2450°F, dissociation of the limestone proceeds gradually inward from the outside surface of the stone particle, like a "growing" veneer or shell. However, for dissociation to penetrate into the interior of the stone pebble or lump, kiln temperatures considerably higher than the dissociation point are often necessary. Generally for a fixed duration of calcination, the larger the diameter of a lump of stone, the higher is the required temperature to calcine the center of the particle. The reason is that the CO_2 gas to be expelled has a longer distance to travel, and often considerable internal pressure is exerted before the gas can force its escape. If dissociation of the lump is incomplete, there remains in the center of the lump a "core" of uncalcined carbonate that may range in size from a miniature rice-like grain to the size of an acorn, contingent upon the linear dimension of the particle and the extent to which calcination is complete. Although "core" is not deleterious, it does vitiate the quantity of quicklime. After the quicklime is hydrated, however, all of the core except the very fine grains is removed by air separation or screening as waste ("tailings"). Its presence is inevitable with under-burned lime. Thus, an obvious objective is to produce a lime of zero to 2% maximum core, if at all possible. Hydrating quicklime of high core content (5 to 15%) is too wasteful, although the lime that is calcined may be of good quality.

On the other hand, if the stone particles are calcined under severe thermal conditions (i.e., high temperature and long retention), the lime may become hard-burned (or even dead-burned at very high sintering temperature). Under such conditions the particles shrink by 25 to 50% of their original size. This shrinkage densifies the resultant lime, narrowing and occluding its micro-pores and fissures, so that hydration reactivity of the lime is reduced in varying degrees and even extinguished (for all practical purposes) with dead-burned lime. Water simply does not penetrate into the constricted pore structure nearly as readily as with softer-burned, porous quicklimes. Thus, the rate of hydration is retarded. On slaking, this type of lime tends to yield coarser hydrate particles that contribute to inferior plasticity. The above principle applies proportionately with either high calcium or dolomitic or impure (possibly slightly hydraulic) limes, the latter two of which are inherently slower to react than the former. In fact, with the latter two limes, closer control over time-temperature conditions is essential to avoid over-burning than with high calcium.

A practical range in kiln temperatures for high calcium lime is 1900 to 2450°F, and for dolomitic, 150 to 200°F less (1750 to 2250°F), depending upon the size, uniformity, crystallinity, and purity of the stone and type of fuel and kiln utilised. Obviously, to secure the desirable soft-burned lime, the lower temperature levels are indicated. Yet, unless a small size of kiln feed is charged into the kiln of 2" maximum size, preferably less, such temperatures would be impractical because of necessarily long retention periods that drastically reduce throughput. Under most circumstances, calcining at the dissociation point would be hopelessly slow and impractical. Therefore, frequently optimum quality conflicts with maximum economy, and a compromise may be the only feasible solution, particularly when there are limitations on the size of stone that the kiln can accommodate.

In accelerating the rate of calcination, an increase in temperature exerts a much greater influence than prolonged retention. Even a 50°F rise in temperature with some stone can reduce calcination time by three to four-fold.

For superior calcination control, the favored practice is to preheat the stone gradually up to the dissociation point and not subject it to thermal shock. The temperature can be elevated gradually to a predetermined optimum calcining temperature adjudged to be most efficient for the given stone, and then retained at this level until calcination is complete. The two extremes of under- and over-burning should be avoided. A soft-burned, porous, highly reactive, thoroughly-calcined product that has shrunk only 5 to 20% is the objective. This means that the lime should not be retained in the kiln after calcination is complete, but that ideally it should be discharged to the kiln cooling zone just as it is fully calcined and then cooled as rapidly as possible. Unfortunately, considerable "trial and error" methods, with adequate instrumentation, are necessary to establish the condition for coordination of this delicate time-temperature relationship. The importance of operating skill predicated on extensive experience is also evident here.

Recarbonation - Another hazard in lime burning, that fortunately manifests itself only under poor calcination conditions, is recarbonation of the quicklime, the reversible phase of the calcination reaction, diagrammed earlier. Naturally, this condition reduces the content of quicklime, just as core does. Recarbonation can occur when large (+6 inch) lumps of limestone are calcined. As the higher temperature heat inflow penetrates well into the lump near its center, dissociation in an atmosphere of pure CO_2 will start to exert considerable pressure. The temperature rises as this pressure increases and causes the already calcined surface to be over-burned. This tends to shrink the pores of the particle more, thereby, impeding the escape of CO_2 and generating more pressure. If this lime is discharged to the cooler before all the core is calcined, there will still be a diffusion of CO_2 from the red-hot core which can be reabsorbed on the surface of the lime. Use of smaller sized stone, complete dissociation in the calcining zone, fast cooling of the lime, and rapid venting of the CO_2 gas up the stack are the best preventatives against this malfunction. Slight traces of recarbonation are almost unavoidable in most kilns; that is why quicklime of zero CO_2 content is almost unattainable. But in efficient operations, reabsorbed CO_2 will not exceed 0.5%. In a dry atmosphere quicklime will not recarbonate except at high temperatures of the order of 700°C.

Loss in weight - With a pure high-calcium stone, there is a theoretical loss in weight of 44%, usually in practice 1 to 2% less than this figure with commercial stone, because of impurities. With magnesian and dolomitic stones there is 1 to 4% greater loss in weight than with high-calcium, depending upon the MgO content (since $MgCO_3$ contains 52.2% CO_2).

Decrepitation - There are types of stone that can never be successfully calcined or are difficult to calcine unless special kilns are utilized. Such stones simply cannot withstand the preheating or calcining temperatures, and they will decrepitate and fracture into fines. The heat causes their crystalline matrix to expand or stresses will occur in these large individual crystals, causing disintegration. There is no dependable rule or formula or test for predicting the suitability of a given stone for calcination. Usually those types that are most prone to decrepitate are the coarsely crystalline and certain soft, chalky stones. The fine-grained dense limestones and other fairly crystalline types resist this thermal expansive force. However, these are simply generalizations. There are other stones that might visually appear to be susceptible to decrepitation, yet may be honeycombed with many microscopic fissures that act as expansion joints, thereby preserving their coherence.

Influence of stone size - Possibly the greatest influences on calcination are stone (kiln feed) size and gradation. Generally, the larger the size, the more difficult it is to calcine properly. Heat penetration into the center of the lump requires much more time. Too often the resulting long retention period causes the exterior of the stone to become hard-burned, or if this is averted, then the lime is incompletely calcined with a high core content. With large stone the "calcining effort" is much greater. A safe rule to observe on calcination is that the calcination time is directly proportional to the square of the stone thickness (or average diameter for irregularly shaped stone). This formula means that it would require about four times as long for stone A of 4 in. thickness to be calcined as stone B of 2 in., assuming both are cubic in shape, although the thicker fraction contains eight times as much volume and the heat has twice as far to penetrate. Stated another way, the small stone absorbs heat twice as fast as the large ones, but the calcining effort is only one-fourth. Thickness of stone rather than width or length or total volume (in irregularly shaped stone) is the main criterion in determining the calcining rate or effort.

The shape of the limestone particle is also somewhat important. Cubical stone rather than flat or laminar pieces are most desired. The type of crushing equipment or adjustment in crushing influence this desired shape.

Stone up to 12 in. is calcined into lime, but for the above reasons 6 in. maximum size is recommended and if possible even smaller sizes down to 1 in. or less, assuming that an appropriate kiln is available. Theoretically, sizes of Nr. 8 to Nr. 40 mesh would be ideal for calcination, but such small fractions are most difficult to burn, except in special, usually costly kilns. So, probably top sizes between 1 to 3 in. may be the most practical to calcine under average conditions.

Production of kiln feed of the same uniform size would be prohibitively costly. But ideally, the stone sizes should be as uniform as can be economically produced, for maximum lime quality. Assuming an even distribution of heat in the kiln, stone of the same or nearly same size will be calcined evenly, leading to great uniformity in quality. But if there is a broad gradation of say, 1 to 6 in., the larger stones will be under-burned when the smaller size is soft-burned and vice versa. Furthermore, in all vertical kilns there must be ample voids (about 35%) between the stone for adequate gas circulation. Wide gradations tend to reduce the voids; whereas close gradations enlarge these voids. Thus, gradations of no more than 100% spread should be utilized, such as 1 to 2 in., 1.5 to 3 in., 3 to 6 in., etc.

Influence of impurities - Impurities in lime are derived primarily from the stone and secondarily from certain fuels. For building lime, concern regarding impurities is more quantitative than qualitative; for chemical lime, on the other hand, there are tolerances on specific impurities for certain uses so that qualitative considerations are usually of equal importance. The typical impurities in lime in order of their approximate magnitude are silica, carbon dioxide, alumina, iron, sulfur, manganese, sodium oxide, and potassium oxide. None of these would be deleterious to a building lime, except Na_2O and K_2O, and that, too, if the combined amount of these exceeds 0.2%. Limits on these alkaline salts are desirable, since their presence in lime-based mortars in excessive amounts will contribute to efflorescence in masonry. This is one of the disadvantages of impure or hydraulic limes, since the argillaceous or silicious limestones from which they are derived, frequently possess much greater amounts of these salts than the purer limestones. The many trace elements that occur in limestone are of no concern.

The reason it is desirable to utilize a stone of low total impurity is that at calcining temperatures the CaO in particular and the MgO to a lesser extent will combine chemically through a fluxing action to form calcium and magnesium silicates, aluminates, and ferrites. The formation of these slag-like compounds tends to reduce the calcination process by clogging the micro-pores in the stone, thereby impeding the expulsion of CO_2 gas. This retards calcination and compels higher temperatures that induce hard-burning and ultimately yields hydrates of inferior plasticity. From a chemical standpoint, it markedly reduces the amount of available lime. As a generalization, an impure limestone of, say, 6% impurities that is subjected to severe calcination conditions, will yield a lime with nearly double (12%) the content of impurities, since the weight of the CO_2 that is evolved is nearly half of the weight of the calcium carbonate. But if these impurities combine with the oxides, then the magnitude of loss of CaO could be as much as 24%. In contrast, a stone with only 2% impurities would vitiate the lime content by no more than 6% by the same reasoning — a vast difference. Even if an impure limestone is calcined skillfully so that it is not relatively hard-burned, its reactivity with water is lower, and it tends to behave like a hard-burned pure lime. Furthermore, the color of the resulting lime hydrate is adversely affected by excessive impurities, tending to be slightly grayish instead of the desired sharp white color.

The secondary source of impurities from fuel occurs mainly with direct firing with solid fuels or in mixed-feed kilns. Silica, carbon, iron, and alumina contained in the ash contaminate the lime in both a free state and by forming silicates and aluminates, and sulfur is often absorbed from the combustion gases. Generally, any appreciable impurity pickup like this discolors the lime. Sulfur is also absorbed from coal-derived producer gas, oil, and natural gas, but generally the quantity involved is no problem with building lime. Of all fuels, wood has the least potential for contaminating lime. In fact, wood, when economically available, is ideal for lime burning, since it is almost impossible to hard-burn lime because of its innately milder heat generative qualities.

Other Modifications - Research with certain limestones have revealed that the addition of salt (NaCl, $CaCl_2$, or Na_2CO_3) to the limestone kiln feed improves calcination by accelerating the reaction at the same temperature or by permitting calcination at lower temperatures, leading to softer burned lime. The amount of salt added ranges between 0.2 to 1% in dry form, or the stone may be simply immersed, or doused with a salt brine. Since there is a virtual absence of adverse reports on this possible additive, it might be worthy of some investigation.

In striving for high quality and a soft-burned lime, control of temperature is essential. In order to prevent temperatures from rising unduly, empirical methods of tempering the flame have been developed by the judicious application of forced or induced draft and/or injection of steam. Such practices contribute to higher thermal consumption but may be economically justified when applied in moderation. Often some steam is generated in any event from use of moist stone or coal, but some plants will inject artificial steam into the kiln as a supplement. Use of artificial steam would appear to be most applicable to those limes that are most difficult to calcine without over-burning, i.e., hig. magnesian, dolomitic, and impure or weakly hydraulic limes.

Heat Requirement - To determine the theoretical calorific requirements for lime burning, it is first necessary to calculate the thermal units required to preheat the stone to the dissociation point. The following formula is used for this calculation:

Calculation:

$$Q = 2000 \times Cp \times (T_2 - T_1).$$

Q Heat required in Btu/t.

Cp Specific heat of limestone in Btu/lb.

T_2 Minimum dissociation temperature stone in °F.

T_1 Starting stone temperature, atmospheric temperature about 50° in °F.

2000 Conversion factor from lbs to tons.

Assume that the specific heat (see Fig. 1) for $CaCO_3$ is 0.255, that the starting temperature of the stone is 50°F, and that the minimum dissociation temperature is 1648°F; then: 0.255 x 2000 x (1648 - 50 or 1598) = 814,980 Btu/ton of limestone. But 44% of the limestone is volatilized as CO_2 so that theoretically 1.79 ton of kiln feed is required to produce 1.0 ton of quicklime; thus 814,980 x 1.79 = 1,458,814 Btu/ton of high calcium quicklime.

The same formula applies to dolomitic limes, but because of their lower dissociation point the thermal requirement is slightly less, in spite of the fact that a greater amount of CO_2 is lost. The heat requirement for dolomite would be about 1,250,000 Btu/ton of lime. Magnesian limes would be intermediate between this value and high calcium.

However, there is another larger thermal requirement for quicklime production. This involves the retention of the dissociation temperature until all of the CO_2 has been expelled and consequant heat-loss in the kiln. General consensus is that the theoretical values for high calcium and dolomitic are 2.77 and 2.60 million Btu/ton, respectively.

All of the above theoretical values are predicated on 100% pure carbonates. As impurities in limestone increase, these thermal requirements are reduced percentage-wise slightly, since there is less carbonate to decompose.

To determine actual thermal efficiency with commercial limestone, the following formula can be employed:

$$\frac{\text{Theoretical Heat Requirement} \times \text{\% available oxide content}}{\text{Total Heat Requirement}} = \text{\% Thermal Efficiency}$$

Thus, if a lime has a 93% available CaO content and total fuel requirements are 6 million Btu/ton, then

$$\frac{2,770,000 \times .93}{6,000,000} = 43\% \text{ (efficiency)}$$

100% efficiency is unattainable, for three reasons: first, there is no commercial stone available that is 100% pure; second, it is impossible to calcine lime without some dissipation of heat; third, production of lime with zero core and zero recarbonation, without hard-burning, is virtually impossible. The initial thermal requirement of preheating the stone to the dissociation point is not included in thermal efficiency studies, since theoretically such heat is only required once, i.e., for the first charge of stone. Heat recuperation at the cooler recovers much of this heat for calcination and preheating of successive stone charges.

Significant improvement can be gained in thermal efficiency with heat balance studies on each kiln that reveals the individual heat losses in various stages of calcination. In the order of their magnitude, heat losses occur as follows:

1. Heat in products of combustion (exhaust gases) — if only 1% each of CO and O_2 are present in the exhaust, there is a resultant calorific loss of 220,000 and 40,000 Btu/ton of lime, respectively. Better co-ordination of fuel input with sources of draft to achieve complete combustion reduces this loss.

2. Heat of radiation and convection — this covers the inevitable loss of some heat through the kiln lining. Increasing the thickness of the refractory brick lining can reduce this loss.

3. Heat in discharged lime — potentially this can be a severe loss of heat if the lime is discharged from the kiln red-hot. Efficient coolers can reduce this loss.

4. Heat to dry stone — most kiln feed, since it is stored outside, contains varying amounts of moisture, from 1 to 10%. Thermal units are required for volatilizing this extraneous moisture.

5. Heat in dust and incombustibles — due to attrition from the movement of the stone through the kiln, there is an accumulation of lime, stone, ash, and refractory lining dust waste that absorbs and wastes a small, usually inconsequential, amount of heat.

6. Heat to dry coal — there is a very small calorific requirement for the heat of dehydration in drying solid fuels.

Lime kilns are operated with widely divergent thermal efficiencies, depending largely upon kiln design and operating skill, from as low as 3.25 to 3.5 million Btu/ton of lime up to 12 to 14 million. However, most modern kilns fall into a range of 4 to 7 million Btu/ton. At one time thermal requirements were described in terms of fuel ratios, such as 1 ton of coal to 4.5 tons of lime, etc. For accurate heat balance studies such ratios are too loose. The coal could possess a fuel value of 12 or 15,000 Btu/lb. Therefore, Btu/ton of lime is the most dependable measure to use, since it is more specific and acts as a common unit for comparisons of diverse fuels, like coal (tons), oil (gallons), natural gas (cu.ft.), and wood (cords). Calorific value ranges for common fuels employed in lime burning are contained in Table III.

Recapitulation — Thus, there are numerous critical variables in lime burning, which are summarized as follows in the approximate order of their importance:

1. Stone size and gradation.
2. Physical characteristics (crystallinity) of stone and tendency to decrepitate.
3. Quantity of impurities in stone.
4. Rate of calcination.
5. Calcination temperature.
6. Duration of calcination.
7. Possibility of recarbonation.
8. Quality and type of fuel.
9. Quality of impurities in stone.

