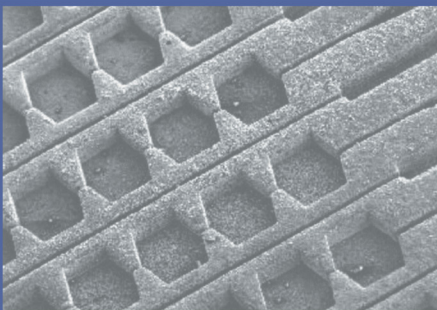




Structure and Performance of Cements

Second Edition

Edited by

J. Bensted and P. Barnes

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Preface

Structure and Performance of Cements was first published in 1983. Much has changed over the last 18 years, but still, a surprisingly large number of the reasons given then for the need for such a book are equally valid today; these include:

- Cements constitute the second largest manufactured commodity (by weight) in the world
- Most peoples' lives are continually dependent upon the properties of cements
- Only a small fraction of income derived from the manufacture and marketing of cements is spent on research into the properties and applications of cements, including new developments

However, although the basic starting materials for the manufacture of most cements have not changed very much, the subject has in fact moved on appreciably. Cements today have a greater number and range of applications than ever before. The various types of cements now available (with and without inclusions of additives/admixtures) have increased significantly in numbers. New techniques of examination have arrived and our understanding of the performance requirements and utilization of many different types of cements has improved.

In particular, wet process manufacture for Portland cements is declining rapidly because of the high energy costs involved in driving off the water from the raw material slurries. Modern developments now permit more environmentally friendly dry process manufacture from soft raw materials like chalk and clay with their significant moisture contents using flash calciners. Also important environmentally friendly uses for materials, previously regarded as industrial wastes in

the manufacture of cements, save substantial amounts of traditional fuels like coal, gas and oil. Such pyrotechnic processes now allow wastes that used to be dumped, to be disposed off safely by burning in cement kilns on a routine basis.

This is complemented by cement extension, which means that industrial by-products such as pulverized fuel ash (pfa), ground granulated blast-furnace slag (ggbs) and condensed silica fume (csf or 'microsilica') can partially replace Portland cement clinker in cements. Such replacement permits substantial benefits in the range of applications of the finished cements in grouts, mortars and concretes.

The second edition of the book has been produced, like the first edition, for those scientists and engineers working in both the cement and general construction industry and for research and development specialists in universities and colleges, who need an up-to-date knowledge in key areas of cement technology that have moved on since 1983. It is not intended to be a standard textbook dealing with the whole range of cement types and their applications. Instead, a focused tome has been produced with contributions by a multinational consortium of authors to indicate the global developments that have arisen over the last seventeen years. Modern cement manufacturing methods, key types of cement extenders and important examining techniques, both new, and developments in existing important methods, have been highlighted for addressing a global audience. This updated book is intended to reflect both current production and research in the cement arena, but, as indicated above, is not intended to be an exhaustive treatise, which would have been unmanageably large.

The order of presentation reflects the evolutionary developments that have arisen, and is divided roughly into three broad categories:

- Basic materials and methods – cement manufacture, cement phase composition, Portland cement hydration, calcium aluminate cements, properties of concrete with admixtures, special cements, various reaction/corrosion mechanisms.
- Cement extenders – ggbs, natural pozzolans, pfa, metakaolin and csf – where there have been considerable developments in terms of quality and application; many other extenders have not been included where there is still much basic work needed.
- Techniques of examination highlighted include the well established X-ray diffraction and electron microscopy, where there have been numerous developments in the last seventeen years, together with more recently introduced

methods (electrical impedance, NMR, synchrotron radiation-based techniques) which, with cement-based composite microstructures, need to be drawn to the attention of a wider audience. Some of the more traditional techniques have been excluded since relatively few novel applications have appeared in recent years.

As the editors, we have endeavoured to obtain a widespread balance of authors from a number of different countries around the world. Many of these authors are well known internationally. They are joined by others who are newer to the field and who help to establish a broader viewpoint, both technically and through wide international coverage. We feel privileged to have succeeded in bringing such a distinguished worldwide group of authors together in one book under the umbrella title of *Structure and Performance of Cements*.

