InfoMine
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Association of independent experts in field of mineral resources,
metallurgy and chemical industry

Lime Market Research in Russia and Central Federal District

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Moscow
October 2007

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Annotation

The report is devoted to studying of lime market in Russia and Central Federal District. The report includes 6 Sections, 146 pages, including 35 Tables, 35 Figures and Appendix.

As information sources, data of Federal Service of State Statistics (Rosstat), Federal Customs Service of Russia (FCS), official domestic railage statistics of Ministry of Railways of Russia, data of companies, received in the course of telephone interviews with their leaders, the sector and regional press, annual and quarterly repots of companies, internet-sites of company-producers of lime were used.

The first Section presents review of modern technologies of lime production, comparative characteristics of lime production facilities description of some Russian and foreign manufacturers of production facilities for lime production and engineering companies.

The second Section is devoted to production of lime in Russia. The report contains official statistics of output of building and technological lime in the country in 1997-2007, data on regional structure of the production and volumes of lime production by various producers. The Section contains description of current standing of leading players of Russian lime market, including ownership pattern, available production capacities, lime roasting (kilning or burning) technologies, volumes of production, range and quality of products, flows (destinations) and volumes of lime supplies. The section also describes plans of the business development: available projects on organizing new and modernisation of operating lime productions.

The third Section analyses data of Federal Customs Service of Russia on foreign trade operations in lime. Irt presents data on volumes of exports and imports of lime in 2000-8 months of 2007 in bulk and in money terms, with data on regional structure of export-import supplies on the whole and by the main Russian exporters and importers of cement.

The fourth Section is devoted to consumption of lime in Russia and Central Federal District and contains supply-demand balance of lime, as well as presents estimate of sectoral ("by end-uses") and regional structure of consumption of lime with analysis of effect of seasonality factor on supplies of lime, as well as estimates regional and sectoral structure of cement consumption in Russia as a whole and Central Federal district (CFD) and seasonality of the supplies.

The fifth Section is devoted to analysis of price conjuncture of Russian lime market. The Section presents dynamics of release prices on lime of Russian producers in 2001-2007, current prices of some producers, analysis of dynamics of export-import prices and forecast of price conjuncture of Russian lime market up to 2010.

The sixth Section presents forecast of lime production in Russia and Central Federal District up to 2015, as well as forecast of consumption of lime in Russia and Central Federal District in 2007-2015, prepared on the basis of forecast of development of lime end-uses.

The Appendix contains contact information on leading Russian producers of lime.

Introduction

Lime (CaO) is a product of burning carbonate rocks and finds wide application in various branches of industry. Lime is one of the most widespread and usable chemicals, produced and consumed all over the world. Unhydrated and hydrated lime has been being used for above 3000 thousand years. Previously lime was mainly used as building material, but now its application was considerably widened. The greatest end-uses of lime are ferrous metallurgy, building industry, pulp-and-paper industry, chemical industry, agriculture, sugar industry. Among other important end-uses of lime is natural environment protection (neutralizing sewage and flue gases).

In developed countries, consumption of lime at present time is around 80 kg per capita. Global lime production, including small producers in developing countries, as well as producers of lime for own needs (for instance, metallurgical and pulp-and-paper productions) estimates 300 mln tpy, of which around 120 mnln tpy are sold at market. In volume of lime production, Russia is one of global leaders, producing above 10 mln tpy lime per year.

1. Review of modern technologies of lime production, engineering companies and producers of equipment

1.1. Review of technologies of lime production

The lime making process consists of the burning of calcium and/or magnesium carbonates at a temperature between 900°C and 1500°C, which is sufficiently high to liberate carbon dioxide, and to obtain the derived oxide:

$CaCO_3 = CaO + CO_2 - Q$

(the reaction is endothermic, for breaking 1 mol of $CaCO_3$, 178.2 kJ of heat is consumed).

For some processes, significantly higher burning temperatures are necessary, for example dead-burned dolomite.

The calcium oxide product from the kiln is generally crushed, milled and/or screened before being conveyed to silo storage. From the silo, the burned lime is either delivered to the end user for use in the form of quicklime, or transferred to a hydrating plant where it is reacted with water to produce hydrated or slaked lime.

Lime processes mainly contains the following basic steps, listed below:

- Winning of limestone
- Limestone storage and preparation
- Fuels storage and preparation
- Calcination of limestone
- Quicklime (unslaked lime) processing
- Quicklime hydration and slaking
- Storage, handling and transport

Winning of limestone.

The raw material for lime production is limestone or, to a lesser extent, dolomite or dolomitic limestone. Dolomite and dolomitic limestone are mixtures of calcium carbonate and up to 44% magnesium carbonate. While limestone deposits are relatively abundant in many countries, only a small proportion are suitable for commercial extraction.

High purity limestone or dolomite is quarried, crushed, and in some cases washed. It is then screened and transported to the kiln. Limestone is normally obtained by surface quarrying, generally adjacent to the lime plant, but in some cases sea dredging or even underground mining are used. A typical mining process includes:

- Removal of the overburden (i.e., the soil, clay and loose rock overlying the deposit).
- Blasting of rock.

Loading and transportation of the blasted rock to the crushing and screening plant.

Limestone preparation and storage.

Limestone is crushed to the appropriate size range, which is normally 5 to 200 mm depending upon the kiln used. Primary crushers receive quarry rocks as large as one meter in diameter and reduce their size down to 100-250 mm. Crushed stone from the primary crushers is transported via conveyors to vibrating screens, where large pieces are separated and recycled while those passing through are used as kiln charge, or may be fed into the secondary crushers located further down the process line.

Secondary crushers yield pebbles of 10 to 50 mm, which after screening are transported on belt conveyors and/or bucket elevators to limestone storage silos or compartments for storage prior to feeding the dryer or the lime kiln.

Depending on the nature of the rock (hardness, lamination, size etc.) various types of primary crushers are used, such as: jaw crushers, gyratory crushers and impact crushers. As the kiln charge does not have to be very fine, jaw and impact crushers are also often used as secondary crushers, as are hammer mills. Sometimes crushing plants are located at the quarry and are mobile.

The particle size distribution must be compatible with the requirements of the kiln. This generally requires the stone to be positively screened to give a size distribution, ideally 2 to 1, or at least 3 to 1.

Washing is sometimes used to remove natural impurities such as silica, clay and the very fine particles of limestone. This washing aids the burning process by leaving free space between the stones for combustion air circulation, thus reducing the amount of excess air and saving electrical energy. Techniques for piling the limestone, for better cleaning, have been developed.

Screened sizes of limestone are stored in bunkers and in outdoor stockpiles. Fine grades are usually stored in sealed bunkers.

In a very limited number of installations (for example, where the calcium carbonate is in the form of a sludge or filter cake), it is necessary to dry the feed material. This is generally done by using the surplus heat from kiln exhaust gases.

Fuels, storage and preparation.

In lime burning, the fuel provides the necessary energy to calcine the lime. It also interacts with the process, and the combustion products react with the quicklime. Many different fuels are used in lime kilns. The common is natural gas, but coal, coke and fuel oil are also widely used. Most kilns can operate on more than one fuel, but some fuels cannot be used in certain kilns. Fuels markedly affect the heat usage, output and product quality. Some fuels require a special refractory kiln lining.

The choice of fuel(s) for a lime-burning operation is important for the following reasons:

a) the cost of fuel per tonne of lime may represent 40% to 50% of the production cost,

b) an inappropriate fuel can cause major operating costs, and

c) the fuel can influence the quality of the lime, notably the residual CO_2 level, the reactivity, and the sulphur content.

In addition, the choice of fuel can affect the levels of emissions of carbon dioxide, carbon monoxide, smoke, dust, sulphur dioxide and oxides of nitrogen, all of which have an environmental impact.

The fuel should be prepared as required for the injection system, which can be of direct or indirect firing type. In the case of solid fuels, this involves delivery at the appropriate particle size for the installed handling system. In the case of liquid and gaseous fuels, the required pressure and (as appropriate) temperature need to be maintained.

Calcining of limestone.

The lime burning process typically involves:

providing sufficient heat at above 800^{o}C to heat the limestone and to cause decarbonation, and holding the quicklime for the requisite time at a sufficiently high temperature (typically in the range 1200 to 1300 ^{o}C to adjust reactivity).