However, there is one more very important variable, the kiln, which is the mainspring of the lime plant. Even slight modifications in the design of most kilns can exert a marked influence on the calcination performance. Yet many kilns are only adaptable to certain sets of conditions and are relatively useless with other kiln feed or fuels or because of economic circumstances.

Types of Kilns - Although lime calcining is chemically a simple operation, there are such a vast number of commercial kilns available that the prospective lime manufacturer will have to make a careful study to determine the best type of kiln to install for making building lime. This initial study is also vital, considering that the kiln investment may represent as much as 50% of the total plant cost. The kiln finally selected will depend primarily upon the type of stone and fuel available, although other factors, such as labor supply and lime market requirements may have a bearing.

The following discourse will consider the major kiln types available; these will be described briefly, but no attempt will be made to go into details of actual kiln design and operation. This information can be obtained from the various kiln manufacturers. It would seem to the writers that because of the general lack of skilled workers in the developing countries, emphasis should be placed on the simpler, less sophisticated types of kilns. Of course, regardless of kiln type, a premium should also be placed on producing a soft-burned reactive lime, which is required for good building lime.

Lime kilns are divided into vertical (or shaft), tunnel and rotary types, but in recent years a growing number of radically different kilns have been introduced. This wide variety of lime kilns represents a striking contrast from the portland cement industry, which mainly utilizes rotary kilns.

Generally, the vertical and horizontal static kilns have the following advantages over rotary kilns: lower capital investment, lower fuel costs, simplicity of construction and operation, low attrition loss of stone, less refractory wear, and greater flexibility (can be shut down over weekends). On the other hand, the principal advantages of the rotary type are: ability to burn small stone readily and to produce a wide range of burn (from soft to dead-burned), more uniform lime quality, greater capacity, and higher output per manhour. In the U.S.A. and Canada, more than 80% of the total commercial lime is produced in rotary kilns, whereas in Europe nearly 95% is produced in shaft kilns.

Vertical Kilns - Revolutionary changes have taken place in vertical kiln design in recent years, and a large number of types are now available: mixed-feed, gas producer, natural gas (with side and center burners), oil-fired, dual- and triple-shaft, double-incline, to name a few. Nearly all of these kilns burn only large stone (over 3 in. and up to 12 in. size); however, some of the newer vertical types are designed primarily for small stone (1 to 2 in.). Generally, with vertical kilns, the use of small stone is more conducive for producing soft-burned lime, although there are exceptions.

Fig. 6 shows a generalized view of a simple vertical shaft kiln. The most widely used kiln has a refractory-lined steel or boiler plate shell, although

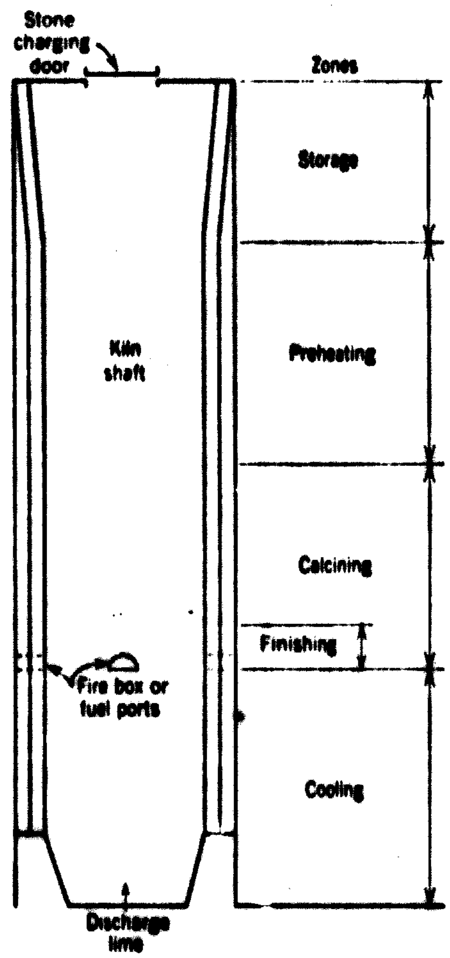
Table III

Calorific value ranges of fuels for lime calcination

Fuel type	Calorific value	Unit
Solid fuels (other than wood)	11,000 - 16,000	Btu/lb.
Natural gas	900 - 1,200	Btu/cu. ft.
Fuel oil	16,000 - 18,000	Btu/lb.
Wood	3,000 - 6,000	Btu/lb.

Figure 6

Diagrammatic section of vertical kiln



stone masonry and reinforced concrete have also been used for the outer shell. The kilns are usually circular in cross-section, although they may be oval, rectangular, or a combination. The most typical diameters vary from 9 to 14 ft., and heights from 50 to 75 ft. (Some kilns are as high as 125 ft. and as much as 24 ft. in diameter.) Capacities vary widely — from a low of 10 tons per day to as high as 500 tpd.

There are four basic zones in a shaft kiln — storage, preheating, calcining, and cooling, although the boundaries are not often distinct. The exact proportioning and contouring of these zones constitutes the "art" of vertical kiln design.

Charging to the storage zone is usually accomplished with skip hoists; or in the case of modern mixed-feed kilns, a special bucket device is used. Some kilns are also charged by a belt conveyor tripper system and circular distributor plate. In most vertical kilns an airtight seal is provided to eliminate fluctuations of draft. The storage zone serves primarily to insure continuous operation of the kiln in the event of breakdown in the stone handling system; it generally holds about 2 hours supply of stone.

In the preheating zone the stone is heated to the dissociation temperature by utilizing hot gases rising upward from the calcining zone. In some kilns the exhaust gases are drawn off by an induced or forced draft from the top of the preheating zone, with some of the gases then being recirculated to the calcining zone (primarily to temper the flame); in other kilns the hot gases are exhausted through the storage zone. In areas where exhaust gases may present a problem, the gases are drawn through a dust collector (dry or wet) before discharge to the stack.

The calcining zone is the most critical segment of the kiln. Too high a temperature in this zone, or too long a retention time, will hard-burn the lime, making it undesirable for building purposes. Several types of firing are utilised in shaft kilns, including mixed-feed, direct-firing with solid fuel, and indirect firing from Dutch ovens, gas producers, and gas or oil burners. These methods will be described later.

The cooling zone is also critical, and most vertical kilns are designed so that practically all of the air for combustion is drawn in through this zone, thus both cooling the quicklime and preheating the combustion air. In modern kilns, the quicklime is cooled to the extent that it can be held without burning the hand — down to 110-125 F.

Discharging methods vary considerably with shaft kilns; the older units still utilize manual methods, the lime being discharged intermittently into carts or wheelbarrows. In contrast, mechanized kilns are discharged automatically and continuously, using pre-set time cycles, vibrating feeders, and weigh-hoppers. The timer actuates a feeder, which operates until a pre-set weight is reached; the feeder then shuts off and the weigh-hopper discharges to a conveyor. Several feeders serve each kiln, working in sequence, thus effecting uniform discharge across the kiln.

Kilns Burning Large Stone - Nearly all of the shaft kilns calcine large stone, generally exceeding 3 in. in diameter, and in some cases ranging up to 10-12 in. These include the following types:

Mixed-feed — There is a great diversity of kilns in this category, ranging from the more primitive pot kiln to the more advanced high capacity coke-fired kiln. The former are constructed of field stone, charged with alternate layers of limestone and anthracite (or coke), and produce up to 15 tpd.; they are operated strictly empirically with no instrumentation. For further discussion on early type kilns refer to the end of this chapter.

The modern coke-fired kilns, on the other hand, are built with refractory-lined steel shells; and they are equipped with automatic charging and discharging devices, recirculatory fans, and various instrumentation controls. Capacities average 125 tpd, although they are as high as 400 tpd. In one German kiln, a modified Seeger, the mixing and charging of the limestone-coke feed is handled by a bucket-like device called a kubel, which has the same diameter as the kiln shaft. As it rotates, it is charged with precise weights of coke and limestone, thus effecting intimate mixing; the kubel is then hoisted to the kiln top, where the feed is discharged uniformly and quickly by the collapse of the bottom by means of radially-hinged doors.

The high capacity mixed-feed kilns have the best average thermal efficiency in the lime industry, operating as low as 3.25 million Btu/ton. Invariably, however, the lime is hard-burned and contains up to 5% core, as well as impurities from the coke. Mixed-feed kilns are often employed captive in the alkali and sugar beet industries, where CO_2 gas from the limestone and coke is recovered for use along with the quicklime in the chemical process. By using coke, it is possible to recover more CO_2.

Direct-fired kilns — Largely due to contamination from fuel ash in the early pot kilns, lime manufacturers developed separate fire boxes or Dutch ovens for burning coal, coke, or wood, with firing done initially by hand methods. Several plants in Ohio still utilize kilns of this type to produce a highly plastic dolomitic lime which is especially suitable for mortar and plaster. These kilns are approximately 12 x 50 ft. in size, and are equipped with four Dutch oven fire boxes which burn 2 x 4 in. soft coal; the heat enters the kiln through six ports located around the periphery. As a means of insuring the production of soft-burned lime, the flame is often tempered by the introduction of artificial steam beneath the grates in the fire box. These kilns are operated with natural draft and produce up to 15 tpd, with a fuel consumption of approximately 7,000,000 Btu/ton (3 tpd. of coal per kiln). The kilns are drawn every four hours.

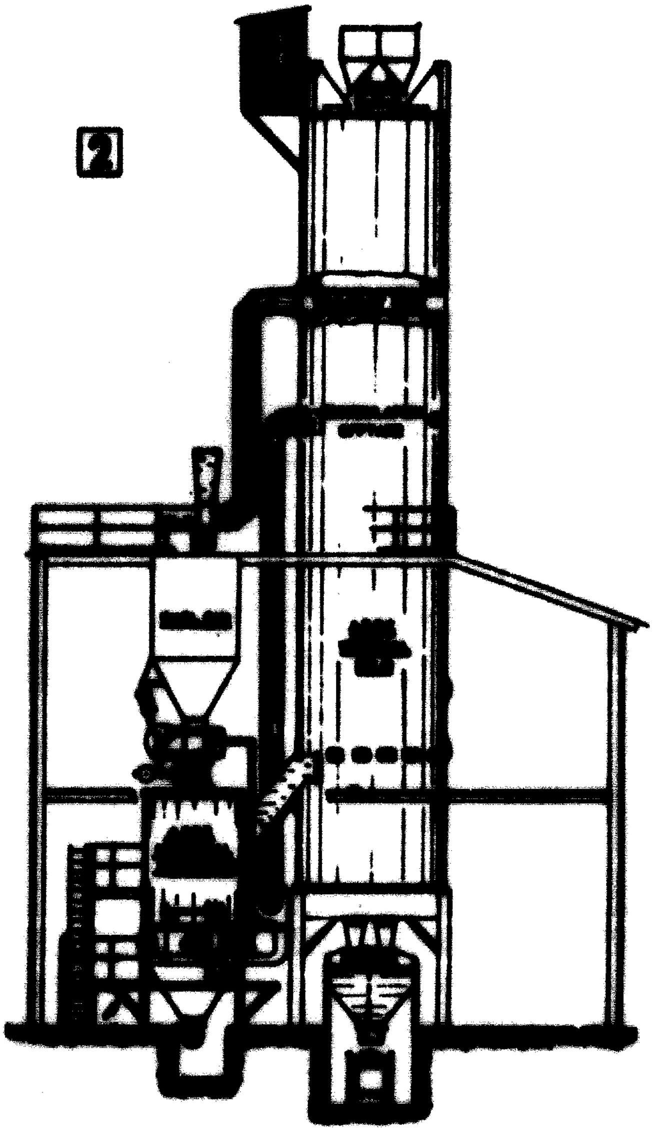
Gas-Fired Kilns - Two types of lime kilns are included here — *producer gas* and *natural gas*. The former, developed historically after the direct-fired kilns, were once popular in the U.S.A., but are seldom used there now; however, they are still prominent in other countries. Natural gas firing, on the other hand, has gained much prominence, particularly in the U.S.A.; and some of the largest capacity vertical kilns are of this type.

Producer gas is generated by burning coal (soft or hard) or wood in a furnace adjacent to the lime kiln, the hot gases being drawn or blown into the kiln through numerous ports or through a center beam. (See Fig. 7.) Most producer gas kilns are small in capacity, although one plant in Brazil, which burns wood, operates at a 130 tpd. rate.

Fig. 8 depicts a simple, unmechanized, and inexpensive producer gas kiln designed by Asbo. It can be hand fired, using coal or wood, although wood is preferred for soft burning. The kiln is 47 ft. high, with a superimposed 12-ft. chimney; the external diameter is 10 ft. but internally it is 6 ft. 3 in. at the calcining zone and 7 ft. 9 in. at the preheating and storage zones, indicating thick insulation at the hottest zone. The hot combustion gases from the adjoinin gas producer enter the kiln through a center burner beam. Stone charging and lime discharging are handled manually, although cable-car charging may be adapted It operates on the following principle, with the stone and lime moving down evenly and with frequent charging and discharging at about half-hour intervals. It

Figure 7

Medium capacity Ãzbe producer gas kiln featuring automatic coal firing



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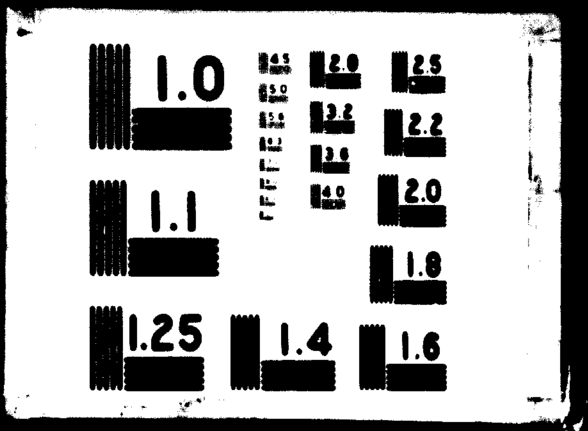

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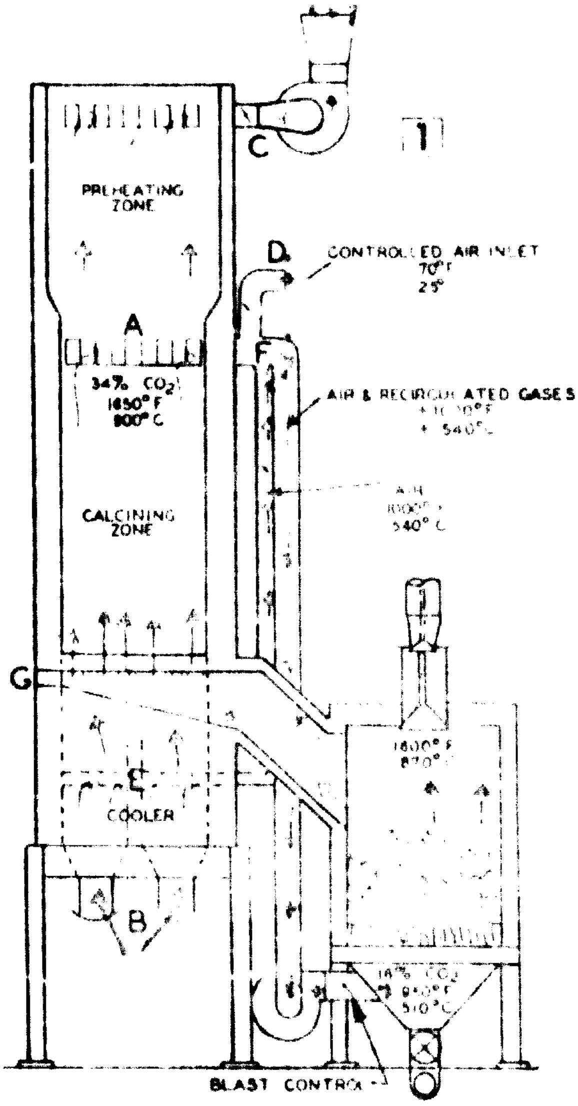
Small capacity Azbe [illegible] wood as fuel



is provided with poke holes to prevent "hanging". Although it can be operated with natural graft, installation of induced draft fans will markedly increase throughput, about doubling capacity from 20 to 35-40 tpd. Kiln feed of 3 x 5 in. is required, and thermal efficiency is reasonably good. This kiln could probably be converted to oil firing, by installing oil burners in the gas producer.

Early natural gas-fired kilns utilized side burners, but the more modern ones, such as the Azbe, are also equipped with center burners for more efficient distribution of heat across the entire kiln cross-section. (See Fig. 9.) When side burners are used, they are located around the kiln periphery at two or more levels in order to effect uniform heat distribution. However, unless high gas velocities are sustained, the gas tends to rise up along the sides, thus causing less heating in the center of the kiln. It is mainly for this reason that center burners have been developed to supplement or even replace the side burners.