Notation

Standard cement chemistry notation is assumed throughout this book:

$A = \text{Al}_2\text{O}_3$	$C = \text{CaO}$	$\bar{C} = \text{CO}_2$	$F = \text{Fe}_2\text{O}_3$	$f = \text{FeO}$
$H = \text{H}_2\text{O}$	$K = \text{K}_2\text{O}$	$M = \text{MgO}$	$N = \text{Na}_2\text{O}$	$S = \text{SiO}_2$
$\bar{S} = \text{SO}_3$	$T = \text{TiO}_2$	C-S-H denotes a variable composition		

AFm denotes a solid solution range within the monosulphate-type structure (i.e. calcium monosulpho-aluminate hydrate to calcium monosulpho-ferrite hydrate).

AFt denotes a solid solution range within the ettringite-type structure (i.e. calcium trisulpho-aluminate hydrate to calcium trisulpho-ferrite hydrate).

Cement manufacture

Wiesław Kurdowski

-
- 1.1 Introduction
 - 1.2 Raw material preparation
 - 1.3 Raw material crushing
 - 1.4 Raw material grinding
 - 1.5 Classifiers
 - 1.6 Homogenization
 - 1.7 Clinker burning
 - 1.8 Coolers
 - 1.9 Cement grinding
 - 1.10 Automation
 - 1.11 Environmental protection
 - 1.12 Acknowledgements
 - 1.13 References
-

1.1 Introduction

Cement technology is very traditional and the basic principles have remained unchanged for a long time. However, very profound changes in the production techniques were introduced leading to the diminishing of energy consumption and decrease in employment as well as fundamental pollution limitations.

Especially quick development was achieved in the last thirty years, which embraced burning and grinding techniques. First, the introduction of precalciners gave a considerable increase in kiln capacity, and the specific capacity increased from $1.5 \text{ t/m}^3 \times 24 \text{ h}$ to 3.5, and even to $5 \text{ t/m}^3 \times 24 \text{ h}$ for extra short kilns.

Second, in the field, the application of the roller press became a general practice and the development of roller mills is noted, which are more and more frequently used for cement grinding. The grinding efficiency was further improved by the

introduction of a new generation of dynamic classifiers.

The introduction of automatic control in all production processes, including kilns, resulted in a drastic fall of employment and during weekends plants are run by two or three people.

Significant progress has been achieved in pollution control. The dust emission decreased to about 0.2–0.3 g/kg of cement. NO_x , SO_2 and CO are of the order 1200, 400 and 500 ppm, respectively, per cubic metre of kiln gases. For the special precalciner NO_x can be as low as 400 ppm. The problem is CO_2 emission, which originates mainly from CaCO_3 decomposition during clinker burning. A partial solution to this problem is the increasing production of cement with additives, chiefly slag, fly ash and limestone. Also, alternative fuels are used to partially replace completely classic fuels giving a decrease of total CO_2 emission from the combustion process.

In the case of alternative fuels utilization, emission of dioxins and furans can be monitored continuously. The industrial experience has shown no increase in these emissions. Long-term measurements have proved that, at least in the case of some alternative fuels, the emission of hazardous gases is lower in comparison with classical fuels. Old tyres must be recognized as being number-one alternative fuels.

Cement kilns are also used for the destruction of hazardous wastes instead of incinerators and the neutralization and destruction of these substances is much more effective.

All these achievements make the cement industry friendly to the environment.

1.2 Raw material preparation

The properties of Portland cement is determined by the mineralogical composition of clinker. The classic Portland clinker has the following mineralogical composition:

$3\text{CaO} \cdot \text{SiO}_2$	alite	55–65%
$2\text{CaO} \cdot \text{SiO}_2$	belite	15–25%
$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	aluminate	8–14%
$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	brownmillerite	8–12%

For special cements the content of C_3A and brownmillerite can differ significantly.

Indispensable conditions for obtaining clinker with this mineralogical composition is the appropriate chemical composition of the bath. The share of main oxides is equal to about 95 per cent and their content is as follows:

CaO	60–70%
SiO_2	18–22%
Al_2O_3	4–6%
Fe_2O_3	2–4%

The entire content of minor components such as MgO , K_2O , TiO_2 , Mn_2O_3 and SO_3 is normally under 5 per cent.

For the raw mix preparation limestone is used and to a lesser degree marl or clay, or even shale or fly ash. As a rule, a small quantity of the iron-bearing component is also added. Sometimes, a small fraction of sand must be used to regulate the silica ratio. It is not a satisfactory solution because quartz, which is the main sand component, is very hard and remains usually in the coarse fraction and is difficult to burn.