A large variety of techniques and kiln designs have been used over the centuries and around the world. Although sales of lime kilns in recent years have been dominated by a relatively small number of designs, many alternatives are available, which may be particularly suitable for specific applications. Stone properties such as strength before and after burning, dust generation and product quality must be considered when choosing kiln technology. Many lime producers operate two or more types of kiln, using different sizes of limestone feed, and producing different qualities of lime.

Heat transfer in lime burning can be divided into three stages:

a) Preheating zone. Limestone is heated from ambient to above 800°C by direct contact with the gases leaving the calcining zone (i.e. products of combustion, excess air and CO_2 from calcination).

b) Calcining zone. Fuel is burned in preheated air from the cooling zone and (depending on the design) in additional "combustion" air added with the fuel. This produces a temperature of over 900 °C and causes dissociation of the limestone into quicklime and carbon dioxide.

c) Cooling zone. Quicklime leaving the calcining zone at 900°C is cooled by direct contact with "cooling" air, part or all of the combustion air, which in return is preheated.

Most of the kilns currently used are based on either the shaft or the rotary design. There are a few other kilns based on different principles. All of these designs incorporate the concept of the three zones. Whereas shaft kilns usually incorporate a preheating zone, some other lime kilns, namely rotary and fluidised bed kilns, are nowadays operated in connection with separate preheaters. Two main types of preheaters are used; vertical shaft and travelling grate.

Most kiln systems are characterised by the counter-current flow of solids and gases, which has implications for the resulting pollutant releases.

Modern lime-kilns can be classified as follows:

1. Shaft kilns:

1.1. Mixed feed;

1.2. External chambers (gasifiers);

1.3. Gas;

1.4. Finelime Kilns (for calcining fine limestone);

1.5. Parallel-flow regenerative kilns.

2. Rotary kilns.

3. Kilns of other types:

3.1. Multiple hearth kilns;

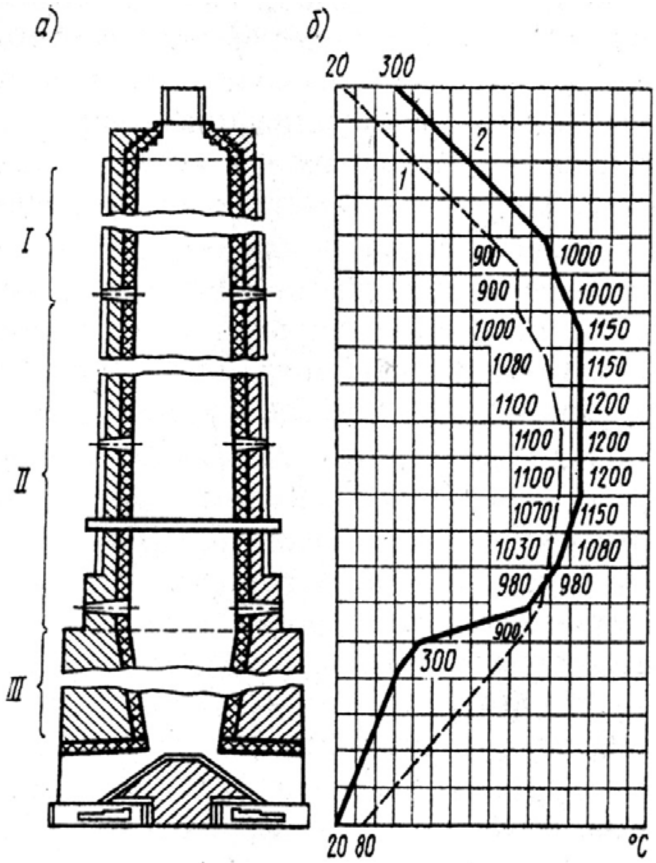
3.2. Fluidised bed kilns;

3.3. Flash calciners (cyclone).

At present time, in burning of lime in Russia, lime-kilns of 2 kinds dominate: shaft (up to 75% of total lime production) and rotary (around 25%). These and other kinds of lime-kilns will be described below.

In **Shaft kiln**, same to others, 3 zones of heat transfer can be distinguished: I) preheating (in upper part of the shaft, filling 55-65% of working height), II) calcining (10-15%, in the middle of the shaft) and III) cooling (25-30% in lower part of the shaft) – see Figure 1. Shaft kiln efficiency ranges 40-75%.

Figure 1: Design and temperature regime in shaft lime-kiln



a) zones of shaft kiln: *I* – preheating, *II* – calcining and *III* – cooling

b) temperature regime of lime burning: 1 – material temperature; 2 – hot gases temperature

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

The major problem with traditional shaft kilns is obtaining uniform heat release and movement of the burden across the shaft. Fuel injected at a wall usually does not penetrate more than 1 m into a packed bed. This limits the kiln effectiveness. To solve the problem, the following measures are applied:

- use of the mixed feed technique
- use of central burners or lances,
- injecting the fuel via tuyères which penetrate approximately 1m into the kiln,
- injection of the fuel underneath arches, or
- injection of air or recycled kiln gas above the fuel.

In general, shaft kilns have relatively low heat use rates because of efficient heat transfer between the gases and the packed bed. However, they retain most of the sulphur in the fuel so low-sulphur fuel is required to produce a low-sulphur product. Older designs tend to produce quicklime with a low to moderate reactivity and a relatively high $CaCO_3$ content. Modern designs incorporate features which enable highly reactive lime to be produced with low $CaCO_3$ levels.

Before describing specific designs of vertical shaft kilns, it is appropriate to consider three important features which are common to all designs, namely charging, drawing and combustion.

Charging of raw material

Single point charging of lump raw material, especially to shaft kilns, can lead to problems in kiln operation. Larger stones tend to roll down the conical heap towards the walls, while the smaller fractions concentrate along the axis of the kiln. As a result, there is a gradation in the resistance to flow of kiln gases from a high level around the central axis to progressively lower levels towards the walls. This results in a greatly reduced flow of gases through the central part of the kiln and as a result part of the burden tends to be under-calcined.

A variety of devices have been developed to mitigate this effect and to minimise the asymmetry of the charging system. In the fixed plate and cone arrangement, the position of the cone and strike plate, relatively to the feed chute and to each other, can be adjusted to produce a more-or-less uniform profile around the kiln. Inevitably, fines tend to concentrate on either side of the feed chute centre line, but the effect on the kiln operation is small. The rotating hopper and bell system is more sophisticated and produces both a more uniform profile and a better dispersion of fines in an annular ring around the kiln.

For mixed feed kilns it is essential that the fuel is dispersed uniformly across the kiln. Therefore rotating hopper and bell systems are used, in which the bell may be fitted with extensions, which typically consist of four quadrants, one deflecting part of the charge towards the centre of the kiln, a second deflecting it further out, and with the third and fourth quadrants deflecting it progressively further away from the axis of the kiln. After each charge, the hopper and the apron are rotated by a fraction of revolution so that, on average, a uniform distribution is obtained.

Drawing of lime

In most cases the drawing system determines the velocity at which the limestone burden descends through the kiln. The drawing system should produce a uniform movement of the burden. Simple systems, using a single discharge point and a conical table, work satisfactorily while the burden moves freely. However, when there is a tendency for part of the kiln to stick or when fused lumps of lime bridge between the table and the wall of the cooling zone, lime is preferentially drawn from the free-flowing parts of the kiln, resulting in further over-heating in the problem area.

A better system uses four discharge points without a central table. If there is a tendency for part of the kiln to stick, the feeder(s) under that part can be operated at a faster rate than the others to help re-establish free movement. Similarly, if one feeder becomes blocked, appropriate action can be taken. Multiple discharge points can also assist with diagnosing problems within a kiln. By operating each in turn, the lime from different segments can be tested separately to identify if a particular segment is under or over-burned.

Still more sophisticated drawing mechanisms are used, such as:

a) hydraulically driven quadrants,

b) a rotating eccentric plate, and

c) a rotating spiral cone with steps and a slope designed to take lime uniformly across the shaft. This design is used on some mixed-feed kilns.