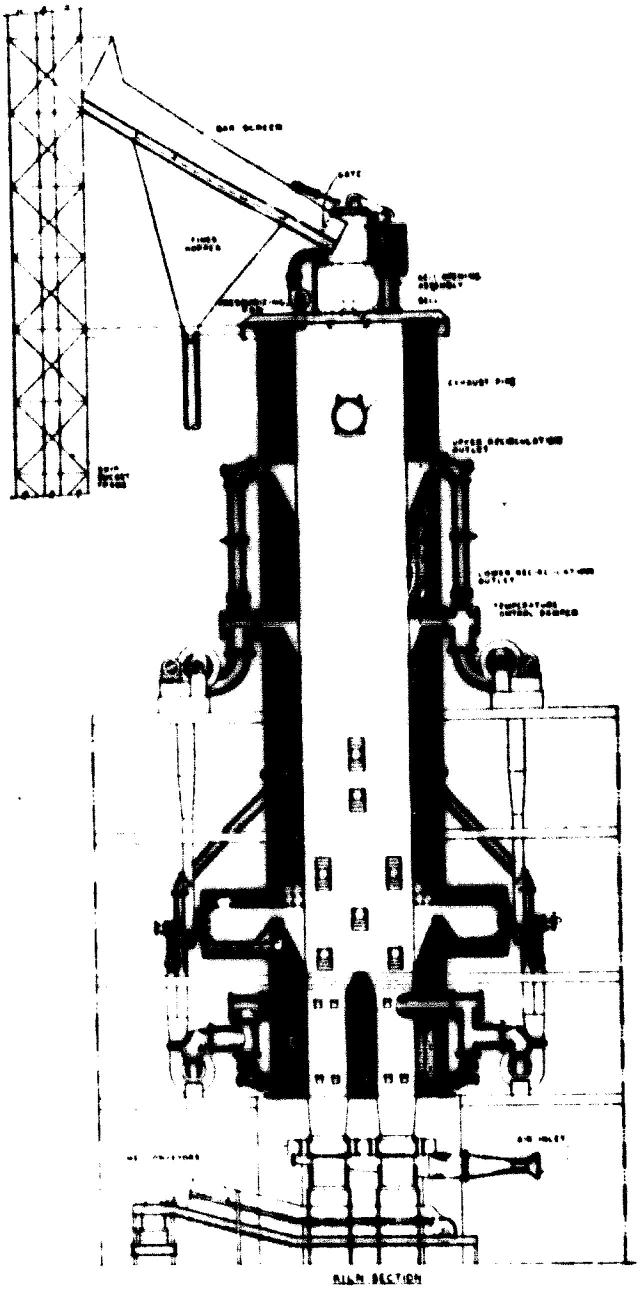
One of the latest center-burner kilns is the Union Carbide Kiln, which houses the burner pipes in water-cooled H-beams extending across the kiln. The burner beams are located at two levels in the calcining zone, with two or three beams per level, depending upon the kiln capacity. Each beam is divided into four burner compartments, each compartment in turn having its own set of burners and a separate air inlet to control the amount of air that combines with the fuel. This kiln is reported to have the largest output of vertical kilns, producing up to 500 tpd.; the larger unit requires a 500 hp. fan to effect a forced draft of 28 in. water-gauge pressure.

Oil-Fired Kilns — A recent vertical kiln innovation, developed largely in Europe, is the oil-fired kiln. The development has been prompted in Europe by the increasing cost of coke and coal, coupled with the general unavailability of natural gas. Of course, the fuel oil has to be vaporized before contacting the stone in the kiln. The main advantage of oil firing over mixed-feed is the production of a more reactive, uniform lime, with the possibility of using a wider range of stone sizes.

One of the most advanced oil-fired shaft kilns that is favoured by the largest European plants is the Beckenbach ring-kiln developed in Germany, which has the largest capacity — up to 325 tpd. for an 18 ft. diameter x 80 ft. high unit. Normally heavy fuel oil (Bunker C) is used, although lighter oils can also be

Figure 9

High capacity natural gas fired kiln equipped with center burners



burned. Kiln feed is 1½ x 3½ in. and thermal efficiency is reported less than 4 million Btu/ton.

Two other oil-fired kilns have been developed in England: West's kiln using the Catagas system and Esbjornsson-type kiln using the Urquhart gasification system. The Catagas unit (Fig. 10) comprises oil injectors mounted on the side of the kiln and refractory-lined chambers inside the kiln. The oil is injected as a solid jet (at 220°F) around the full circumference of the chamber, where it flash vaporizes from the radiant heat; the oil vapors, together with the primary air also introduced through the injector, then rise directly into the calcining zone where combustion is completed. The West's kiln is available in 50 and 100 tpd. sizes; 3 x 5 in. stone is used, with a heat input reported to be less than 5 million Btu/ton. Oil consumption (heavy oil) ranges from 24-28 gals./ton.

In the Urquhart system, gasification occurs in the unit itself, which is mounted at the lower firing level; the heavy fuel oil is first atomized, then converted to a gas at about 1400°C. Before entering the kiln, however, the gas is cooled to 1000°C by means of water spray jets located in the duct between the gasifier and kiln. The gas enters the kiln at two levels through a total of 16 ports. Fuel consumption for this 50 tpd. kiln, utilizing 5 x 8 in. stone, is 27-30 gal./ton.

<u>Kilns Burning Small Stone</u> - Much research and experimentation has been carried out to utilize small stone (2 in. size and under) in vertical kilns, but only a few kiln designs to date have been successful. Two of these which successfully burn small stone are the double-incline (cascade) and the Wopfing parallel-flow regenerative (double- and triple-shaft) type. Both are of European development and of moderate capacity; the former burns a combination of coke and fuel oil/or natural gas, and the latter utilizes natural gas or fuel oil (no coke).

The <u>double incline kiln</u>, developed by Warmestelle Steine : Erde (Germany), is rectangular in cross-section and widens into two firing chambers, arranged one below the other. (See Fig. 11.) The feed consists of a mixture of coke and limestone (generally 1 x 1½ in. size, although the absolute size range is 3/8 to 2-3/8 in.). The coke provides about 40% of the fuel requirement, and fuel oil, the balance. Two high pressure oil burners are mounted at each firing level, each pair being opposite one of the two inclined beds in the shaft. The

Figure 10

British vertical kiln equipped with Catagas oil burners

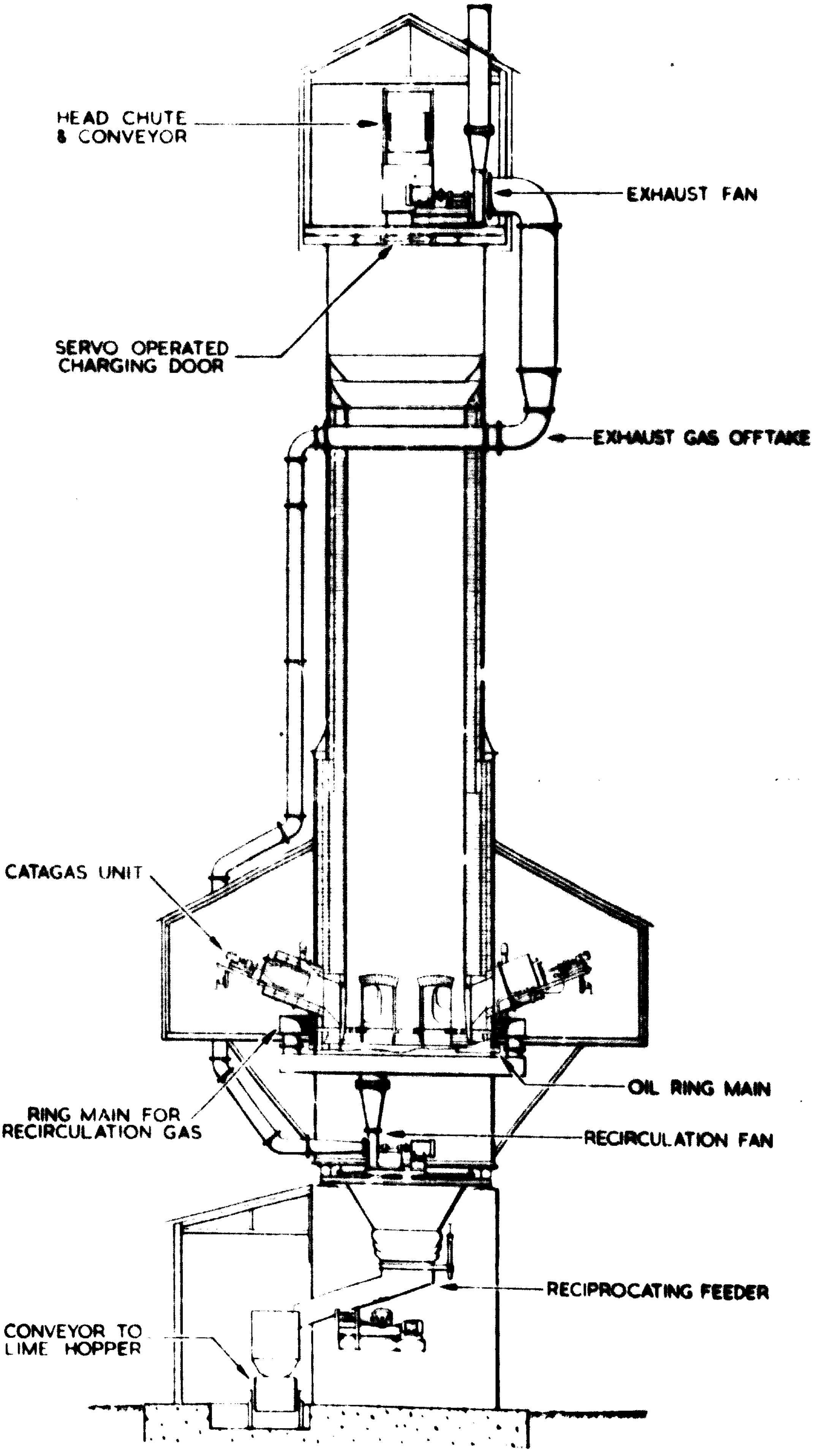
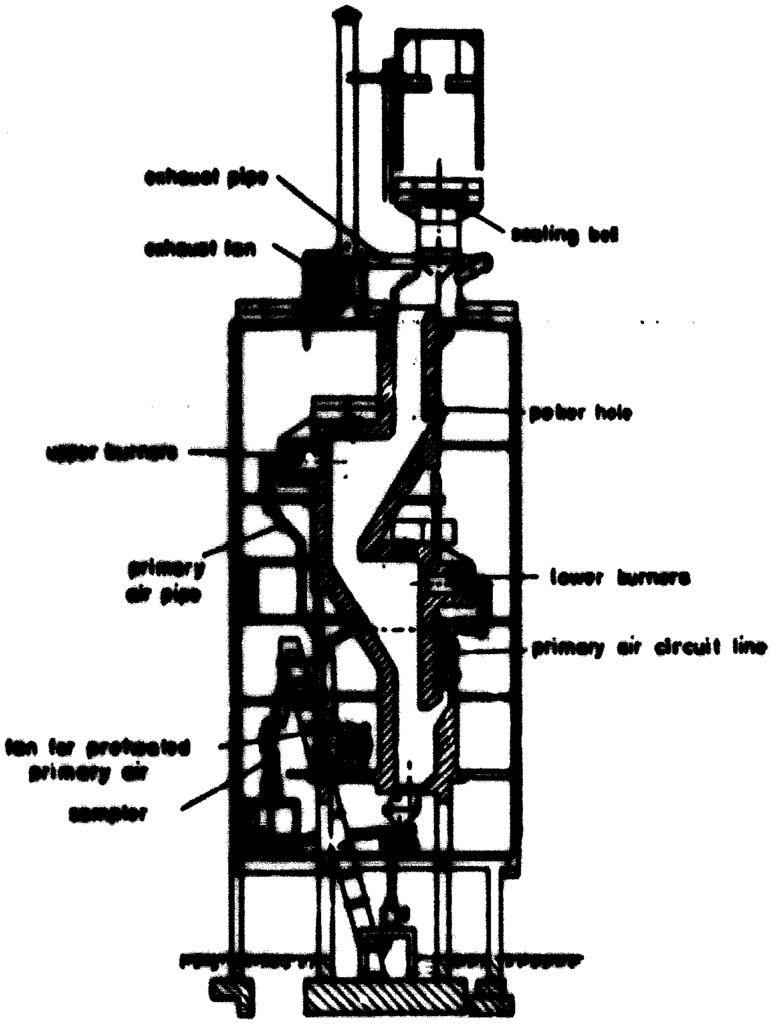


Figure 11

German double-incline kiln for burning small stone, fired with coke and natural gas



kiln works on the following principle: as the material leaves the storage zone, the coke ignites, thus preheating the stone; then the material layer flows down the first inclined bed, meeting the gas flames from the top oil burners. Next, the material passes to the second inclined bed, where it turns over (cascades) due to diametric position of the bed; thus the remaining limestone now faces the flames of the bottom oil burners (by this time the coke has been consumed). Leaving the lower firing chamber, the lime enters the cooling zone at a temperature of 800°C.

The kiln is about 75 ft. high and has a capacity of 150 tpd. The fuel consumption of about 4.1 million Btu/ton is higher than modern coke-fired kilns, due largely to radiation losses at the cascade sections. The lime is of good quality — soft-burned and minimum core.

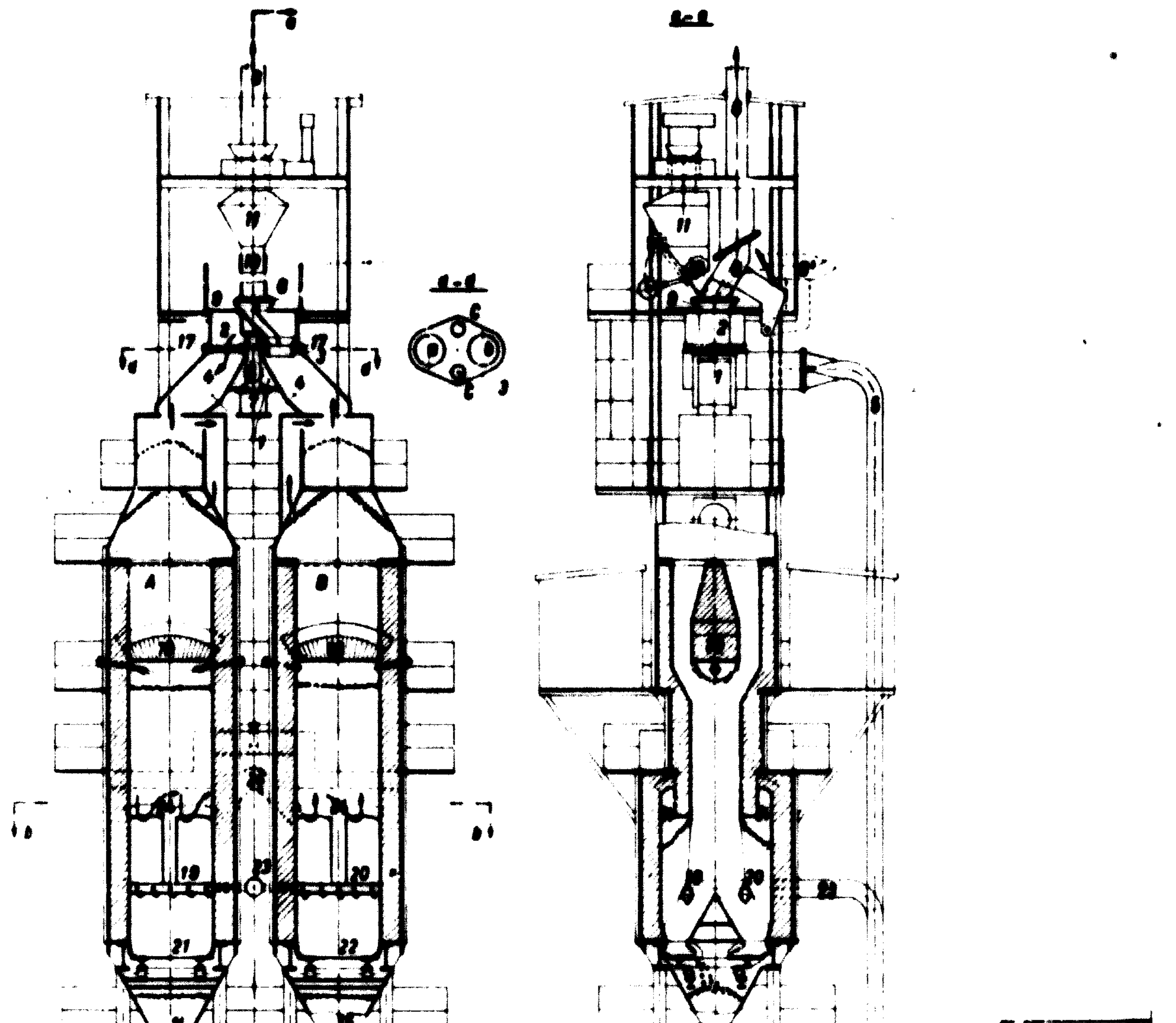
The parallel-flow regenerative kiln was developed by Schmid (Austria), and comprises two-shaft (Fig. 12) and three-shaft units with capacities of 100 and 150 tpd., respectively. Next to the modern coke-fired kiln, this vertical has the lowest heat consumption — under 3.5 million Btu/ton. Another advantage is production of soft-burned lime, utilizing kiln feed of 1 x 2 in. in the triple shaft and 2 x 4 in. in the double shaft. Either natural gas or oil can be used.