The cement plant is located near the limestone deposit which very often contains, in some deposits, rock of higher clay minerals content called 'marl'. In cases where limestone is rich in calcium carbonate such as silica and alumina bearing components, clay is used which deposits can be found, as a rule, in the proximity of the limestone deposits.

The raw mix composition can be calculated on the basis of the chosen mineralogical composition of clinker. However, to simplify the control of the chemical composition of raw meal and kiln feed, several ratios were introduced. The most important

TABLE 1.1 LSF, S_R and A_R of clinker produced in Germany

1988	Highest value	Mean value	Lowest value
LSF*	101	96	90
S_R	4.2	2.5	1.4
A_R	4.2	2.3	0.6

* German LSF = Lime standard $I = C/2.8 S + 1.1 A + 0.7 F$.

is the lime saturation factor (LSF):

$$\text{LSF} = \frac{\text{CaO}}{2.8 \text{SiO}_2 + 1.2 \text{Al}_2\text{O}_3 + 0.65 \text{Fe}_2\text{O}_3}$$

where CaO , SiO_2 etc. are the oxide contents in the raw mix on the ignition-free basis.

The detailed foundation of LSF is given by Lea [1].

Other ratios are as follows:

$$\text{Silica ratio: } S_R = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$

$$\text{Alumina ratio: } A_R = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$$

For A_R lower than 0.64 the clinker does not contain the C_3A phase but only C_4AF and C_2F . The content of the latter increases with the lowering of A_R .

In Table 1.1 the ratios occurring in the German cement industry are shown [2].

1.3 Raw material crushing

There have been no major changes in the technology of primary crushing of raw materials in recent years. As a rule, mainly the single- and twin-rotor hammer crushers and impact crushers are used for the primary size reduction. Jaw crushers, also in combination with roll crushers and gyratory crushers, are applied, especially for hard as well as for softer materials. For the latter, a crushing department equipped with roll crushers, arranged in two stages, is frequently used.

The most recent improvements in the construction of hammer and impact crushers consist in increasing the maximum feed size and raising the

maximum feed moisture content of the raw material. For the latest construction of the twin-rotor hammer crusher, the permissible feed moisture content has been doubled from 10 to 20 per cent and the mass of the individual lumps of feed material has been increased to about 7 tonnes [3]. Simultaneously, the crusher itself has a lower weight and for a unit of throughput of 1100 t/h the mass is about 160 t.

In the limestone quarry, very often a mobile installation is used which provides the most economical solution. Orenstein and Koppel have furnished the mobile crusher with a very high capacity, namely 4500 t/h [3]. Depending on the terrain conditions and the required mobility, these crushers can travel with the aid of a hydraulically powered walking mechanism or can be mounted on rubber tyres or rails. The development of mobile crushing installations have been associated with a drastic weight reduction of the crusher which has become lighter by 30 per cent and more [3].

1.4. Raw material grinding

For wet and dry grinding of the raw materials, ball mills are used which operate either as open-circuit mills or in closed circuit, in case of the dry process with an air classifier. By wet grinding the process is closed through the vibrating screen or arc-screen. The quick elimination of the fine fraction in closed circuit increases the grinding efficiency by about 20 per cent.

The granulometric composition of the feed greatly influences the energy consumption. To diminish the coarse fraction, the preliminary grinding is applied. For this purpose, Aerofall autogenic mills are installed which can be used for dry or wet grinding. These are one of the methods of modernization of the grinding department.

The energy consumption in ball mills is also heavily influenced by the grinding media filling ratio, by the design of the mill liners and by grinding media classification in the last chamber. For the solution of the grinding media classification the so-called autoclassifying liners are used.

Because of the predominance of the dry method of clinker production, in the dry grinding

technology more new achievements have been introduced. In the first place, the development of roller presses for preliminary grinding has been very often used recently. For grinding installations containing the roller press, a good solution is the application of the so-called V-separator (Figure 1.1) [4,5]. This static separator is extremely well suited for operations in grinding systems equipped with roller presses. This technology has been applied for several years in Hundai Cement Company's Young Wol plant for cement grinding and for raw material grinding. The operation data for raw material grinding are given in Table 1.2.

There are efficient installations using hammer or impact crushers for pregrinding of the material. These solutions are also convenient for raw materials drying. The hot gases from the kiln passing through the crusher transport the material to the classifier, where 70–85 per cent of the crushed material returns to the ball mill, the rest having suitable granulometry joins the product. These installations cannot be used for a very hard material because the short life of elements of the crusher can negatively influence the efficiency of the ball mill.