Combustion

In all combustion processes there is an optimum air to fuel ratio which gives the highest efficiency of combustion. A ratio lower than optimum results in incomplete combustion and increased levels of carbon monoxide, while a higher ratio results in the products of combustion being diluted and cooled by the additional quantities of air.

Combustion within the packed bed in vertical lime kilns is particularly problematical as mixing of gasified fuel and air under these conditions is more difficult. From the viewpoint of combustion efficiency, the fuel and air should, ideally, be distributed uniformly across the shaft. However, regardless of the firing system, variations in the air-fuel ratio occur.

Various techniques have been used to moderate temperatures in the calcining zone. Use of an overall deficiency of air is effective but increases fuel usage and can cause the emission of dark smoke. Recirculation of kiln gases is practiced with some kilns to moderate kiln temperatures, particularly at the walls. In the annular shaft and parallel-flow regenerative kilns part or all of the combustion gases pass down part of the shaft in co-current flow with the lime. This results in a comparatively low temperature in the finishing section of the calcining zone.

Shaft kiln are distinguished by kinds and methods of fuel burning. Modern ***mixed-feed shaft kilns*** use limestone with a top size in the range of 60 to 200 mm (fuel – 40-60 mm) and a size ratio of approximately 2:1. The most widely used fuel is a dense grade of coke with low reactivity and low ash content. The coke size is only slightly smaller than that of the stone so that it moves with it rather than trickling through the interstices. The stone and the coke are mixed and charged into the kiln in such a way as to minimize segregation.

The quality of the quicklime tends to be moderate, with the reactivity being considerably lower than that obtained by rotary kilns at the same $CaCO_3$ level. The retention of sulphur from the fuel is high.

In ***kilns with external chambers***, positioned along outer perimeter of the kiln, high-volatile-containing fuel (brown coal, peat, slate coal) are used. The exhaust gases are fed to calcining zone via special hollows in kiln walls. Around 15% of manufactured lime are calcined in this kind kilns.

In ***gas kilns***, natural gas is used as fuel. Calcining with the use of natural gas allows to increase quality of finished product, to increase lime-kiln productivity and simplifies automation of the process. This kind kilns yield around 305 of total lime manufactured. Among these kilns advantages are also low cost of lime calcinations equipment, relatively low specific consumption of conventional fuel (160-180 kg/t), low dust emission, small land plot required, simplicity of design and maintenance.

The main disadvantages of the mentioned types lime-kilns are as follows:

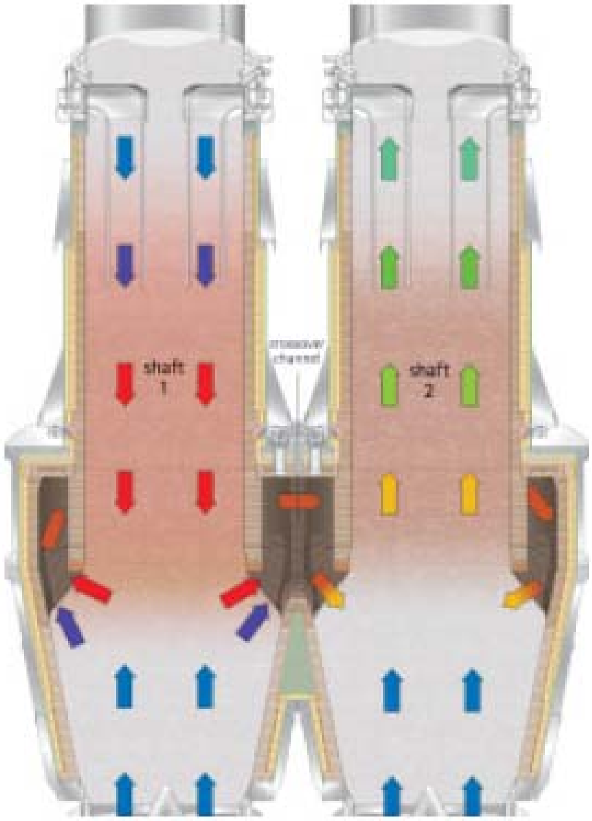
- calcinations irregularity, which increases with increasing diameter and decreasing height of lime-kiln;
- insufficiently high decarbonization degree (95-97% maximum as rule);
- rather strict requirements, imposed on uniformity of resources in strength and granulometry, as well as in content of clay impurities;
- limited productivity (100 tpd maximum to provide uniform calcining, including central zone of lime-kiln).

Shaft kiln PFR Maerz® for calcining lime and dolomite (Parallel Flow Regenerative Lime Kiln)

This kiln system, which was developed for the production of highly-reactive quicklime by MAERZ -Ofenbau AG (Zürich) in the 1960s and marketed with great success ever since throughout the world, is based on the parallel flow regenerative principle.

The two vertical shafts are connected with each other by means of a crossover channel of typical design geometry (Figure 2) – a system which makes it differ substantially from other vertical lime-kilns.

Figure 2: Principle of operation of PFR kilns Maerz



Source: Maerz AG

By means of cyclic alternation of the burning process in the two shafts, the combustion gases are passed through the limestone to be de-carbonated alternately in parallel or counter-current flow.

Batches of limestone are charged alternately to each shaft and pass downwards through a preheating/regenerative heat exchange zone, past the fuel lances and into the calcining zone. From the calcining zone they pass to the cooling zone.

The operation of the kiln consists of two equal periods, which last from 8 to 15 minutes at full output.

In the first period, fuel is injected through the lances in shaft 1 and burns in the combustion air blown down this shaft. The heat released is partly absorbed by the calcination of limestone in shaft 1. Air is blown into the base of each shaft to cool the lime. The cooling air in shaft 1, together with the combustion gases and the carbon dioxide from calcination, pass through the interconnecting cross-duct into shaft 2 at a temperature of about 1050 °C. In shaft 2, the gases from shaft 1 mix with the cooling air blown into the base of shaft 2 and pass upwards. In so doing, they heat the stone in the preheating zone of shaft 2.

If the above mode of operation were to continue, the exhaust gas temperature would rise to well over 500 °C. However, after a period of 8 to 15 minutes, the fuel and air flows to shaft 1 are stopped, and "reversal" occurs. After charging limestone to shaft 1, fuel and air are injected to shaft 2 and the exhaust gases are vented from the top of shaft 1.

The method of operation described above incorporates two key principles:

a) The stone-packed preheating zone in each shaft acts as a regenerative heat exchanger, in addition to preheating the stone to calcining temperature. The surplus heat in the gases is transferred to the stone in shaft 2 during the first stage of the process. It is then recovered from the stone to the combustion air in the second. As a result, the combustion air is preheated to about 800 °C.