The high fuel efficiency is due to a novel heat regeneration system which permits burning at relatively low temperature — the shafts are interconnected at the lower end of the burning zone, and while one shaft is being fired, the other is being preheated. Fuel and combustion air are supplied to the burning shaft from above, ignite at the upper end of the burning zone, and calcine the lime in uniflow. The exhaust gases then pass into the second (adjoining) shaft, preheating the stone in counterflow. After a 10-15 min. interval, the shaft firing is reversed. Cooling air is blown into both shafts simultaneously. In the three shaft units, one shaft is operated as the burning shaft, while the other two are being preheated. The length of reversal time is determined primarily by the production level desired (the kiln can be operated as low as one fifth of capacity). An indication of the high fuel efficiency is the low exhaust temperature — only 100°C.

The kiln is almost completely automated, and all reversal, charging, and discharging devices are hydraulically operated. Power consumption is about 15 kwh per ton at full capacity.

Figure 12

Austrian parallel-flow double-shaft kiln for burning small stone, fired with natural gas and fuel oil



Rotary Kilns - Unlike shaft kilns which operate essentially fully charged, the rotary kiln has about 90% of its volume filled with flame and hot gases. As the kiln rotates, new surfaces of stone are constantly exposed to the hot gases, but the area exposed is relatively small and there is little passage of gases through the solids; hence, the heat exchange is relatively inefficient. In spite of the lower fuel efficiency, however, rotary kiln installations have increased greatly during the past quarter century, particularly where fuel is cheap, labor is costly, and large production of uniform, soft-burned lime is required.

The rotary kiln has the advantage of burning stone as small as 3/8 in., but can also handle stone as large as 2¼ in. Generally, however, the stone fed to any one kiln is confined to fairly narrow limits, e.g. 3/8 x 3/4 in., 3/4 x 1½ in., etc.; otherwise segregation would occur and the finer stone would sift to the bottom of the kiln and remain largely uncalcined.

Rotary kilns vary greatly in size, ranging from 6 x 80 ft. to 12 x 450 ft., with capacities from 25 to 600 tpd. The most typical sizes in North America are between 8 to 10 ft. in diameter and 150 to 200 ft. long, producing 200-250 tpd. (See Fig. 13.) Rotaries are mounted on two or more tires, slopes from 3/8 to 3/4 in. per foot, and operated at 40-60 rph.; the speed of rotation is determined primarily by the production and degree of burn required. Types of fuel used include pulverized soft coal, natural gas, and fuel oil, or combinations. In modern kiln installations, instrumentation is highly developed, enabling one man to operate two or more kilns efficiently.

When rotary kilns were first used in the lime industry, fuel ratios exceeded 12 million Btu/ton. This has gradually been lowered to a minimum of about 6 million Btu/ton, largely through the use of shaft or grate-type preheaters, internal heat exchangers and dams, recuperative-type coolers, and elaborate instrumentation. The modern trend is away from the long kilns to the use of medium-sized kilns incorporating various heat-saving devices, particularly the preheater.

One of the most widely used preheaters is the Kennedy Van Saun shaft type, which is a 7 ft. high rectangular box mounted below an enclosed raw stone bin. Exhaust gases from the kiln are drawn through the stone, preheating it to about 1600°F. The retention time is about 2 hours, during which time about 10%

calcination is accomplished. The stone is then fed to the kiln at a pre-determined rate by means of a reciprocating bar feeder and feed pipe.

Several internal devices for improving heat transfer within the kiln have also been developed. The most prominent are the trefoil, quadrant, or sexpartite recuperator sections, generally mounted at the feed end, which turn over the stone more effectively and increase the turbulence of the hot gases. (See Fig. 14.) One or more dams may also be used, primarily in the calcining zone, which slow the passage of the stone and also create turbulence of the flame and hot gases.

Three principal types of coolers are used with rotaries -- the shaft or contact, the planetary, and the rotary cooler. In each type, hot gases are returned to the kiln as secondary air, thus increasing fuel efficiency. The most prevalent type is the contact (counterflow), which is mounted beneath the kiln hood. The Marblehead-Niems cooler, one major type, is a refractory-lined steel box incorporating four discharge pockets; cooling air is provided by a medium-sized fan sufficient to reduce the lime temperature to 150°F. or less. The KVS contact cooler is conical shaped, and the Krupp (German) cooler utilizes double cross-current action.

The planetary cooler, including the Unax and Warner types, consist of eight or more approximately 4-ft. dia. x 20-ft. tubes, mounted at the discharge end of the kiln (Fig. 13). The lime is moved in each tube by integral conveyor flights counterflow to the cooling air; chains may also be used for heat transfer. The rotary cooler is not as effective as the other two types, and a further disadvantage is attrition loss caused during rotation.

<u>Grate-Kiln System</u> -- A fairly recent calcining development by Allis-Chalmers is known as the Grate-Kiln system, which incorporates three units: a single pass, down-draft, enclosed traveling grate preheater; a relatively short, large diameter kiln; and a revolving counterflow contact cooler. A feature of the system is the calcining of the finer stone and preheating of the coarser stone in the grate section (at about 1500°F). This is made possible by means of a conical chute distributor which places the coarsest stone on the grates and the finer sizes on top. The smaller stone begins to calcine by direct contact with the hot gases that pass downward through the grate. The coarser sizes are then calcined in the rotary kiln, while the smaller sizes are protected from overburning because they sink into the rotary kiln load due to the sifting action.

Figure 13

Medium-sized rotary kiln equipped with satellite coolers

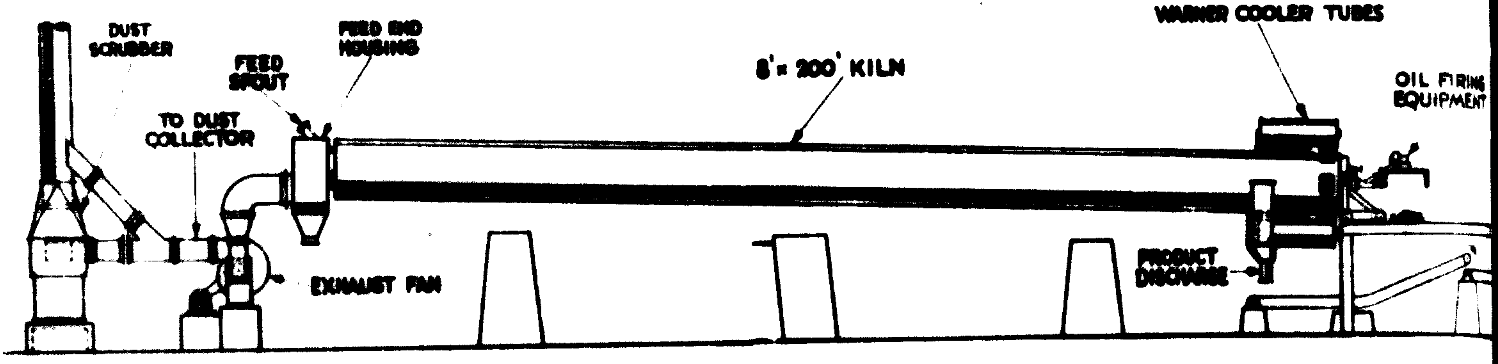
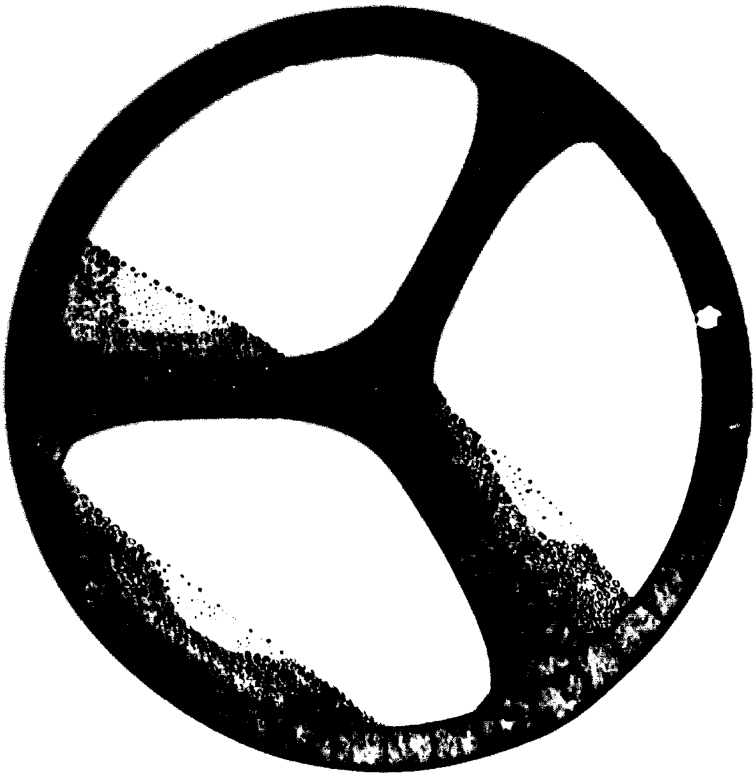


Figure 14

Cross-section of rotary kiln showing trefoil section for effecting better heat distribution



Grate-Kiln systems in operation include a 600 tpd. plant incorporating a $12\frac{1}{2}$ x 60 ft. grate and $11\frac{1}{2}$ x 160 ft. rotary, which burns pulverized coal, and two 300 tpd. plants incorporating 6 x 46 ft. grates and 10 x 110 ft. rotaries (one gas-fired and one oil-fired). These kilns operate at about 5,500,000 Btu/ton of lime, producing a uniform, soft-burned lime. One distinct disadvantage of this system has been the excessive maintenance on the grate castings.

Other Kilns - One of the most revolutionary of the new lime kilns is the Calcimatic, which consists of a preheater, circular hearth, and cooler, all refractory-lined. (See Fig. 15.) The stone is carried on the hearth in a thin layer, and one revolution of the hearth constitutes the calcining cycle; an average cycle is about 90 min. Stone from 4 in. down to dust can be burned, although a gradation of not greater than 3:1 (e.g. $\frac{1}{2}$ x $1\frac{1}{2}$ in.) is recommended for optimum results. The kiln is fired from 20 to 32 burners located inside and outside the hearth, utilizing natural gas, fuel oil, or coke-oven gas. Exhaust gases pass through the preheater, heating stone feed to about 1000°F. The hearth, driven with only a 3 hp. motor, rotates within the limits of the stationary walls. There is little hearth maintenance required since the walls and roof are not in contact with the stone, and there is no attrition loss.

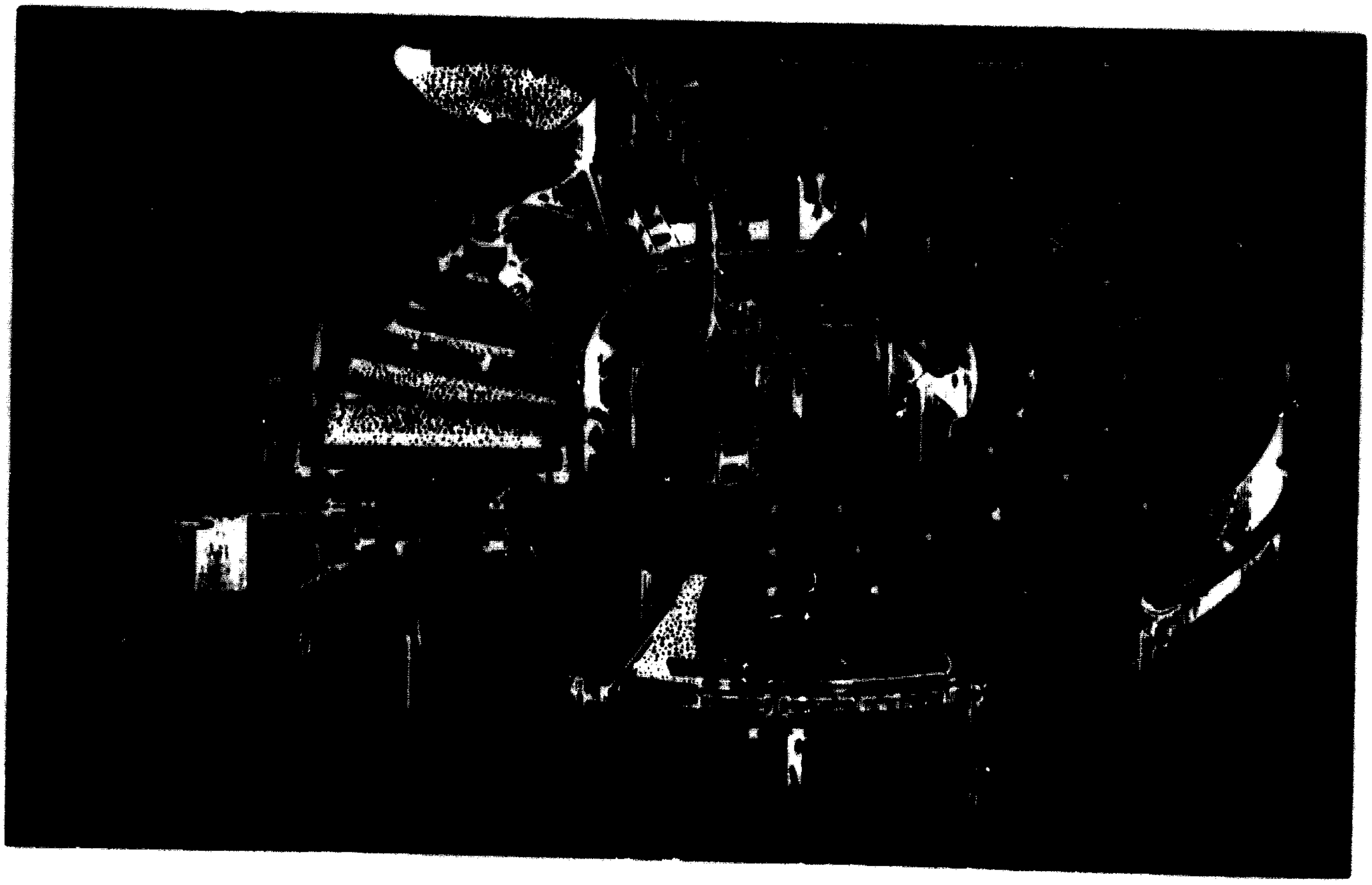
Several kilns of 100 and 200 tpd. capacity are in operation. Fuel requirement averages 5 million Btu/ton. The key feature of the Calcimatic is the controllability available to the operator, which permits the production of a wide range of lime quality. Among the controls are speed of revolution, temperature in the various zones, thickness of bed, change in feed size, etc. The kiln can also be shut down and started up in a matter of hours. Another advantage is the compactness of the unit, requiring a relatively small amount of space. (The 100 tpd. unit has an O.D. of 52 ft. and I.D. of 20 ft.)

Corson Kiln - A potentially interesting 50 to 100 tpd. kiln is the patented Corson inclined-vibratory kiln that is under commercial development. It is a very compact unit and offers the prospect of low capital investment per ton of lime capacity. Further details on this kiln are proprietary at this time.

Kilns Burning Pulverized Stone - For limestone that is friable or decrepitates during calcining, the Dorrco FluoSolids Kiln has been used successfully for producing reactive, soft-burned lime. In this process the material is maintained in dense suspension in a rising current of hot gases. The system incorporates a Fluo-Dry unit, which dries the 6 x 65 mesh kiln feed, and a FluoSolids reactor

Figure 15

Calcimatic circular hearth kiln



or calciner. The latter, resembling a vertical kiln, is approximately 15 x 90 ft. in size, it is divided by perforated domed refractory constriction plates into five compartments, including three preheating zones, a calcining zone, and a cooling zone. The reactor is fired with Bunker C oil, with the calcining temperature being maintained at about 1800°F, thereby insuring a soft-burned product. Fuel consumption is about 30 gal /ton, or about 5,000,000 Btu/ton. The system is completely automatic and permits close calcining control; it has also been used for calcining water softening sludge.

Another version of the FluoSolids kiln, called the Fluo-Radiation, has been installed at a lime plant in California. It also has a 200 tpd. capacity.