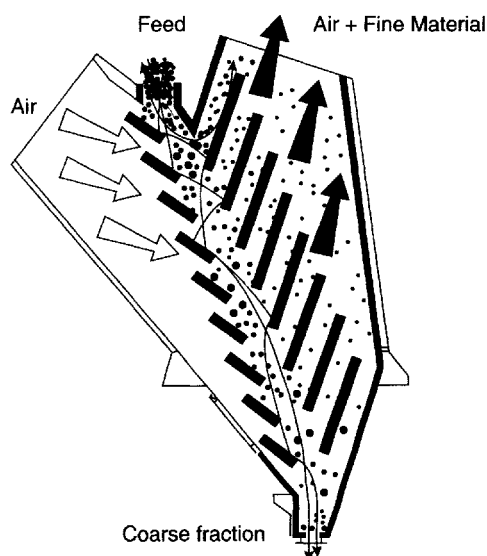


FIGURE 1.1 V-separator-principle scheme [5].

In the last decade, the application of roller mills increased because of the lower energy consumption of about 10 kWh/t in comparison with ball mills. Large quantities of gas conveying the material to the classifier enable drying of the feed up to 20 per cent of humidity.

In the past, there were some problems with the service life of the grinding elements, especially in the case of raw materials containing quartz [6]. In recent years, because of improvements in wear-resistant engineering materials, the service life has been substantially increased and, depending on the abrasiveness of the raw material, values ranging from 6000 to 16,000 h are reported [3].

A special high-drying capacity characterizes Loesche roller mills [7]. These mills can work with a very high gas temperature in the range of 600°C. Practical experience gathered during the exploitation of raw materials and coal grinding can be summarized as follows:

- for dry grinding of coal slurry with more than 30 per cent water content, operation temperatures of 700°C were used;
- for dry grinding of raw materials with 23 per cent water content, the hot gas temperature of 560°C has been used.

Among the various advantages of roller mills, the smaller dimensions and the lower capital cost (by about 10 per cent) in comparison with ball mills are worth mentioning.

TABLE 1.2 Characteristic operation data: raw mill no. 3, Young Wol plant [5]

Operation mode of roller press	Finish grinding	Semi-finish grinding
Production rate tph	175	300
Raw mix fineness		
90 ($\mu\text{m}\%$ R)	15–17	15–17
212 ($\mu\text{m}\%$ R)	2–3	2–3
Specific energy consumption (kWh/t)		
Roller press	9.4	5.9
Ball mill	—	7.0
Separator SKS-L	0.7	0.4
Separator fan	4.6	2.7
Bucket elevators	0.9	1.0
Total	15.6	17.0

The main goal of the grinding process is to ensure the suitable raw-meal granulometric composition, which usually corresponds to the residue of 1 per cent on 200 μm sieve and 12 per cent on 90 μm sieve. The large influence on raw-meal burnability is exerted by the coarse grains of quartz. Fundal [8] found that each per cent of silica grains larger than 44 μm increases the free lime content of the clinker by about 0.9 per cent. So the content of quartz greater than 44 μm should be lower than 2 per cent. Also the coarse grains of calcite, larger than 150 μm , should be under 2 per cent. Additionally, the raw-meal moisture must be very low, as a rule below 1 per cent, commonly 0.5–0.8 per cent. The higher moisture content negatively influences the flowing properties of raw meal.

1.5 Classifiers

A classifier exerts significant influence on mill efficiency and consequently on energy consumption. It is well documented by the curves showed in Figure 1.23 [47]. For the product containing 90 per cent of the fraction under 30 μm , the energy consumption of the ball mill is 65 kWh/t when the classifier efficiency is 25 per cent, but falls to 35 kWh/t for 100 per cent classifier efficiency.

Traditionally, two kinds of separators were used: the so-called grit separators and mechanical separators [9]. Air-swept mills are normally equipped with a grit separator and cyclone (Figure 1.2).