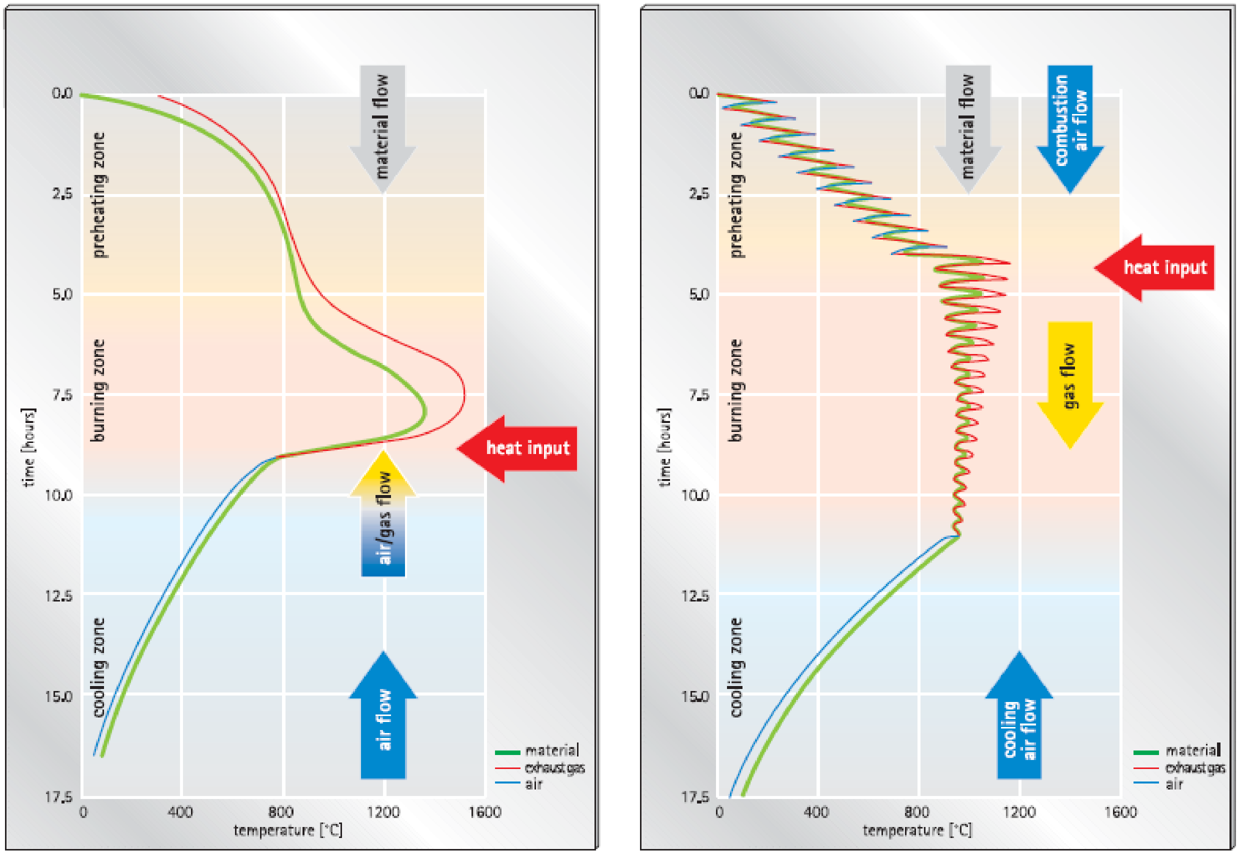
b) The calcination of the quicklime is completed at the level of the cross-duct at a moderate temperature of about 1100 °C. This favours the production of a highly reactive quicklime, which may, if required, be produced with a low CaCO3 content.

Because the kiln is designed to operate with a high level of excess air (none of the cooling air is required for combustion), the level of CO2 in the exhaust gases is low -about 20% by volume (dry).

The kiln can be fired with gas, oil or solid fuel (in the case of solid fuel, its characteristics must be carefully selected). A modified design (the "finelime" kiln) is able to accept a feedstone in the range 10 to 30 mm, provided that the limestone is suitable.

In Figure 3, plots of temperature variation with height of shaft in common shaft kilns, operating by counterflow principle (*a*), and in PFR kilns Maerz (*b*).

Figure 3: Temperature trend by zones (in height of shaft) in shaft kilns of various types



a *b*

a – common shaft kiln; *b* – PFR kiln Maerz

Source: Maerz AG

Kiln PFR Maerz® with rectangular shafts is of simplest design; appearance of the kiln is presented in Fig. 4 *a*. The simplest design of a PFR-Kiln is to place two shafts with rectangular cross section side by side lengthwise in such a manner that the kiln gases can flow directly from one shaft to the other via a direct crossover channel. Because of its geometry this kiln type is simple to manufacture with reduced requirements for steel structure and refractory materials.

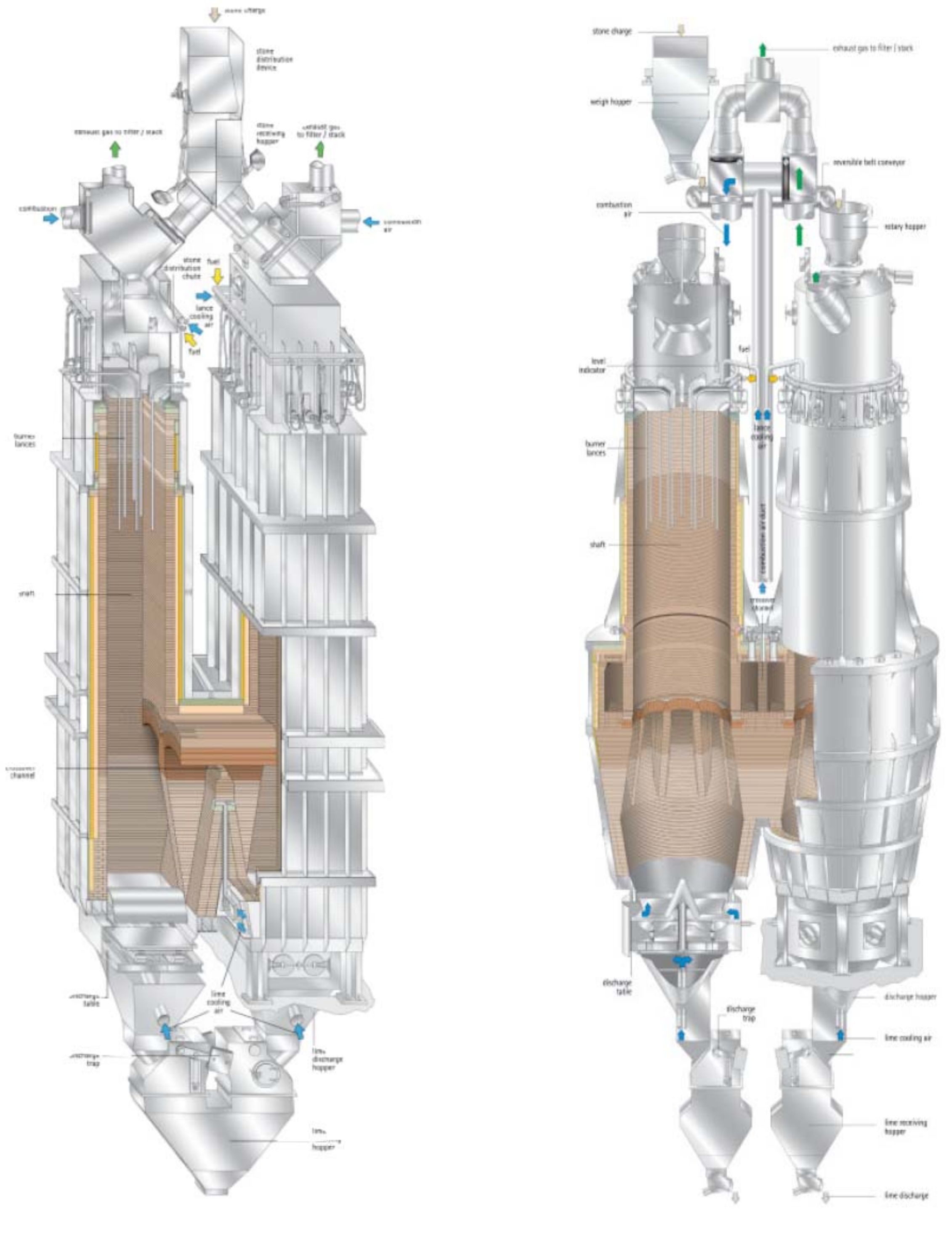
This simple and cost efficient kiln type is mainly applied for output rates up to 400 tons of burned lime or dolomite per day. For larger kiln capacities Maerz has developed a special patented flap type stone charging system which allows an efficient control of the limestone grain size distribution in the shafts and thus uniform gas flow, a pre-condition for consistent and high quality of the product.

Since 1966 Maerz has built world-wide more than 170 rectangular Maerz Kilns operating with gaseous, liquid and pulverised solid fuels.

For larger capacities, e.g. from 300 to 800 tons per day, Maerz® elaborated kilns of circular cross section are recommended ***(circular PFR kilns)***. Appearance of the kiln is presented in Fig. 4 b. These kilns have circular ring channels collecting the combustion gases before they enter the non-burning shaft via the crossover channel. The gases exit the burning shaft and enter the non-burning shaft radially around the complete shaft perimeter thereby guaranteeing an absolute even heat distribution.

A bucket positioned vertically above each shaft is used for charging raw stone into the kiln shafts. Stone distribution is further improved by rotating the bucket during charging from the conveyor belts or vibrating feeders. The circular shaft design facilitates uniform stone and fuel distribution during charging and calcination throughout the complete shaft cross section. As a result this kiln type produces the best product quality of all PFR-Kiln types.