Another system for calcining friable stone has recently been developed in New Zealand. where the fine material is mixed with coal and pelletized before calcining. Soft limestone screenings are first dried, then mixed with $\frac{1}{4}$ in. soft coal in a ratio of 39 lb. coal to 450 lb. stone; the mixture is then ball-milled to 85% passing 100 mesh, followed by pelletizing into $\frac{1}{2}$ in. balls. The kiln is only 7½ x 18 ft. high, yet it is reported to produce 75 tpd. The preheating level is very critical, since too low a temperature causes condensation and the pellets stick, and too high a temperature bursts the pellets. Combustion is completed within 6 ft. of the top, and the lime is discharged cold, with the pellets showing very little attrition loss. This kiln, as well as the Fluo-Solids, may also have potential for burning limestone spalls.

Summarization of Kilns - To facilitate consideration of the many kiln types just reviewed — their pros and cons, limitations, attributes — a summarization is contained in Table IV. The values and ratings contained therein do not necessarily represent absolute minima and maxima, but more of typical ranges. The summarized items are defined below and should be reviewed for proper comprehension of the tabulated data presented.

Kiln capacity - This indicates the range of capacities in short tons per day that have been authenticated for currently operating kilns and does not necessarily represent absolute extremes. Some kiln designers and manufacturers are planning larger capacity kilns than indicated.

Size of stone - The values indicate the approximate range in minimum and maximum sizes that can be calcined -- not necessarily the gradation of the stone. For example, with the rotary kiln, actual gradations would be: 3/8 to 3/4 in., 1 to 2 in., etc., and not 3/8 to 2-1/4 in., the range that is cited.

TABLE IV - SUMMARY OF LIME KILNS

Kiln	Kiln Capacity, TPD	Size of Stone, in.	Gradation of Kiln Feed	Type of Fuel	Thermal Consump. (Mill.Btu/ton)	Control of Calcining	Capital Cost	Automation	Flexibility
Vertical									
Old Type Mixed-Feed (Pot)	5– 20	5 - 12	Medium	Solid	8 - 12	Low	Medium	Low	—
Modern German Mixed-Feed	75–400	3 - 8	Narrow	Coke	3½–4½	Low	Medium	Medium-High	Medium-High
Direct-Fired (Coal)	5– 25	4 - 12	Medium	Solid, Wood	7 - 12	Low	Medium	Low	Medium-High
Direct-Fired (Dutch-Oven)	5– 25	4 - [illegible]	Medium	Coal, Wood	6½– 8	Low-Medium	Medium	Low	Medium-High
Large Producer Gas	25–150	3 - 8	Medium	Varied	4 - 7½	Low-Medium	Medium	Medium-High	Medium-High
Small Producer Gas (Azbe)	20– 40	3 - 5	Narrow	Varied	5 - 6	Low	Low	Low	Medium
Natural Gas	50–500	3 - 8	Medium	Nat. Gas	4 - 6½	Medium	Medium	Medium-High	Medium-High
Fuel - Oil	50–325	3 - 6	Narrow	Oil	5 - 6	Medium	Low-Medium	High	Medium-High
Double Incline	100–150	1 - 2½	Narrow	Coke & Oil Coke & Gas	4 - 5	Medium-High	High	High	Medium
Multiple Shaft (Wopfing)	100–150	1 - 5	Medium	Gas or Oil	3½– 4	High	High	High	High
Rotary									
Simple Rotary	100–400	3/8–2¼	Medium	Varied	8 - 12	High	Very High	High	Low
Rotary, with Recuperation	100–550	3/8–2¼	Medium	Varied	6 - 7½	High	Very High	High	Low
Grate-Kiln Syste	300–600	1/4–2	Broad	Varied	5¼– 6	High	Very High	High	Low
Miscellaneous									
Calcimatic	100–225	1/4–4	Broad	Oil or Gas	5 - 5½	High	High	High	Very High
FluoSolids	100–225	#6–#65 mesh	Narrow	Oil or Gas	5 - 5¼	High	High	High	Medium
New Zealand (Pelletized)	50– 75	1/2 pellets	Narrow	Coal	—	—	—	Medium	High
Corson	75–100	—	—	Gas	—	High	Low	Medium-High	Medium

Gradation of kiln feed - This indicates whether the gradation must be restricted or can be broad for efficient operation. "Narrow" would be defined as less than a 1:2 ratio in size, such as 3 x 5 in., or a particulate distribution such as Nr. 6 x Nr. 65 mesh. "Medium" would be about a 1:2 ratio plus or minus 10-15%, except for pulverized kiln feed; and "broad" would be more than a 1:2.25 ratio, such as 1/4 x 2 in., etc.

Type of fuel - This indicates whether the kiln has some flexibility in using more than one type of fuel, and also which fuels can be used. Those that are listed as "varied" can be operated efficiently with three or more different fuels; naturally such latitude offers an advantage.

Thermal consumption - These values simply indicate an approximate range of fuel consumption in millions of Btu/ton of lime that have been authenticated. These values do not necessarily encompass both extremes. Two major reasons for the range in values are variations in kiln design and operating skill.

Control of calcining - Controllability in calcination is important for lime quality, and this indicates those kilns that can be controlled most readily to produce uniformly a soft or hard-burned lime or intermediate calcine or so called "tailor-made" lime. With certain kilns it is difficult to produce other than a hard-burned lime or a lime of high core content. Thus, control has a great influence on lime quality.

Capital cost - On the basis of tons/day of lime capacity, there is a tremendous difference in capital equipment costs. Yet, as a generalization, the lowest cost kilns are frequently the most costly to operate in spite of low depreciation, and they tend to produce the poorest quality lime, thereby impeding its saleability. So by no means are the lowest cost units necessarily the best to purchase. The many other pros and cons should be carefully weighed, in arriving at the wisest choice for a specific situation.

Automation - This pertains to the degree of mechanization that these kilns possess and its relation to manpower, specifically the amount of tons of lime per manhour that can be produced. In areas of low wages this ratio may be irrelevant.

Flexibility - This refers primarily to continuity of operation. If kilns must be shut-down due to lack of demand, accident, or maintenance, certain kilns can be started up again faster and more inexpensively than others, reducing "down" time. This also refers to the ability to produce lime economically at reduced operating rates — another distinct advantage; some kilns only operate efficiently at near to maximum capacity.

Early-Type Kilns -- For those nations that lack the capital to build modern lime kilns and where labor is plentiful and very cheap, it is possible to build inexpensive type kilns which can be operated intermittently or continuously. As a general rule, however, the lime quality is considerably below that produced in the more modern kilns. Three such types are the field kiln (intermittent) the stone vertical (mixed feed) kiln, and the horizontal or ring kiln (Hoffman).

Field Kiln -- This kiln, depicted in Fig. 16, is operated intermittently, each production cycle consisting of placing the stone, firing, cooling, and removal of the lime. The kiln stone is built up as an arch within the confines of the refractory-lined circular kiln wall. Great care is taken in placing the large pieces to form the arch and also to form a type of 'chimney" leading to the top of the kiln charge. The stones are placed individually to give a keying action so that the structure will not collapse during calcining. The firing is accomplished directly below the arch, using wood, coal, or coke. For the purpose of increasing draft, the kiln is equipped with a sheet iron ring which acts as a windbreak.

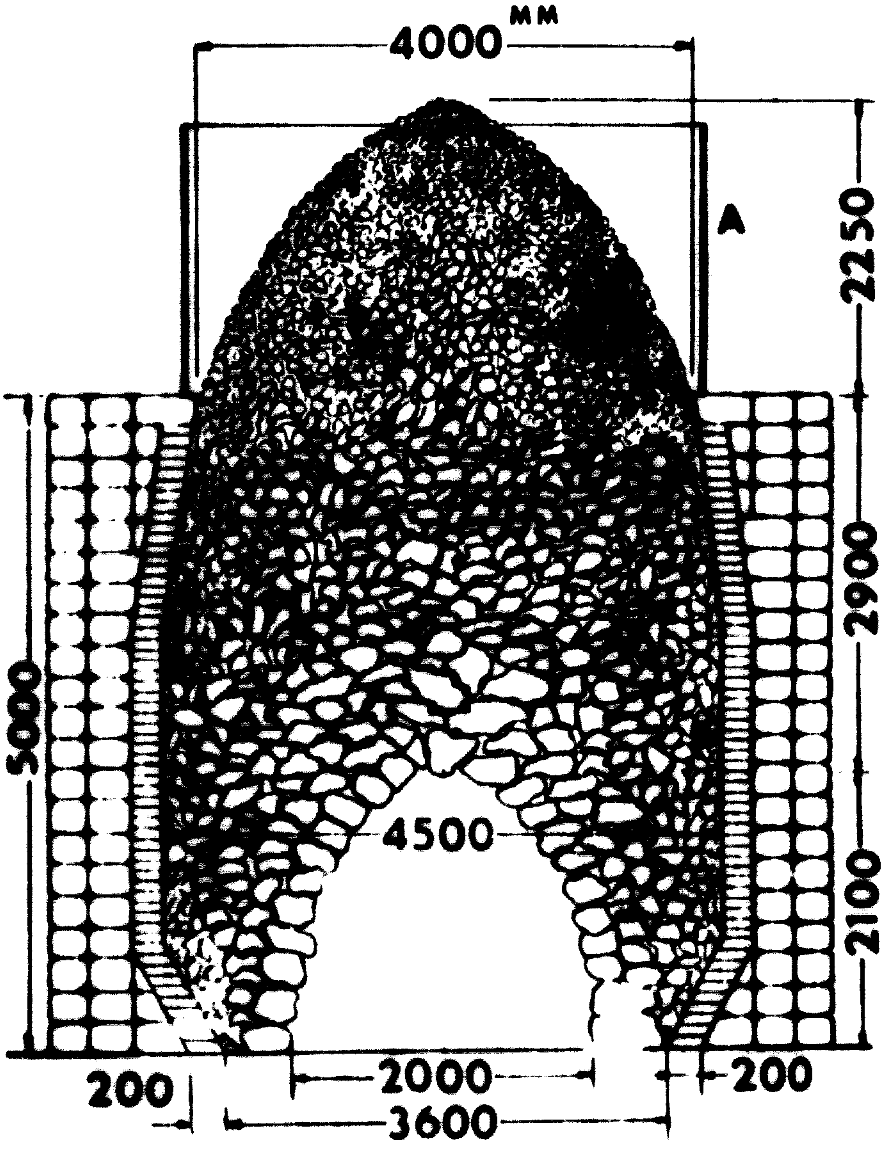
The production cycle requires 1 - 3 days for charging the stone, the exact number depending upon the kiln size and number of workers; several days of firing; and one day of cooling. While the kiln walls are still hot, the kiln is emptied of the hot lime, this operation also taking several days. After the walls cool off, the cycle is repeated.

One variation to the above involves the combination of firing from below with the use of mixed feed, i.e., the kiln charge is built up with alternating layers of fuel (wood or coal) and stone, with supplemental direct firing from below. In some field kiln operations the top of the stone charge is plastered with mud (all but the central 'chimney' section) to increase the natural draft.

The principal disadvantage of the field kiln is the great care and time needed to build the stone arch and the balance of the stone charge for each cycle. Generally, skilled masons were required for this operation. The waste of fuel is also excessive, since the kiln walls must be cooled down during each cycle to permit recharging.

Figure 16

Field kiln



Although field kilns were popular in the U.S. prior to the 20th century, they have been replaced by modern kilns. However, they are still used in many other parts of the world.

Mixed-Feed Stone Kiln -- The intermittent field kiln was followed in history by the continuous stone kiln, utilizing the mixed feed principle, with wood, coal, or coke being used as fuel. This kiln is a solid stone structure built of field stone, preferably a refractory stone like sandstone, quartzite, or granite which obviates a refractory lining. If limestone is used for the outer shell, however, then a refractory lining, up to 12 in. thick, is desirable. Unlike the typical vertical kiln depicted in Fig. 6, this kiln has an open top, and it also lacks fire boxes or fuel ports. It is generally built along a hillside to facilitate charging of the layers of stone and fuel from the top.

As with lime kilns in general, the early stone shaft kilns vary considerably in size, design, type of fuel, etc. In one eastern U.S. plant specializing in agricultural lime production, these stone kilns are about 12 ft. dia. x 50 ft. high, with the lower 10 ft. interior section being tapered to a diameter of 4 ft. at the discharge opening. A ¼ in. boiler plate lining is incorporated in the lower part of the conical discharge section. Discharge is effected with a manually operated, inclined shaker grate bolted to the boiler plate.

The stone feed is 2½ - 7 in. size, and the fuel is 3/4 - 1¼ in. coke. Each charge consists of a 5000 lbs. layer of limestone and 600-800 lb. layer of coke. Charging and discharging are handled by one worker operating a front end loader.

Each kiln produces about 10 t.p.d., with the lime being drawn and charged intermittently. Generally, the passage of stone through the kiln requires about 7 days. Nearly all of the combustion air is drawn in from the top.

Tunnel or Ring Kiln -- Extensively used in Europe and some parts of Asia at one time was the so-called Hoffman Kiln, a tunnel-like, ring kiln. Since World War II this kiln has largely disappeared from use in Europe due primarily to the great amount of manpower that is essential to its operation. Its use is only feasible in areas of very low wages -- 25c/hr. or less.

Although there are many modifications in its design, essentially it is a horizontal process consisting of a refractory-lined tunnel, circular or elliptical in shape, in which hot gases from the direct firing of solid fuel slowly travel through the tunnel circuit, preheating and calcining the stone charge. The tunner of 8 to 10 ft. in height is divided into 12 to 20 imaginary or partially constructed chambers of about 10 to 12 ft. in length. The kiln feed is charged into each chamber through openings in the roof of the tunnel, forming piles. Layers of small sized coal are added to the stone piles, and through an intricate network of flues the hot gases ignite the coal in succeeding chambers. Fans induce cool air into the tunnel for cooling the red-hot, calcined lime, and the resulting hot air preheats stone in the adjoining chambers in a regenerative manner. In a 20-chamber kiln, under ideal conditions, one chamber will be empty, one chamber will be charging, seven chambers will be preheating, four chambers will be under fire (calcining), six chambers will be cooling, and one chamber will be discharging by hand from side openings in the tunnel. The hot combustion gases move through the tunnel at 2 to 4 ft./hour; the hearth is stationary.

It is obvious from the above that a tremendous amount of manhours is required for charging and discharging; also extreme (strictly empirical) operating skill is necessary to produce good quality lime. Yet, in the first part of the 20th century it was regarded as the most thermally efficient kiln in use — 4.5 to 5 million Btu/ton. Capacities of this kiln ranged between 25 to 80 tons/day. Capital costs for the kiln were considered very expensive.

CHAPTER VI - HYDRATION AND MILLING

As pointed out in Chapter I, quicklime can be used as building lime simply by slaking it into a putty, preparatory to making mortar, plaster, or stucco. But quicklime alone should not be the sole objective. During lime calcining and handling of the quicklime, a certain amount of fines are inevitable, which may not be marketable. The next logical step, therefore, is to hydrate these fines, producing the second important lime product - hydrated lime.

In modern building construction, hydrated lime is generally preferred, mainly because it can be used directly, i.e., without slaking. It is also a more refined product (due to air separation) and it stores better. In addition, hydrate is much less caustic and, therefore, easier to handle, with less chance of workers getting burned. This safety problem is particularly aggravated during hot weather, when workers normally perspire profusely. Since many of the developing nations are located in tropical regions, this is all the more reason why hydrated lime (and not quicklime) should be made available for building purposes.

Theory of Hydration - Quicklime's strong affinity for moisture is the basis on which hydrated lime is predicated. Accompanying hydration of the lime oxides is the evolution of considerable heat, called heat of hydration. This exothermic reaction which is also reversible, is diagrammed chemically as follows:

High Calcium Hydrate

$$\overset{56}{\mathrm{CaO}}\ \text{(h.c. quicklime)} + \overset{18}{\mathrm{H_2O}} \rightleftarrows \overset{74}{\mathrm{Ca(OH)_2}} + \text{heat}\uparrow$$

Normal dolomitic hydrate

$$\overset{96.3}{\mathrm{CaO.MgO}}\ \text{(dol.quicklime)} + \overset{18}{\mathrm{H_2O}} \rightleftarrows \overset{74}{\mathrm{Ca(OH}_2} \,.\, \overset{40.3}{\mathrm{MgO}}\ \text{(mono. hydrate)} + \text{heat}\uparrow$$

Highly hydrated dolomitic lime

$$\overset{96.3}{\mathrm{CaO\ .\ MgO}}\ \text{(dol. quicklime)} + \overset{36}{\mathrm{2H_2O}} + \text{pressure} \rightleftarrows \overset{74}{\mathrm{Ca(OH)_2}} \,.\, \overset{58.3}{\mathrm{Mg(OH)_2}} + \text{heat}\uparrow$$

As seen above and mentioned previously, the high calcium types will hydrate more completely and with greater celerity than dolomitic products. The more reactive high calcium limes will actually hydrate explosively. As the water penetrates the pores of the quicklime fragment, the rapid rise in temperature exerts great internal expansive force within the particle and causes it to fracture and disintegrate completely into countless microparticles, either as a crystalline powder or as a colloidal suspension, the difference being contingent on the amount of water added.

Amount of Water - For complete hydration high calcium types require theoretically 24.3% water; dolomitic monohydrate, 16 to 17%; and highly hydrated dolomitic, 26-27%. This water is chemically combined and adds about one-third more weight to the quicklime, but the volume of the resultant hydrate more than doubles. Practically, however, more water is required than the theoretical values cited above, since considerable water in varying amounts is volatilized as steam due to the heat of hydration. For a reactive high calcium quicklime, the minimum amount of water that must be added would be about 50-55%, indicating that over 50% of this amount is evaporated. Normal dolomitic and magnesian quicklimes will require less water, since not as much is chemically combined, and less moisture is evaporated due to the slower, less turbulent hydration. The exact amount for a given lime should be determined empirically because of lime's varying capacity for water.

With respect to the amount of water used, two extremes should be avoided. If a large excess of water is added rapidly (or at one time), an adverse reaction may occur in which the lime is "drowned". Following initial hydration of the surface of the particle, there is a loss in slaking temperature. This impedes the expansive force that shatters the particle. The result is incomplete hydration or long delayed hydration, and the resulting putty after some drying resembles a thin, watery paste of poor plasticity. Such hydrates would also be unsound because of the danger of delayed hydration. This malpractice would apply more to slaked quicklime putties for structural use and occurs most commonly with hard-burned lime.

The other extreme would be to add insufficient water to the lime, causing the hydrate to be "burned". With highly reactive limes, excessive slaking temperatures of 400 to 550°F are obtained under these conditions that may even partially dehydrate some of the lime that has initially hydrated.

More often the hydration on the surface due to localized over-heating impedes penetration of subsequent water into the interior, causing delayed or incomplete hydration. The result is a coarse, non-plastic hydrate with suspect soundness.

Rate of Hydration - Many factors influence the rapidity of hydration, which are enumerated as follows:

1. Purity. High chemical purity abets rapid hydration. Generally, the greater the impurities, the slower the rate, since water has more difficulty in penetrating the clogged pores.

2. MgO Content. Increasing increments of MgO have a retarding effect on slaking. A very impure dolomitic lime would be the slowest, almost impossible to hydrate completely.

3. Size. Generally, the smaller the quicklime particle, the more rapid is the hydration.

4. Temperature. The rate accelerates with increasing temperatures of both reactants, particularly water, and with most lime reaches a zenith in steam.

5. Amount of Water. Increasing the amount of water retards the rate of hydration.

6. Agitation. of the lime and water markedly accelerates the reaction.

7. Air slaked quicklime hydrates sluggishly. Thus, both the quicklime and the freshly made dry hydrate or putty should be confined so as to prevent undue exposure and absorption of carbon dioxide from the atmosphere.

In dry-hydrating a reactive quicklime the most rapid slaking methods are usually not the best for building lime; a reasonably rapid hydration rate is more rewarding. The exact amount of water should be carefully pre-determined by tests, but it should range between 50 - 70%. Often it is more advantageous to add the excess water in several small distinct increments instead of all at once or in a continual light sprinkle. There is disagreement on whether greater hydrating control is exercised by adding water to the lime or vice versa, but a slender majority favors the former. Use of ground quicklime of ¼ inch top size down to No. 10 mesh is recommended for soft-burned types. With less reactive limes, smaller sized particles should be employed. However, fine pulverization is undesirable since the comminuted impurities cannot be removed by air separation.

Maintaining a maximum hydration temperature of [illegible] - [illegible]°F (or ideally just a few degrees below the boiling point) is recommended. Such a temperature can be controlled by such variables as the volume, temperature, and rate of introduction of the water; temperature and particle size of the lime; and rate and means of venting off steam. Rapid cooling of the hydrate immediately after termination of slaking is highly desirable.

With soft-burned magnesian and monohydrate dolomitic limes, generally the above procedure is also applicable, except that allowance must be made for the slower slaking rate. To produce highly hydrated dolomitic lime, a different technique must be employed, which will be described later in the chapter.

With slaked quicklime putty, additional water, of course, is needed, since it will contain about 35 to 40% *free* water in addition to that which is chemically combined. Curing of the putty for at least a day or longer increases its plasticity markedly.

A logical question is: how does one know by laboratory test whether a good building hydrate is produced and what are its characteristics? Measurement of the following physical properties with limits cited will answer such a question:

Fine particle size - Maxima of ½% and 15% retained respectively on No. 30 mesh and No. 200 mesh sieves, respectively; predominant percent of particles of 5 microns or less, with some submicron sizes. Such a particle size distribution indicates high *chemical purity*.

Specific surface area - High surface areas of at least 20-25,000 sq.cm/g., as determined by the Blaine Air Permeability test (ASTM C 204).

Shape of particle - As determined by microscopy, plate-like, laminar-shaped particles should predominate over spherical shapes.

Putty volume - High yield of putty that increases the volume at least 40 to 45% over that of the dry hydrate. (This is not to be confused with putty yield from quicklime which will increase 100-140%).

Water retentivity - At least 85%, as determined in test prescribed by ASTM C-110 (See p.21).

Slow settling - When using a 10% suspension, a high specific surface lime will require 2 to 4 hours to settle, whereas a lime of low surface area will settle in less than 1½ hours.

Plasticity - Lastly and most important - high plasticity - an Emley value of 200 or more, as determined by the Emley Plasticimeter test described in ASTM C-110 (See p.19).

Manufacturing Methods - Similar to calcining, hydration is a relatively simple chemical process; yet there are numerous methods and types of equipment available, thus necessitating again a careful study to determine the best hydration system for producing a dry hydrate, conforming to the above properties.

To produce a high grade uniform lime, mechanical hydration is required, followed by pulverizing and air separation. Before the introduction of mechanical hydrators early in 1900, two principal hydrating methods were employed: hand operation and silo-retention. In the former the lump lime was simply spread on a floor and watered heavily from hoses, followed by hand mixing and sifting. The silo method was somewhat similar, except that crushed or pulverized lime was used, which was mixed with a slight excess of moisture, and the material dumped into a silo. The lime then "aged" or "matured" for 24 hours or longer, in some cases up to a month. The silo or aging method is unsuitable to hydrate a soft-burned or reactive lime. The rapid rise in temperature increases the loss of moisture through evaporation, with the result that frequently there is a deficiency of water remaining for complete hydration. As a consequence, "burning" of the hydrate usually occurs to some extent, and the plasticity and soundness of the product are impaired. Adding secondary water to the lime hydrating in the silo would be difficult to control. So, this method is practical for quicklimes, that slake slowly or sluggishly, such as dolomitic, hard-burned, and/or impure (hydraulic) types. With some of these slowest slaking limes, boiling water or steam is added to accelerate hydration to prevent long periods of curing. Finer pulverization of the quicklime also stimulates the reaction. With limes of erratic or non-uniform reactivity, frequently too much water is added - in excess of the evaporation loss. The resulting moist hydrate (with free water) is difficult to remove from the silo and is more prone to recarbonate. Air separation is almost essential to dry and completely hydrated, screening through No.30 and No.40 mesh screens can be employed in lieu of air separation. However, obviously both of these methods are crude, and it is difficult to obtain a uniform hydrate of high purity and minute particle size.

With the development of mechanical hydration, lime quality was improved greatly. Hydration capacity likewise was augmented, and today some hydrators produce up to 25 tph.

A typical modern hydrating plant, as diagrammed in Fig. 17, comprises the following unit operation:

1. Hammermill, or similar type crusher, for reducing lump or pebble lime to small size (i.e., - ¼ in.); some hydrators, however, can handle pebble size lime.

2. Surge bin or hopper for pulverized material; high and low level indicators are generally provided for automatic filling of bin.

3. Weighing (or volumetric) feeder for lime and flowmeter for water, which are synchronized.

4. High speed pre-mixer (may be part of hydrator).

5. Mechanical hydrator, either batch or continuous, pressure or non-pressure (atmospheric).

6. Pulverizer, generally equipped with integral classifier.

7. Centrifugal air separator for classifying hydrate, with tailings being rejected.

8. Tube or ball mill, which is optional; this mill is used to increase plasticity by flattening and agglomerating the particles.

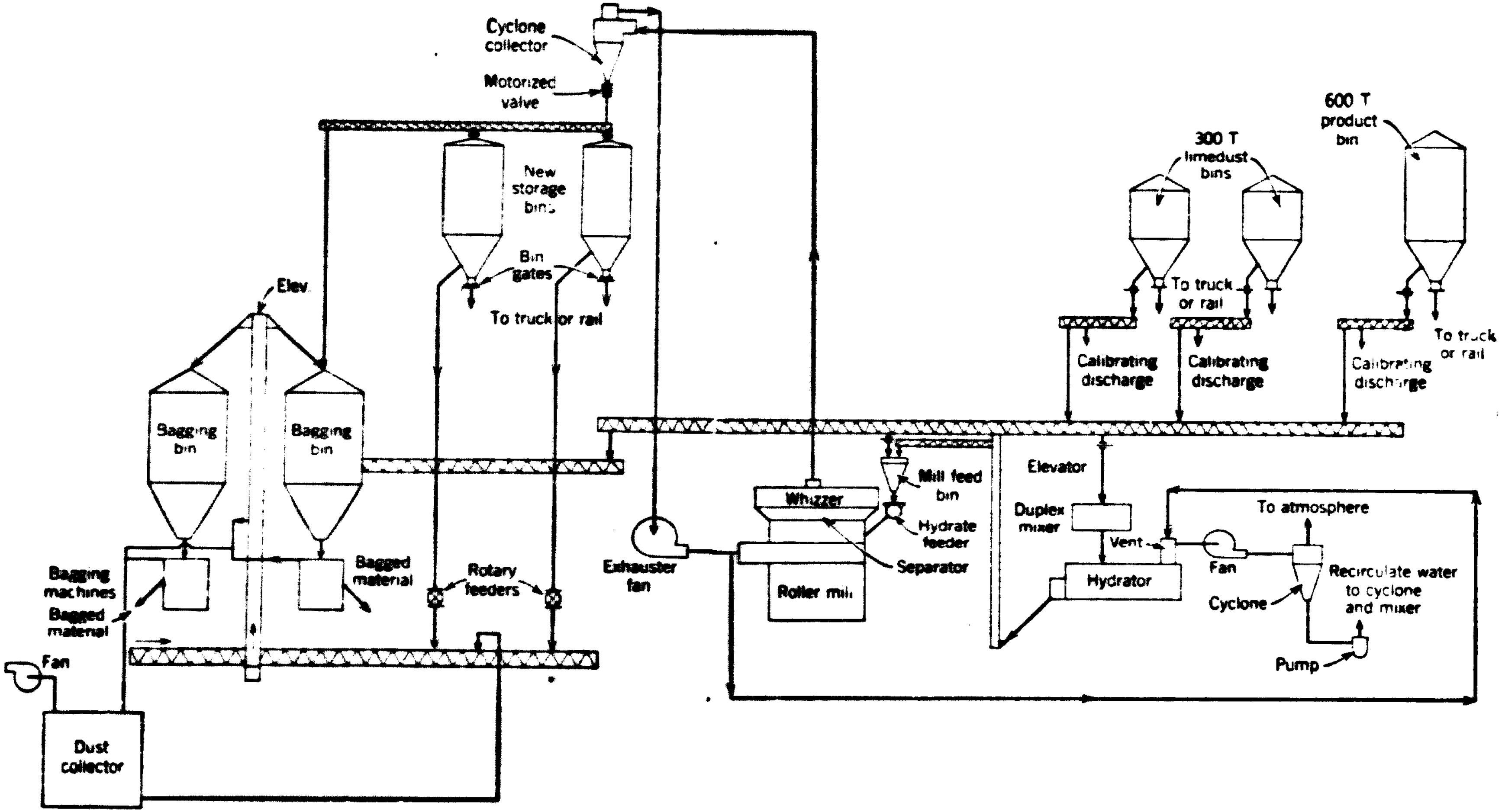
9. Silos for storing various hydrate products.

10. Bagging machine.

11. Conveying equipment used in the hydrating plant includes enclosed drag chain or screw conveyors, bucket elevators, and more recently pneumatic units, including pump and air-slide conveyors.

Figure 17

Flow diagram of a modern, high capacity hydrated lime plant



The hydrator, the key to the plant, is equipped with paddles or plows for obtaining thorough agitation of the lime-water mixture. A stack is generally provided for venting excess heat and steam resulting from the heat of hydration, with the dust particles being collected, scrubbed, and returned to the hydrator as milk-of-lime.

Early mechanical hydrators were of the non-selective type, i.e., the quicklime, regardless of whether it was hard-or-soft-burned, remained in the unit for a certain length of time before being discharged. Thus, not all of the hard-burned quicklime was hydrated. The modern hydrators, on the other hand, are selective or differentiate between the hard and soft lime particles. This is accomplished by means of a weir in the hydrating chamber, which permits only the completely hydrated particles, because of their lightness, to overflow and be discharged. The slower reacting particles remain in the unit as long as necessary to virtually complete hydration.

Hydrator Types - Hydrators are classified into non-pressure and pressure types, the latter being used primarily with dolomitic quicklime to produce a highly hydrated lime. Under normal hydration, the magnesia portion of dolomitic lime is slow to hydrate (due to being hard burned), but with pressures of 40 - 100 psi, the hydration is forced to virtual completion.

Atmospheric Pressure - Several types of atmospheric pressure hydrators are utilized, including both batch and continuous. A commonly used batch hydrator is the Clyde, which is simply a horizontal, revolving pan-type mixer provided with a series of plows on rotating arms. Because of low capacity (about 2 tph.) and high labor requirements, the batch systems have been largely replaced by continuous hydrators. The latter also invariably produce a more uniform hydrate.

Among the principal continuous atmospheric pressure hydrators are the Kritzer, Schaffer, Knibbs, Hardinge, and Kennedy Van Saun, which have capacities up to 15 tph (some to 25 tph.). The Kritzer consists of a pre-mixer and six horizontal tubes which are mounted one above the other and connected in series. Each tube contains a rotating paddle for mixing, with hydration progressing through the six stages of mixing. Water is fed to the pre-mixer through a series of nozzles in the exhaust stack, thus relieving dusting conditions.

The Schaffer hydrator is a vertical unit resembling a multi-stage ore roaster; it is divided into several compartments, each being provided with a revolving disc and a stationary disc. Each disc in turn contains numerous plows, which are arranged to turn the lime over and keep it agitated and moving continuously from compartment to compartment. Water is introduced through the exhaust stack, where it entraps the lime dust and forms a hot milk-of-lime which is then discharged into the pre-mixing chamber along with the quicklime feed.

The Hardinge hydrator (Fig.18) is essentially a large, single, fixed, horizontal cylinder having a horizontal rotating shaft running the length of the hydrator. The shaft has series of paddles which constantly agitate the lime during its passage through the unit. Like the Schaffer, the water is fed through a condenser stack as milk-of-lime, and the lime is introduced through a weighing feeder. Rotary hydrators, resembling small rotary kilns or driers, are also used for lime hydration. Lime and water enter at the feed end, and hydration occurs as the material moves slowly to the discharge end. Paddles are not needed for agitation.

Production of Highly Hydrated Dolomitic Lime - Two types of continuous hydrating systems are used for producing highly hydrated dolomitic lime - the pressure (autoclave) as typified by the Corson process, and the Kennedy-Van Saun, which is atmospheric. These two hydrators, which have also been applied to calcitic and magnesian limes, are generally operated in conjunction with special milling units for the production of highly plastic type S lime.