Since 1966 roughly 200 circular Maerz® Kilns operating with gaseous, liquid and pulverised solid fuels or a combination of these, have been built world-wide.



a *b*

a – rectangular PFR kiln*; b* – circular PFR kiln
Source: Maerz AG

Figure 4: Appearance of rectangular and circular PFR kilns Maerz

Finelime Kiln Maerz® (for calcining fine limestone)

Typical stone sizes processed in conventional vertical shaft kilns are larger than 30 mm. Stone sizes of 6 to 30 mm can be calcined in rotary kilns, however, with poor thermal efficiency. To solve this shortcoming Maerz has developed a patented special type of PFR-Kiln to burn stone sized between approx. 10 and 40 mm at thermal efficiencies even better than in conventional PFR-Kilns.

In the course of laboratory and field test runs the following parameters proved to be critical when processing small size raw material in a shaft kiln:

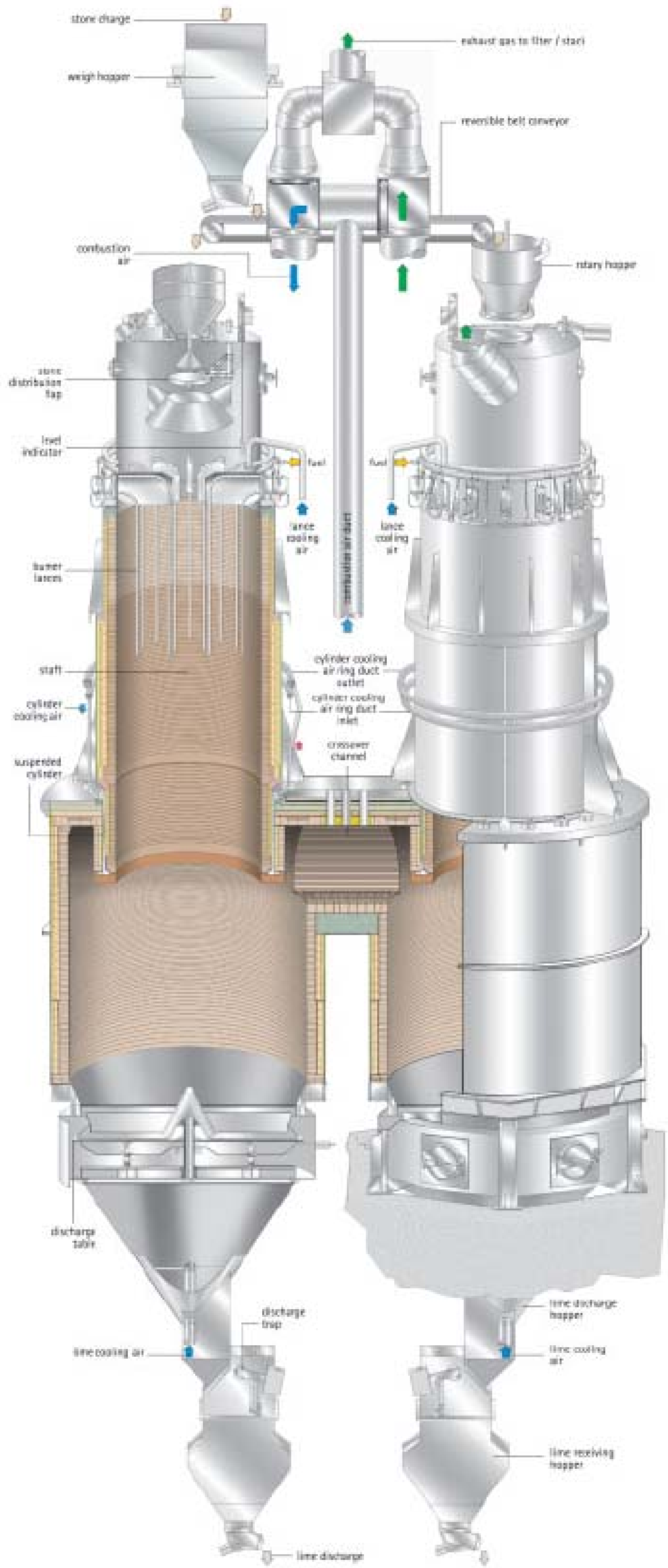
- Segregation phenomena in the stone charge
- Fuel distribution over the shaft cross section
- Interior shape of the refractory kiln lining.

These critical factors have been given particular attention in the subsequent development and design of this kiln type, while maintaining the unique features of PFR-Kiln principles, i.e. the parallel flow of material and combustion gases in the burning zone and the regenerative preheating of combustion air.

Appearance of PFR kiln for calcining fine limestone is presented in Fig. 5.

Notice that these type kilns are capable to calcine also 40-80 lump limestone and even mix of fractions 10-40 mm and 40-80 mm, which are loaded layer-by-layer independently of each other by “sandwich” method.

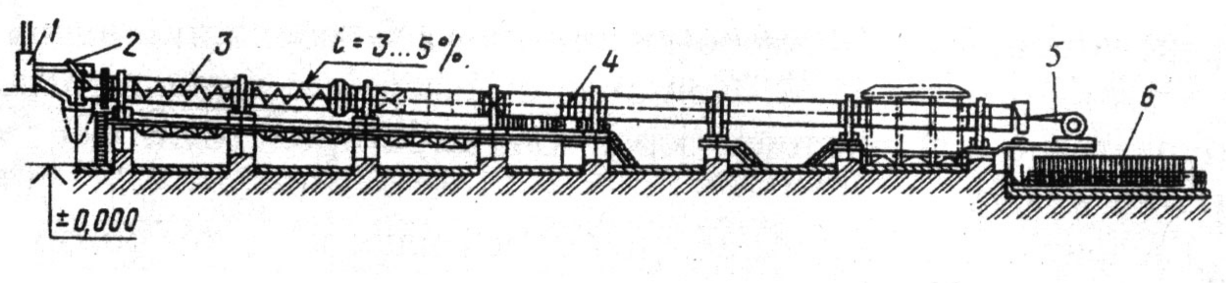
Figure 5: Appearance of kiln PFR for calcining fine limestone



Source: Maerz AG

Rotary kiln appears as steel drum, composed of envelopes, joint by welding or riveting, and has inner refractory lining (Figure 6).

Figure 6: Design of rotary kiln



1 – smoke exhauster; 2 – feeder for feeding slime; 3 – drum; 4 – drive; 5 – ventilator with burner nozzle for blowing of fuel; 6 – grate cooler

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

Section of the kiln can be both cylindrical and complicated with widened zones to prolong time of occurring the roasted material in them.

Kiln, installed at angle of 3-5^{o}, rotates with frequency 0.5-1.5 min^{-1} (rpm). Rotary kiln mainly operate by principle of counterflow. Resources go from upper (cold) end, whereas fuel-air mix, burning out throughout 20-30 m of the kiln length, arrives from lower (hot) end of the kiln. The hot gases heat the charge up to required temperature. Duration of the material stay in the kiln depends on frequency of its rotation and tilting angle, constituting, for instance, in kiln 5×185 m from 2 to 4 hours.

Flame and hot gases heat both the material and lining of the kiln. In turn, the lining gives the heat to the roasted material by direct contact. At each rotation of the kiln, in the process of contact with gas flow, temperature of kiln lining increases, and, at contact with the roasted material, the temperature decreases.

Productivity of rotary kiln depends on its inner volume, tilting angle of kiln and rotation frequency, temperature rate of gases moving quality of resources and other factors.

An important advantage of rotary kilns is their technological universality, owed by possibility to use resources of various kinds. In burning lime, small lumps of limestone (up to 30 mm) and chalk rocks with moisture up to 20% are processed in rotary kilns by dry method, whereas chalk rocks of higher moisture are processed by wet method as slime with moisture 36-42%. Technological characteristics of rotary kilns, operating by wet and dry methods, are presented in Table 1.

Table 1: Comparative specifications of rotary kilns of production JSC "Volgotsemmash"

Parameter	*Value for kilns of sizes, m*			
	5.0×110	3.6×75	2.5×75	3.0×60
Design productivity, tpd	300	360	115	240
Mass of kiln without lining, t	567	574	443	509.2

Source: JSC "Volgotsemmash"

Sizes of rotary kilns are determined by kind of burnt (roasted) product, required temperature and duration of roasting. Length of rotary kilns for roasting lime is 70-150 m, diameter – 2.5-4 m.