Pressure Hydration - The principal continuous pressure system for producing highly hydrated dolomitic lime is the Corson autoclave, which is used in the U.S.A. and several other countries (Fig.19). In this process ground dolomitic lime and water are automatically fed in constant proportions to a high-speed slurry mixer, then to an insulated 7 x 20 ft. pressure vessel (autoclave), which is equipped with an agitator. Operated in an excess of water and at about 75 psi and 300°F, the autoclave virtually completes the hydration in 30-45 minutes retention time. The hydrate, which is extremely fine in size, is then discharged continuously through a small pipe to a special heated cyclone collector. Because this unit is operated at atmospheric pressure, the autoclaved product virtually explodes, thereby drying the hydrate (spray drying principle) and reducing its particle size even further. After drying,

Figure 18

General arrangement of hydrating plant utilizing horizontal puddle-type hydrator

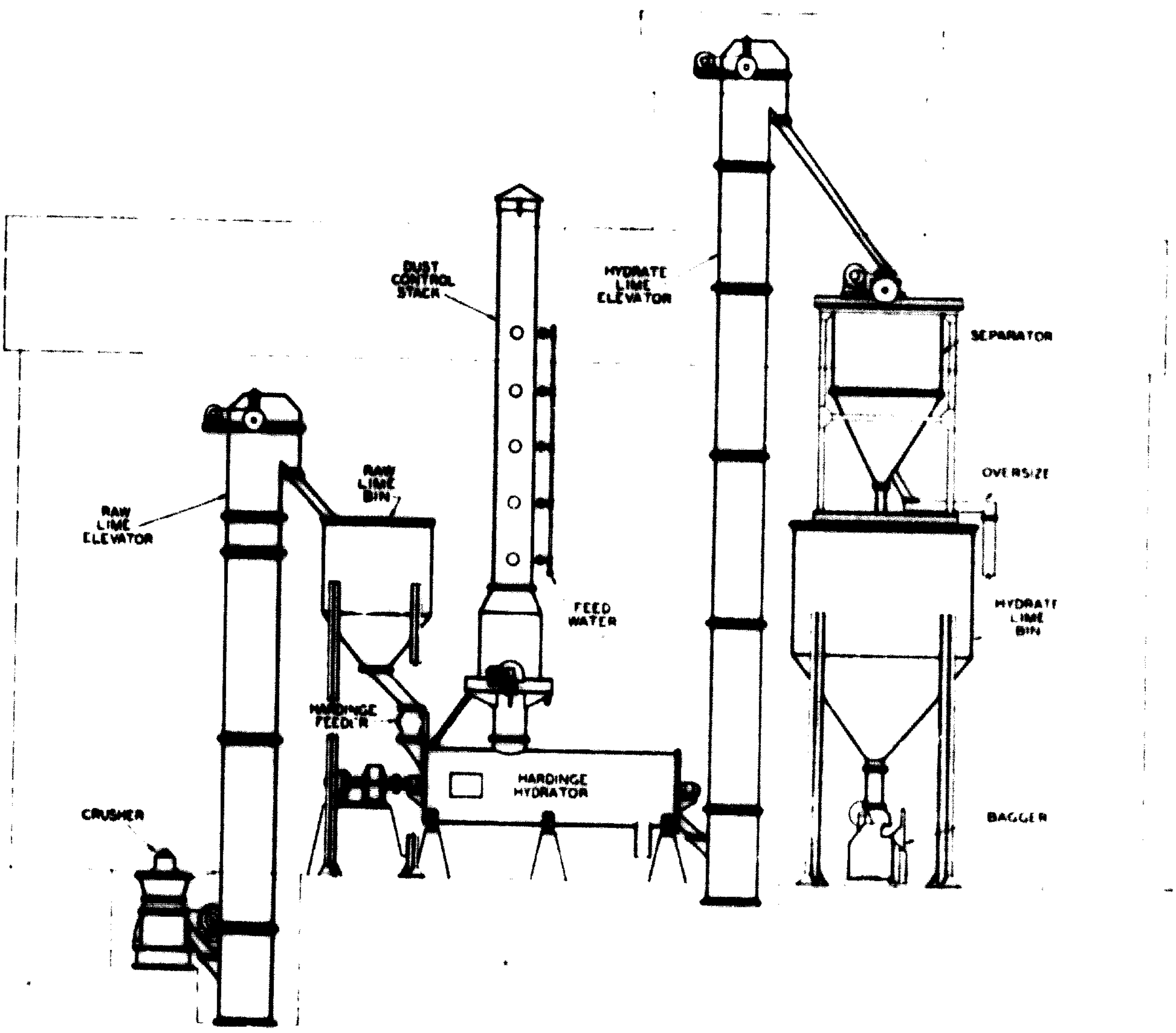
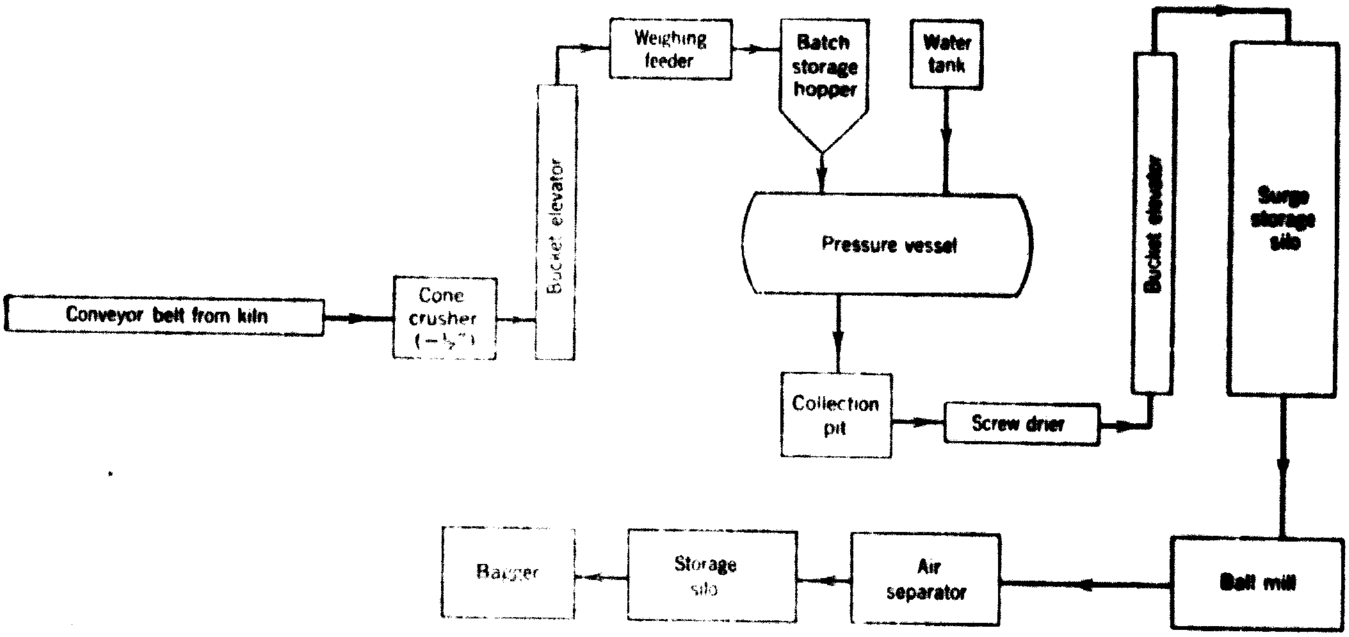


Figure 19

Simplified flow diagram of hydrating plant utilizing pressure hydration and Ball milling to produce Type S lime



the hydrate is fed to a ball mill, not to be ground finer, but rather for agglomeration to increase the plasticity. After milling, the core and impurities are removed with a centrifugal air separator.

A more recent process for manufacturing highly hydrated dolomitic lime involves the Kennedy Van Saun non-pressure hydrator. Key units in this system include a high-speed mixer, a 6 x 20 ft. cylindrical seasoning chamber, a cooling and drying screw conveyor, and a KVS "plasticitor" mill utilizing $1\frac{1}{2}$ in. rods as plasticizing media. The hydrating chamber incorporates a slowly rotating agitator and an adjustable weir at the discharge end for controlling retention time to about one hour. The key feature, however, is an oil jacket surrounding the chamber, which acts as a heat exchanger, transferring the heat released from the hydration of CaO in the initital portion of the seasoner to the opposite end for heating the lime and forcing MgO particles to hydrate. As in the Corson system, small particle size is achieved by hydrating with an excess of water; however, unlike the Corson, the excess water is removed in an enclosed 3 ft. dia. x 14 ft. ribbon screw conveyor, which also cools the hydrate to 140°F by air being drawn through it.

Producing Type S High Calcium Lime - Since calcium oxide hydrates readily at atmospheric pressure, all hydrators can produce high calcium hydrate which easily meets the soundness requirement of Type S lime, i.e., less than 8% unhydrated oxides. But not all hydrating systems will readily yield a high calcium lime meeting the other Type S requirements, i.e., Emley plasticity value of 200 or more and water retention of 85% or more, both being attained within 30 minutes after mixing (high early plasticity). To achieve the quick plastic properties, several manufacturers have developed or patented special hydrating systems. One such system incorporates a continuous hydrator know as the Hydraclave. Another system involves a modified Knibbs continuous hydrator. In this system highly plastic agglomerates are produced in two ways. (1) By hydrating with excess moisture, then feeding the coarser hydrator product to a flash cage mill drier, followed by grinding in a Raymond "Imp" mill. (The fine product that overflows the weir is air separated and marketed as chemical lime). (2) Hydrating with sufficient moisture for complete hydration, then air classifying, producing approximately 65% agglomerates and 35% fines. The agglomerates are then milled, producing a highly plastic lime, with the fines being used for chemical markets.

In all four of the above Type S lime processes, the hydrates develop Emley plasticities well over 200, and in some cases over 500, and water retention values are as high as 95%. As a consequence these hydrates are premium building lime products.

Milling, Air Separation, and Bagging - Description of the above Type S processes indicated the importance of various refining methods following hydration. In the case of building lime, three product improvements are desired - increasing the particle fineness, removing impurities, and agglomerating the fine particles into laminar shapes. In most plants the hydrator product is first pulverized in a roller mill like the Raymond, which also incorporates either a small mechanical or centrifugal (Whizzer) air separator, the coarse fractions being recirculted for further pulverization. The separator fines may then represent finished product, or are more likely to be further processed in a large centrifugal air separator for removal of core and impurities. In this unit the hydrate particles are lifted by strong ascending air currents generated by a fan, with the fine particles dropping out in the separator's outer cone and the coarse fractions in the inner cone. The separator can be adjusted readily to produce virtually any size desired, and in the case of spray hydrate for insecticide use, as much as 99% will pass a No. 325 mesh sieve.

Rejects (tailings) from the separator are usually wasted, along with hydrator rejects, although if the amount is appreciable, particularly if some lime is included, the tailings may be re-processed by scrubbing. The gritty material is then removed, and the milk-of-lime returned to the pre-mixer of the hydrator.

Where a high degree of agglomeration is desired, the ball or tube mill rather than the roller mill is often used for grinding, with the product then being air separated. One disadvantage of ball milling, however, is the high cost of operation, due to wear of the grinding media and high power requirements.

Bagging machines are a necessity in a building lime plant, since it is not practical to handle bulk lime on building construction projects, mainly because requirements are generally too small. Various modern, highly automated, power-driven bagging machines are available, that accommodate various types of multi-wall bags, like the pasted valve, pasted open mouth, sewn-valve, and sewn open-mouth type. The machines [illegible] two or more filling spouts, and one operator can fill as many as fifteen 50 lb. bags per minute using a modern machine. Loading to truck or box car in modern plants is generally handled by push-button 'power-curve' conveyors that have enough flexibility to transport the bags around curves. Where labor is cheap, however, hand carts are used. Bag sizes can be varied to suit the particular weight system used in each country.

CHAPTER VII - ECONOMIC FACTORS IN LIME PRODUCTION

Past chapters have reviewed the various ways of quarrying, stone processing, calcining, and hydrating, all of which emphasized the many variations in these operations, including equipment. There is no single foolproof blueprint available for any lime plant. Each situation is different, and careful study is essential to determine an economically feasible plant. Usually the final selection will be a compromise between various desirable extremes, for example, to secure the desired lime quality, optimum thermal efficiency may have to be sacrificed. If labor is extremely cheap, then a plant with minimum automation is economically indicated, and vice versa if labor cost is high. On the other hand, with rock that is difficult to calcine, there may be only limited choice between kilns and processing equipment.

Capital Equipment (Plant) Cost - In view of the circumstances cited above, any specific predicted investment cost for a lime plant, complete with supporting quarry and stone plant, would be irresponsible. About all that can be presented is the possible range or magnitude of this capital investment on the basis of U.S. and European costs (1966), but not including transportation.

Let us assume that the objective is to produce a reasonably high quality soft-burned quicklime that is suitable for making a good structural hydrate, and secondarily for chemical lime. A high calcium limestone of suitable purity is available. A daily plant capacity of 100 tons of quicklime is desired, with auxiliary hydration facilities of 5 tons per hour. All equipment is new. Real estate costs are not included.

Since approximately 2 tons of limestone are needed to produce 1 ton of quicklime, the stone operation would have to be at least 200 tpd in size. However, because of the spalls and fines produced during quarrying and crushing, an absolute minimum of 300 tpd would have to be quarried and processed, and actually a 400 tpd operation would be safer and highly advisable, particularly for vertical kiln plants which normally utilize large sizes. Theoretically, for the 400 tpd operation, there would be about 200 tpd of by-product stone (minus kiln feed sizes) that could be marketed.

The major minimal equipment needed for such a modern stone operation would include the following: one or two wagon drills and pneumatic hammers; a power shovel or a front-end loader of 3/4 to 1 cu.yd. capacity; a small tractor bulldozer; two or three off-highway trucks; a 2-x 3-ft. jaw crusher with an apron feeder (or comparable crusher); a primary belt conveyor (approximately 30" wide x 150' long); a 4-x-8' vibrating screen; a cone-crusher for possible secondary crushing; about 500 feet of miscellaneous belt conveyors (closed-circuit, stockpile, and reclaim); vibrating feeders in reclaiming tunnel; and structural steel supports for the stone-processing plant.

The estimated cost would be about $65,000 for the quarry equipment, $135,000 for stone processing equipment, and about $70,000 for installation of these facilities. This is a total of $270,000, or $675/ton of daily stone capacity (based on 400 tpd), or $1350/ton of daily quicklime capacity (assuming 2 tons of stone for 1 ton of lime, and disregarding by-product stone sales).

Actually, however, with the above facilities, production could easily reach 100 tph, which for an 8 hr. operation, would reduce the above ratios by about half. By operating at the 800 tpd rate, one 8-hr. shift would easily produce two full days of kiln feed. This being the case, the stone plant could be run on a half time basis, or else be operated intermittently; i.e., week on, week off, etc. For the latter operation, a kiln feed stockpile and reclaiming tunnel belt conveyor would be advisable.

As an alternate, a portable crushing and screening plant could be used instead of the permanent stone processing facility, which would be less expensive in capital cost. Two basic units would be needed - a primary plant consisting of an apron feeder, jaw crusher (or comparable crusher), and conveyor, which could be set up adjacent to the power shovel, and a primary screening plant, consisting of a single (or double) deck screen, with two (or three) product conveyors. The principal product, the kiln feed, could be trucked from the quarry directly to the kiln, or to a stockpile serving the kiln. The two portable units needed would cost about $85,000. If additional stone sizes are desired, a secondary crushing and screening plant could also be set up following the primary screening plant.

Like the permanent plant discussed earlier, the portable primary plant would also have a capacity of 100 tph or more, and thus could be operated on an intermittent basis to maintain the 100 tpd lime plant.

Obviously if some of the above quarry or stone plant equipment and machinery is replaced by cheap hand labor, as is conceivable in the developing countries, the above capital investment costs could be drastically reduced. The degree of mechanization required would be based on the individual circumstances.

For the calcination plant, the capital equipment cost might range between $1,250 to as much as $7,000/ton of quicklime/day. The plant equipment would essentially comprise: the kiln(s); stone conveying and charging equipment; quicklime discharge mechanism and auxiliary conveyor; screen for classifying quicklime; lime storage silo(s), and auxiliary conveyor.

One of the lowest cost kilns available is the small producer-gas vertical shown in Fig. 7, that could be fired with either solid fuel or wood. Such a kiln operated with natural draft would produce 20 tpd, and would cost about $40,000. The same size kiln, equipped with induced draft fan and a few design refinements, would produce about twice as much lime, or 40 tpd, and at a cost of about $50,000. Thus, on the basis of capacity/ton the second kiln would be the best - $1,250/ton/day as compared to $2,000/ton/day for the lower capacity kiln. These kilns, however, have no mechanization, and charging and discharging are carried out manually. Three of the larger capacity kilns, complete with quicklime storage and conveyor, would cost an estimated $165,000 for the complete calcining facilities, or about $1,375/ton of daily capacity.

In contrast, a larger natural gas- or oil-fired vertical of 100 tpd capacity and with mechanized charging and discharging might be obtained for as low as $175,000 or $1,750/ton/day capacity. The same capacity kiln with a gas producer (for solid fuel) would be 15 - 25% more costly or a minimum of $2,000/ton/day capacity. Other special verticals, like the Double-Incline and Multiple-Shaft would be even more expensive - about $3,000 to $3,500/ton/day. However, as a generalization the more expensive vertical kilns are also more highly automated and offer the possibility of better thermal efficiency and more uniform lime quality, including softer burned lime.

Other kilns, like the rotary, are inherently much more costly per ton of capacity, and this disadvantage is accentuated in (for them) small capacity kilns of 100 tpd. At 200-400 tpd capacities, however, these kilns would be less costly to install per ton of capacity. The difference between moderate to large rotaries versus the small (100 tpd) would be approximately $5,000 - $6,000 per ton per day as compared to $6,000 - $7,000, depending upon type of kiln and number and type of auxiliary recuperative appurtenances.

A 100 tpd Calcimatic kiln plant would cost about $4,000/ton/day, including preheater and cooler. The FluoSolids kiln plant would be even higher, approaching the rotary in total cost on an equivalent capacity basis. Like the rotary, these latter kilns are less costly per ton of capacity with larger units, such as 200 tpd.

For the hydration plant of 5 tons per hour capacity, the average cost should approximate $200,000 for atmospheric pressure hydration. This includes the essential equipment itemized in the hydration chapter. With pressure hydration, the capital cost is higher because of extra milling equipment, added expense for the pressure vessel (autoclave), and larger equipment needed for the same capacity because of longer retention time. Again, the same principle applies that, with larger hydrating systems the capital cost/ton will diminish.

Table V presents a summary of the above capital cost considerations, based on the hypothetical 100 tpd lime plant and associated quarry. All figures are in $/ton of daily quicklime capacity, but not including transportation cost of machinery.

Table V - Summary of Estimated Lime Plant Costs

Kiln Types	Cost of Stone Plant and Quarry Equipment*	Cost of Calcining Plant	Cost of Hydration**	Total Cost
Small unmechanized Vertical	1350	1375	2000	4725
Large automated Vertical	1350	2000-3500	2000	5350-6850
Rotary	1350	5000-7000	2000	8350-10,350
Miscellaneous (Special)	1350	4000-5000	2000	7350-8350

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* This figure would be considerably less when credit is given to by-product stone sales. The stone plant for the rotary and special kiln operations may be slightly higher due to need for a secondary crusher to produce small kiln feed stone.

** Based on 5 tph hydration capacity.

Manufacturing Costs - Just as capital equipment costs vary considerably throughout the lime industry, operating costs for producing kiln feed, quicklime, and hydrated lime also vary greatly. The table below, developed by R. S. Boynton,* shows the approximate ranges in American costs as of 1964 for the principal cost categories. Since American cost data is fragmentary in nature, the figures presented are estimates, and do not necessarily represent absolute minimal or maximal values.

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* Boynton, Robert S., "Chemistry and Technology of Lime and Limestone", John Wiley & Sons, New York, (1966).

Table VI - Costs per Net Short Ton of Quicklime

		Min.	Max.
Kiln Feed		1.30	5.00
Fuel		1.50	4.50
Labor		1.25	3.75
Miscellaneous*		2.00	3.00
	TOTAL	6.05	16.25

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* Includes interest, depreciation, insurance, taxes, power, refractories, maintenance, testing, and administrative, but not sales.

The kiln feed costs are based on stone costs of $0.65 to $2.50/ton, respectively, assuming the two tons of stone to one tone of lime ratio. The highest figure pertains to plants purchasing their stone from outside sources (generally by boat or rail haul) or to those having difficult quarry problems (extensive overburden, stone dirt, necessitating elaborate washing, need for selective quarrying or deep mining, etc.). The lowest figures are typical of large, highly mechanized operations, particularly where the overburden is thin and the deposit thick and uniform throughout. Generally, the quarrying costs exceed the stone processing costs, and in some cases may even be three to five times more costly. The above costs are offset somewhat by the sale of by-product spalls or fines. With most stone products, the selling prices approximates that of the kiln feed, although certain specialty products, like pulverized limestone, command a price approaching that of quicklime.

The great variation in fuel costs cited in Table VI is due to a combination of factors, including the type of fuel used (whether natural gas, producer gas, coal, coke, or oil), the cost of the fuel itself (the spread from area to area may be 100%), and thermal efficiency attained (varies from 4.5 - 12 million Btu/ton in the U.S.A.). Generally, fuel is relatively cheap in the U.S.A. so less emphasis is placed on thermal efficiency than in Europe; as a consequence, rotary kilns predominate. Where fuel costs are exceptionally high, however, the rotaries are equipped with various heat recuperative devices.

Labor cost per ton of quicklime also varies widely due to a more than 100% spread in wage rates from area to area, and also the varying degree of mechanization and automation. Some plants with the highest wages counterbalance this disadvantage with the ultimate in mechanization. In contrast, other plants with low wages and limited automation and appreciable hand labor conclude that the capital investment for the requisite labor-saving equipment is unwarranted. The most efficient American plant operate with less than 0.5 manhour/ton of quicklime, but the majority are between 1.25-2.0 manhours/ton.

It should not be construed from Table VI that any plant has the minimum or maximum cost indicated, although it is plausible that the small, old plants may approach the maximum cost. This vast divergence in lime operating costs is far more pronounced than in other industries. Generally, unit costs decline as output increases, and larger plants enjoy substantially lower costs per ton than to produce smaller plants - as well as lower capital cost/ton of capacity. As in most industries, operation at 90-95% of capacity stimulates the lowest operating cost/ton. It is believed that lime operating costs in Western Europe are about 10 - 20% less on an average than in the U.S.A.

Hydrating costs are not included in this discussion, since the value added generally exceeds the processing cost entailed, making the hydrate a more profitable item than quicklime. With normal hydrate the total sales return is 40 - 50% greater than with its equivalent as quicklime, based upon (1) 4 tons of quicklime will make 5 tons of hydrate, less about 5% of the weight due to tailings, and
(2) the hydrate is generally sold at about 15% higher price per ton on a comparable bulk basis. With pressure and other special hydrates, profit may be even greater. Bagging adds about $3.50-$4.00/ton more to the cost of production and the selling price.

Manpower Requirements - A wide range of manpower requirements exist in the lime industry - from the highly skilled combustion engineer and maintenance mechanic to the lesser skilled laborer handling routine, often back-breaking chores. All of the employees must be rugged to withstand the rigors of the job - working under all types of weather conditions and contending not only witn a dusty environment but also with a product having caustic properties.

In view of the latter factor, workers must be instructed in safety to avoid lime burns. They must also be taught how to work safely around all of the heavy equipment characteristic of the lime plant and quarry.

In order to insure an efficient operation with consistently high quality lime being produced, several key men are vital. These include the general superintendent, lime plant engineer, maintenance foreman, and plant chemist. The superintendent must be a well-rounded individual - a mechanical engineer who knows the how and why of each processing unit, an operator who can run every piece of equipment, an expert in labor relations, and lastly a teacher who can demonstrate the right way to perform the various jobs. The lime plant engineer should be an expert on the design and operation of the kiln and hydrator, as well as the auxiliary equipment. Lime quality and production costs are largely in his hand.

The maintenance mechanic is of great importance because the quarry and lime plant machinery and equipment are subject to extremely hard wear, necessitating continual maintenance and repair. This job is especially vital in underdeveloped countries where replacement parts and equipment may be difficult to procure. The maintenance man should be an expert welder and electrician, as well as having the know-how for repairing mobile and other equipment. The plant chemist has the important job of checking quality of both the limestone and lime products, as well as providing technical service to the company's sales organization. A background in geology or mining engineering will be helpful in connection with quarry development.

The manpower requirements will vary considerably from plant to plant, depending primarily on type of quarrying operation and kiln used, lime products made, manpower available, and of course, degree of mechanization. In the most efficient, highly mechanized American plants, as low as 0.5 manhours are required to produce 1 ton of lime. At the other extreme are the simple plants in some parts of the world where the entire quarrying operation, from drilling to loading quarry cars, is carried out with manual labor; where the kilns are loaded and drawn by hand, and where the hydrate is produced by hosing quicklime spread on a floor.

Where a high degree of mechanization is carried out, the following are the approximate manpower needs for the 100 tpd lime plant cited above, assuming the quarry and stone plant operating one shift of 8 - 10 hr. per day, the calcining plant operating round the clock (3 shifts per day), and the hydrator plant 1 - 3 shifts per day.

Stripping - Varies according to extent of overburden (generally 1 or 2 scraper operators, or 1 dragline operator and 2 or 3 truck drivers, with several laborers for final cleanup).

Quarry - 1 shovel operator, 2 or 3 truck drivers, 1 or 2 drillers, who would also handle the blasting, and 1 bulldozer - dropball operator.

Stone plant - 1 crusher and screen operator and 1 laborer.

Calcining Dept. - 1 kiln operator and 1 helper per 2 - 3 kilns per shift.

Hydrating - Bagging Dept. - 1 hydrator operator, 1 mill operator, and 1 laborer per shift; and 1 or 2 bagger operators and 2 or 3 loaders for one shift only.

Maintenance Dept. - 1 or 2 mechanics and 1 helper.

Supervisory Staff - 1 general superintendent, 1 quarry foreman, 1 plant foreman and 1 chemist.

Thus, there are a total of 22-28 production employees, plus the supervisory personnel. The number would be slightly more for a vertical kiln plant, since in addition there would probably be one or more drawmen and several lime pickers needed; the latter manually reject the large pieces containing core following cooling. On the other hand, there may be fewer workers on stone production, since less crushing and screening would be required.

Of the above workers, the shovel, kiln, and hydrator operators and the maintenance men would be considered skilled workers, the truck driver, bulldozer operator, drillers, crusher and mill operator, and bagger would be semi-skilled, and the balance unskilled.

In underdeveloped countries where skilled workers are generally lacking, all but the laboring jobs would undoubtedly be handled by imported skilled workers. Some of these jobs, however, may be taken over by local workers as the skills are learned through intensive job training. The importance of job training cannot be overemphasized, since mistakes made through lack of knowledge and experience may result in costly breakdowns and repairs. Even the more menial tasks should involve adequate training, particularly with regard to safety precautions. The length of training, of course, will depend upon the job difficulty; some jobs can be learned in a matter of days, while others may take a month or longer.

Safety - Safety instruction should be centered around three principal characteristics of the lime industry:

1. It is a heavy industry.
2. The work is largely out-of-doors.
3. Quicklime is highly caustic and hydrated lime slightly caustic.

The heavy nature of the industry is indicated by the high incidence of back strains occurring among workers; e.g., in the U.S.A. about one fifth of all disabling injuries are back cases, nearly all of which are the result of improper lifting. This is paradoxical, in view of the high degree of mechanization in America. Much of these injuries could have been avoided by instruction on proper lifting, proper use of tools, etc.

Outside work, too, creates special problems, particularly under extreme conditions of temperature and weather. Heat stroke can become a problem unless special precautions are taken. Blowing dust is not only a source of discomfort, but can lead to eye injuries. Quarry or mines also create hazardous conditions, particularly with respect to blasting, falling and flying rock, stone haulage, etc. However, silicosis is not a problem, since the limestone used in lime burning is relatively pure and contains little or no silica.

Undoubtedly, the greatest emphasis in safety training has to be directed to avoiding skin or eye burns due to lime's alkalinity or causticity. The U.S.A. lime safety statistics indicate that burn cases comprise about 20% of all disabling injuries. Most of the burn cases involve eyes, and are largely the result of safety goggles not being worn or not fitting properly. The skin burns usually occur in areas where the clothes chafe or rub, e.g., neck, wrists, and ankles. The problem is especially acute with quicklime, due to its great affinity for water and resultant heat of hydration. With hydrated lime, a burn will not occur unless the skin is chafed badly or actually open (due to a cut); with quicklime, however, a burn can occur if the body is perspiring, due to the heat released during the rapid hydration.

Yet, lime burns can be avoided if a few simple precautions are taken. The worker should be fully clothed (short sleeved shirts not permitted); wear high top shoes, with trouser legs extending over (preferably tied) shoe tops; and wear cap and gauntlet gloves. Clothes should not bind too tightly around the neck, wrists, or ankles. If prolonged exposure to dust is inevitable, the worker should use a protective cream like Vaseline on the neck, face, wrists, and ankles. He should also wear thight-fitting safety goggles, fitted with side shields; and if the environment is very dusty, he may need a filter mask or respirator. However, it should be realized that inhalation of hydrated lime dust is not injurious, although quicklime dust could cause internal burns. After work the employee should shower to remove the lime dust and protective cream.

If burns do occur, first aid treatment is required immediately. The affected area should be washed with soap and warm water, then treated with a burn ointment, and kept bandaged to prevent infection. If lime gets in the eyes, they should be flushed out immediately with copious amounts of water. If a worker is found to be allergic to lime dust, obviously he should be dismissed.

Besides being required to wear safety goggles, workers should also be provided with various personal protective equipment, such as hard hats, safety shoes, safety lenses, raingear and boots where needed, etc. The plant should also devote a great effort to accident prevention work, either by hiring a safety engineer or else forming a safety committee. No "short cuts" should be permitted where safety is concerned. It is only through diligent and dedicated safety work that injuries can be reduced to a low level.

<u>Conclusions</u> - Several broad generalizations are evident from this relatively quick glimpse of the lime industry.

(1) Although the chemistry of quicklime and hydrated lime is simple, the production of these two basic products is somewhat complicated, particularly when a uniformly high quality material is desired at a reasonable cost of production. A great variety of kilns and hydrators are available, necessitating a careful study to determine the best types of production units to use.

(2) Although lime is one of the lowest cost building materials and chemicals available today, the lime plant itself is not a low cost facility. Even a low capacity operation would require a capital investment in excess of $0.5 million, perhaps closer to $1 million. Large plants will cost several millions of dollars.

(3) Building lime should be highly plastic, sound, and have high water retention. A good building lime can be produced readily by using high purity limestone and by burning at relatively low temperatures to yield a soft-burned product. Hydrating to produce a fine particle size, followed by grinding to produce agglomerates leads to a highly plastic hydrate.

(4) A developing country should not build a lime plant solely to produce building lime. Other potential markets should also be considered, which may materially affect the lime plant design.

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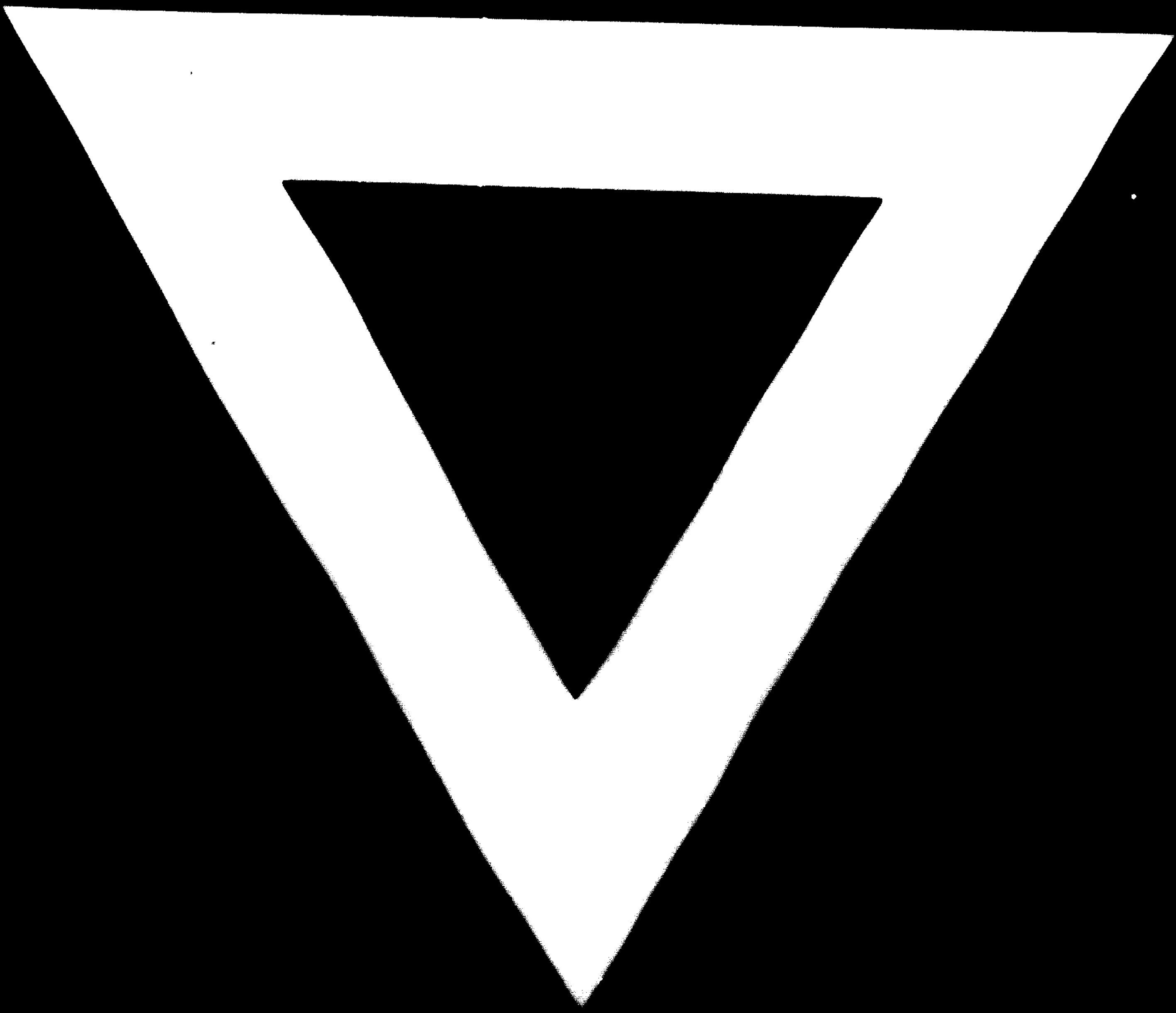

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