The best results are reached when using gaseous fuel. A feature of lime burning in rotary kilns is great (up to 15%) dust flue loss that increases fuel consumption and requires applying effective dust catchers.

Productivity of rotary kilns achieves 400-500 tpd and more, i.e. 2-4 times above that of shaft furnaces. Applying rotary kilns allows reaching the highest degree of resources decarbonization (up to 99.5%), and, thus, the highest quality of products. The technology provides conducting soft burning. The obtained lime is fine-crystalline of high reaction ability. Use of rotary kilns provides stepless regulation of productivity of equipment and quality of products. The kilns are most often used for production of flux lime for metallurgy. According to expert estimates, the kilns yield at least 25% of total lime production in Russia.

Effective use of heat in rotary kilns is provided by installing system of intra-kiln and external heat-exchange devices.

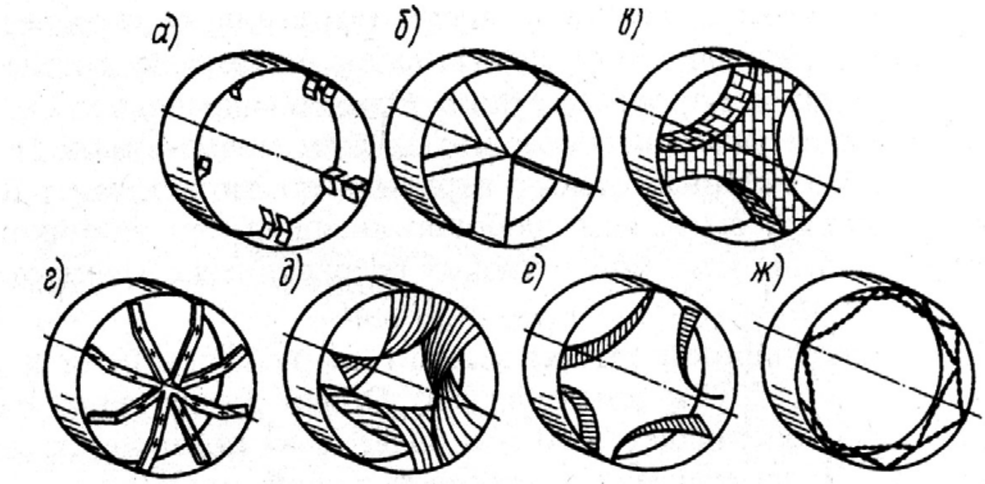
Intra-kiln heat exchangers have developed surface to provide improved heat exchange and, thus, to economize heat; in addition, the facilities facilitate process of mixing and decrease dusting.

In wet method of cement production, the most applicable intra-kiln heat-exchangers are chain curtains, providing heating and drying slime to moisture 8-10% after the curtain. Chain curtains of common chain types and of festoons type (festoons of chain) are applied. The latter is around 2 times less metal-consuming at the same heating effectiveness and lower hydraulic resistance and dusting.

Length of chain curtain part of kiln is around 25-60 m, depending on kiln size. Total length of chains in modern kilns is 2000 m and more; their surface area reaches 1500 m^2. Optimal area of chain surface is to be set – to provide optimal moisture of slime at minimizing heat consumption and dusting Temperature of gases at chain curtain part of kiln of 700-800^oC. Further increasing the temperature results in burning out chains.

For zone with higher temperatures, heat-exchangers of special design are designated (Figure 7). The simplest kind is lifting vanes, made of metal of ceramics, providing increasing height of the material lifting, change a part of the material into flash (suspension) standing, decreasing thickness of layer.

Figure 7: Designs of inner heat exchangers of rotary kilns



а – interspersing (lifting) vanes; б, в – cellular; г – link; д – arc; е – cycloid; ж - chain

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

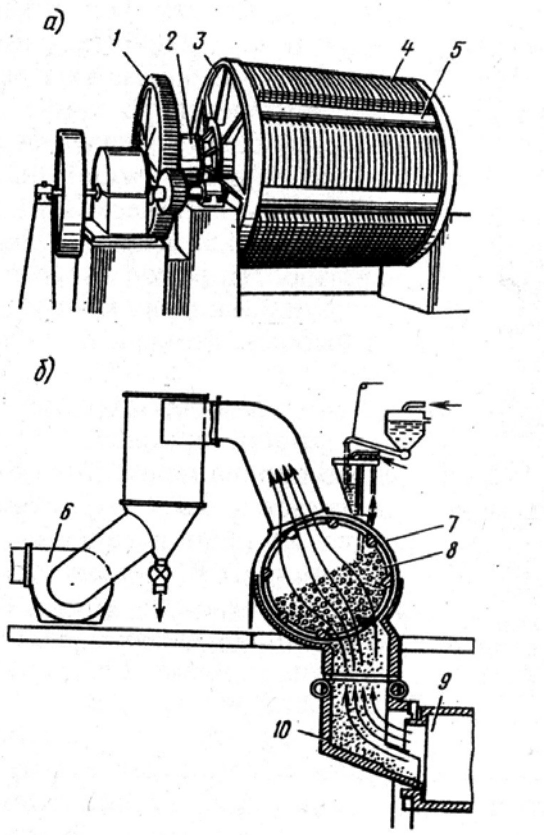
In cellular heat exchangers, being roasted material is divided into several flows to increase surface of contact with hot gases. These type heat-exchangers are installed after chain curtains: metals heat-exchangers in zone of temperatures 700-1000^{o}C, ceramic ones - 1200-1400^{o}C.

Link heat-exchangers are presented by a set of massive links, joint with each other by pin hinge; heated by gases links gives heat to the resources mix when immersing in its layer. Such heat exchangers serve as protecting shields for chain curtains, preventing their burning out. Link heat exchangers are made of heat-resistant steels and can operate up to 1100^{o}C. Besides, arc, cycloid and other kinds of heat-exchangers are applied.

As possibilities of placing intra-kiln heat exchangers are restricted (they fail at high temperatures), in some cases for utilizing hot gases, external heat exchangers are used, for instance, slime concentrators.

Slime concentrator is a rotary drum of grates, fixed in supporting beams (Figure 8).

Figure 8: Slime concentrator of rotary kiln



a – slime concentrator; *b* – scheme of connection of slime concentrator with loading end of rotary kiln

1 – drive of drum; 2 – hollow trunnion; 3 – steel bottom; 4 – grates; 5 – steel beams; 6 – smoke exhauster; 7 – frame of concentrator; 8 – filling bodies; 9 – kiln; 10 – adapter discharge hopper

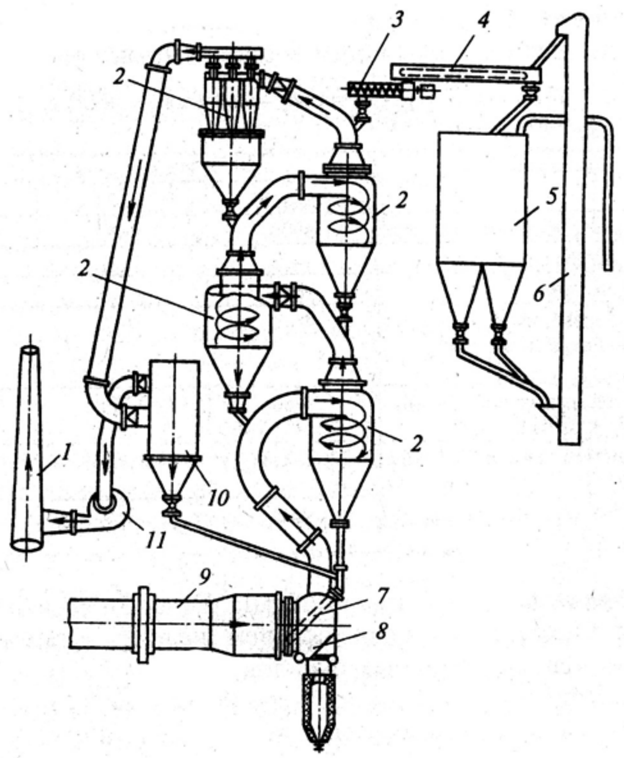
Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

Inner part of drum is filled by 60% with cylinders 100-200 in diameter and 120-250 mm long. The drum is covered by steel jacket, lined inside with refractory brick.

Drying process in concentrator is intensified by sharp increasing heat-transfer surface, provided by availability of the metal filler-bodies, sprayed by slime and hot gases. Temperature of the gases decreases here from 500-600 to 120-150^{o}C, and the slime moisture decreases to 8-12%. The concentrator on its outlet yields granules of the material at temperature around 100^{o}C. Applying of concentrator allows to increase productivity of kilns by 20-25% with decreasing specific heat consumption by 15-20%, however, its use results also in increasing dusting (up to 20%).

Kiln for roasting of dry resource mixes are commonly equipped with external ***cyclone heat-exchangers***. Their design is based on principle of heat exchange between exhaust gases and ground resources mix is suspension (Figure 9).

Figure 9: Scheme of external cyclone heat-exchanger



1 – chimney; 2 – cyclone heat-exchangers; 3 – screw feeder; 4 – scraping conveyer; 5 – feed hopper for ground resources; 6 – ladle elevator; 7 – discharge hopper; 8 – adapter; 9 – rotary kiln; 10 – dust collectors; 11 - smoke exhauster

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

The resources mix in system of cyclone heat-exchangers moves towards flow of exhaust gases from rotary kiln with temperature 900-1100^{o}C. Average rate of the gases movement in gas conduits is 15-20 m/s that much higher than speed of the mix movement. So the mix particles are involved by the flow of exhausted gases into placed above cyclone heat exchanger. As diameter of the heat exchanger is much higher than that of gas conduit, speed of gas movement drops considerably, and the mix particles precipitate, and then go to gas conduit up to the next cyclone. Thus, the mix gradually sinks, passing consequently through several stages of cyclones and gas conduits, starting from relatively cold and finishing in hot one. The heat exchange process is conducted by 80% in gas conduits and only by 20% in cyclones.

Time of being of the resources mix in cyclone heat-exchanger is 25-30 sec maximum;, nevertheless, this is enough for heating the mix up to 700-800^{o}C and its complete dehydration and decarbonization by 25-35%.

Disadvantages of this type kilns are high power consumption and relatively low resistance of lining, as well as high sensibility to changing regime of operation and fluctuations of resources composition.

Cooling of calcined materials

Outcoming from rotary kiln material has temperature around 1000°C. Returning heat of the material into kiln can decrease considerably fuel consumption. This is achieved at the expense of cooling the material by air, fed then into kiln for burning fuel. Regime of cooling influences on both further technological process and properties of finished products. Fast cooling of clinker promote glass and fine-crystalline clinker structure formation. Such clinker is more easily milled that finally increases grade of cement.

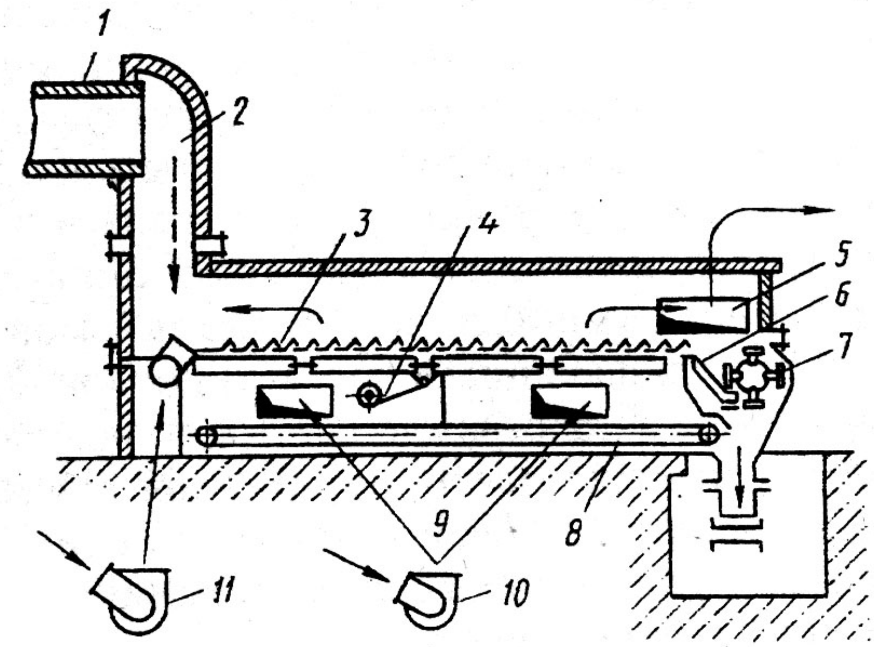
At present time, 3 types of coolers are applied: rotary, recuperator and grate.

Rotary coolers constitute rotary steel drum 15-30 long and 2.5-3.0 m in diameter. Hot mix goes from Kiln to the drum and to its bottom end inside rotating drum. Cooling is conducted by air, moving towards the mix flow. The cooler provides cooling the mix to 200-300°C, at heat recuperation degree up to 50%. The design defects are large sizes and need in individual drive. Rotary coolers, equipped with a set of intra-drum heat exchangers, can be installed after high-efficient dry method kilns.

Recuperator coolers are composed of several steel drums, positioned symmetrically circular relative to the kiln from its hot end. The drums are connected with inner part of the kiln by sprinkles, through which hot clinker arrives. Inside the recuperator, interspersing chains and vanes are installed. Degree of cooling increases with increasing quantity of drums. Air for cooling is sucked in recuperator, goes through it, cooling the roasted product, and, heated, goes to kiln. Applying this type coolers allows decreasing temperature of the material to 130°C. Heat efficiency of recuperator coolers is 65-70%. At present time, recuperator coolers with productivity of 4000 t/day are exploited.

Grate re-pushing (movable) coolers (Figure 10) are used in modern powerful rotary kilns. Horizontal fire grate is geared by cranky mechanism, and the cooled product moves through the cooling chamber with permanent mixing. Initially the hot mix is subjected to overgrate blast (10-12 kPa) that provides regular spreading of arriving material on the whole grate and fast initial cooling.

Figure 10: Grate re-pushing coole



1 – rotary kiln; 2 – takeup shaft; 3 – fire grate; 4 – drive; 5 – window for discharge of surplus exhausted air to atmosphere; 6 – screen; 7 – hammer crusher; 8 – scraping conveyer; 9 – windows for general blast; 10 – ventilator of general blast; 11 – ventilator of "overgrate blast"

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005

The obtained hot air with temperature 450^{o}C is sucked in kiln, where is used for fuel burning as secondary air. In outlet end of the cooler, hammer crusher is installed for crushing lumps of product.

Advantages of grate coolers are high rate and degree of cooling (to 40-60^{o}C), high efficiency, low specific consumption of power.

The **Multiple Hearth Furnace**, elaborated by RCE company, is able to process very small raw material grain sizes as well as filter cakes and allows the adjustment of an accurate temperature profile. It can be applied in virtually all calcination processes where high quality end products are required. Multiple Hearth Furnaces provide calcinations of resources, containing up to 50% of water (chalk slimes). The furnace design provides precise temperature control (±5^{o}C) to ensure high quality of lime. The technology is also suitable for production of fine lime.

Main characteristics of Multiple Hearth Furnace:

• Moisture content levels over 50% in the feed material (e.g. filter cake) are acceptable
• High flexibility and exact control of temperature profile (± 5 °C) to achieve highest product quality
• Suitable for processing very small grain sizes
• Insensitive to fluctuations in chemical and physical properties and moisture content of the feed
• Application temperatures up to 1100 °C

- Suitable for oxidation and reduction processes
- Suitable for liquid and gaseous (incl. low calorific value gas) fuels
- Highest up-time and service life
- Low maintenance costs.

The Furnace description:

The RCE Multiple Hearth Furnace consists of a steel shell lined with refractory bricks and refractory lined hearths. The movement of the material through the furnace is carried out by rabble teeth supported by rabble arms which are attached to a central rotating shaft supported between bearings and driven by an external drive mechanism. In order to withstand temperatures of up to 1100 °C, the rabble system is cooled by air. The heated-up air leaves the furnace top through the hollow centre shaft from where a part of the hot cooling air is recycled to the burner system by a fan for further use as combustion air.

The design of the furnace permits an excellent contact between solids and gases. The furnace hearths are designed alternatively as “outhearths” and “in-hearths” depending on the way they are charged. On an “in-hearth” the raw material is charged to the periphery of the hearth from where it travels to the inside finally falling through the “in-drop hole” onto the next “outhearth” located underneath. Here the material is spirally rabbled outwards until it falls through the “out-drop hole” onto the following “in-hearth”. This pattern is repeated until the calcined material is discharged from the periphery of the bottom hearth.

The quality of the final product (i.e. reactivity, specific surface area, LOI, residual CO_2) can be adjusted by controlling and varying the temperatures hearth by hearth. The fired hearths are equipped with up to four gas or oil burners each. In cases where direct flame contact with the product has to be avoided, the burners are arranged in external burning chambers. The dust collected in a precipitator can be returned by a conveying system to one or several hearths of the furnace thus reducing the product losses with the exhaust gases.

Principal layout and performance data:

Furnace type: ML1 to ML4
MS1 to MS4
Outside diameter (m): 4.3 to 7.8
Number of hearths: 6 to 19
Daily output (tons): 25 to 300
Stone grain size (mm): 0 to 30
Fuels: gaseous and liquid fuels

Another approach to calcining lime is fluidized bed. **Fluidised bed kiln** is characterized by high lime yield at relatively low fuel consumption.

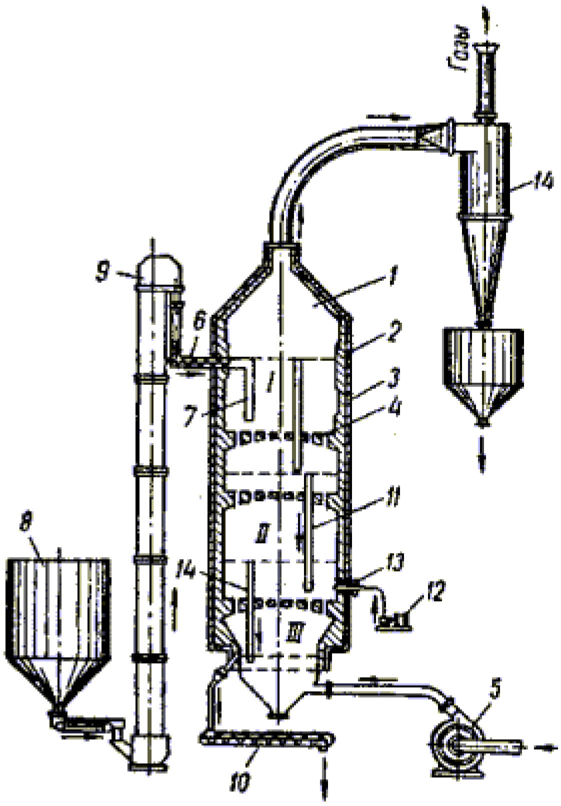
These units are perfect for small production or small sized stone. These units produce up to 120 tpd. These systems can be fired on gas or coal. Efficiency is slightly below other types of kiln systems. Company Metso minerals can build this type of plant turnkey. A system could come with feed and product material handling and storage system, a feed preheater, a fluid bed calciner, waste heat recovery, a fluid bed product cooler and a dust collection system. Controls are from a single control area.

The application of suspension or fluid bed calciners has been in use well over 60 years old. Prescreened 4 mm x 1 mm limestone is fed to the surge hopper. The hopper distributes the stone into a four compartment preheater through which hot gases at 950 degrees C drawn from the kiln. This preheater is a spouted bed type, which quickly quenches the exhaust gases from 950 degrees C to 580 degrees C, thereby circumventing the critical transition temperature. Any buildup occurs on the feed particles and not on the walls or ducts of the processing equipment.

A controlled percentage of the kiln exhaust gases bypass the preheater and mix with the preheater exhaust gases and then pass to a recuperator. The recuperator is a combustion air to gas heat exchanger, where the combustion air is preheated. Fuel is injected into the bed of the calciner zone by means of a number of injectors to raise the temperature to that required for calcination. For coal firing, a pre screened coal of 1 mm x 4 mm is injected along with the limestone into the calciner freeboard. The product is cooled in a fluid bed cooler, either as an indirect water tube cooler or as a direct fluid bed cooler with exhaust gases going to a dust collector.

Design of fluidised bed kiln for calcining limestone is presented in Fig. 11. The kiln appears as vertical metal drum, lined inside with chamotte brick.

Figure 11: Design of fluidized bed kiln



1 – reactor; 2 – refractory brick; 3 – steel case; 4 – grate roof; 5 – ventilator; 6 – screw feed ; 7 – limestone feed pipe; 8 – bunker for grinding resources; 9 – elevator; 10 – screw for drawing lime; 11 – pipes for transferring material from upper to lower zones; 12 – pump for fuel oil feed; 13 – burner nozzles; 14 – cyclone for cleaning gases of dust

Source: B.V.Manikhin "Building lime and materials on its basis" – Khabarovsk: DVGUPS, 2001

At present time, this type kilns have not wide application and are mainly used at metallurgical combines.

<u>Flash-calcining kilns (flash calciners)</u>

Calcining is conducted not only in reactors, but also at other facilities, for instance, in calcining pipes, in which fine-grinded particles of carbonate resources are carried by hot gas flow and are calcined in the flow. The burned lime is precipitated from gas fдow in cyclones and filters. This type kilns are not used in Russia for commercial-scale lime production.

Comparative economic performance of lime-kilns of various types are presented in Table 2.

Table 2: Comparative economic performance of lime-kilns of various types

Type of kiln	*Productivity, tpd*	*Specific yield of lime, kg/m³ per day*	*Specific consumption of conditional fuel, MJ/kg of lime*	*Specific consumption of power, kWh/t of lime*
Shaft:				
Mixed feed	30-200	500-900	3.5-5.0	5-10
With external gasifiers (semi-gas)	7-100	500-800	4.4-5.8	8-12
gas	15-200	500-900	4.1-6.2	-
PFR kiln Maerz	80-850	n. a.*	around 3.6	n. a.
PFR kiln Maerz for calcining fine-lump limestone	200-500	n. a.	around 3.43	n. a.
Rotary	100-500	400-600	5.3-8.8	14-20
Fluidised bed	100-200	1800-2000	5.3-5.9	

** n. a. means "data are not available"*

Source: Sulimenko L.M. "Technology of mineral binding materials and articles on their base" – M: Vysshaya shkola, 2005; B.V.Manikhin "Building lime and materials on its basis" – Khabarovsk: DVGUPS, 2001; Maerz AG

Production of hydrated lime

The hydration of lime is described by equation:

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

The hydration of lime proceeds by stages. At the first stage, oxyhydrate $CaO{\cdot}2H_2O$ originates, which then, at the second stage, is broken in accordance with equation:

$$CaO{\cdot}2H_2O \rightarrow Ca(OH)_2 + H_2O.$$

At the next – final – stage, $Ca(OH)_2$ crystals aggregation proceeds to form hydrated lime.

The hydration of lime involves the addition of water in a hydrator. The quantity of water added is about twice the stoichiometric amount required for the hydration reaction. The excess water is added to moderate the temperature generated by the heat of reaction by conversion to steam. The steam, which is laden with particulates, passes through abatement equipment prior to discharge to atmosphere.

There are many designs of equipment but technically the hydrator consists of pairs of contra-rotating screw paddles which vigorously agitate the lime in the presence of water. A strong exothermic reaction takes place generating 1160 kJ per kg CaO. The average residence time of the solids in the main reactor is about 15 minutes.

The heat release causes a vigorous boiling action which creates a partially fluidised bed. Dust is entrained in the steam evolved during the process. If this dust is collected in a wet scrubber a milk of lime suspension is produced, which is normally returned to the hydrator.

After hydration the product is transferred to an air-swept classifier where the coarse and fine fractions are separated using a recycling air stream. Some or the entire coarse fraction may be ground and recycled. The fine fraction is conveyed to storage silos. From here it is either discharged to bulk transport or transferred to a packing plant where it is packed in sacks or intermediate bulk containers.