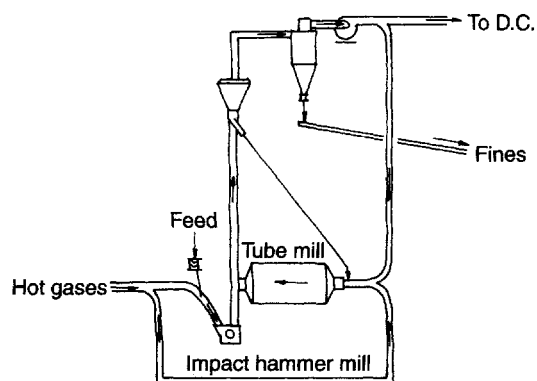


FIGURE 1.2 Scheme of the tandem drying-grinding plant.

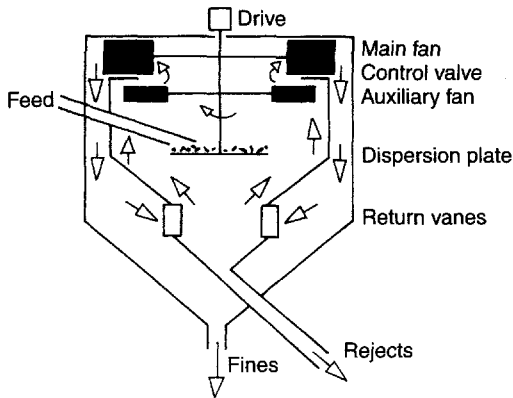


FIGURE 1.3 Scheme of mechanical separator.

Grit separators have no moving parts and the separation effect is due to diminishing of dust-entrained air and its tangential flow induced by guide vanes.

The main part of the mechanical separator is a rotating dispersion plate and two fans: the main fan and auxiliary fan. Coarse particles either fall directly from the dispersion plate or are rejected between the auxiliary fan blades and the control valve (Figure 1.3). The fines fall into the separation volume between two vessels and drop down under inertia forces. The air stream changes the direction forcibly and returns through the vanes and auxiliary fan, forming a closed circuit.

The mechanical separators have low efficiency in fine recovery, which is clearly seen on Tromp curve (Figure 1.4) [10]. To improve this efficiency a new generation of classifiers was introduced in the 1970s. The main part of this classifier is the rotor and tangential vanes (Figure 1.5). They ensure the even air velocity distribution along the full height of the rotor, which is a prerequisite for sharp separation classification. The new classifiers have a very good performance, and in comparison with classic separators produce an almost perfect Tromp curve (Figure 1.4). These separators significantly increase the mill capacity and decrease energy consumption. For example, Burgan [11] stated that the installation of a new classifier O-Sepa increased the cement mill capacity

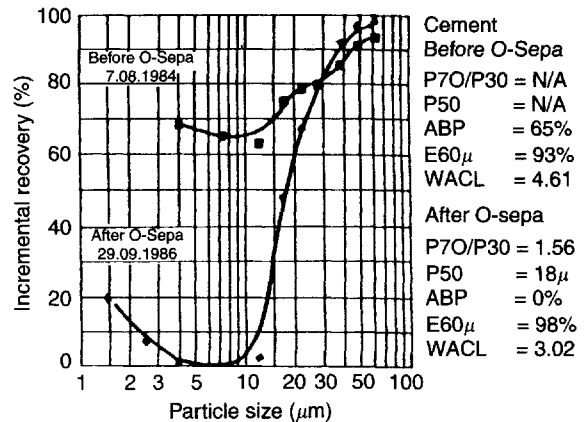


FIGURE 1.4 Tromp curves for classic and O-Sepa classifier [10].

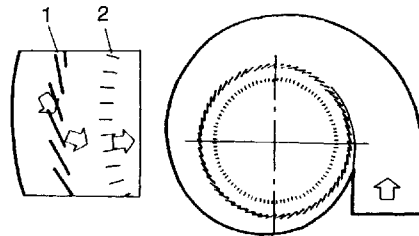


FIGURE 1.5 Principle of new classifier: (1) vertical guide vanes, (2) rotor blade.

by 30–32 per cent and a reduction of energy consumption by 20–30 per cent.

1.6 Homogenization

Raw material homogenization is a very important technological operation because the kiln feed should have a very stable chemical composition. The variations of chemical composition of raw mix influence unfavourably the kiln exploitation and clinker quality. For a stable kiln operation, the LSF factor fluctuations should be lower than one point. Each technological operation should increase the stability of raw materials (Figure 1.6) [12].

When raw materials of a very changeable composition are used, the prehomogenization is a very effective method. However, this technology is expensive with the capital cost being about 10 per cent of total expenditure for a new plant.

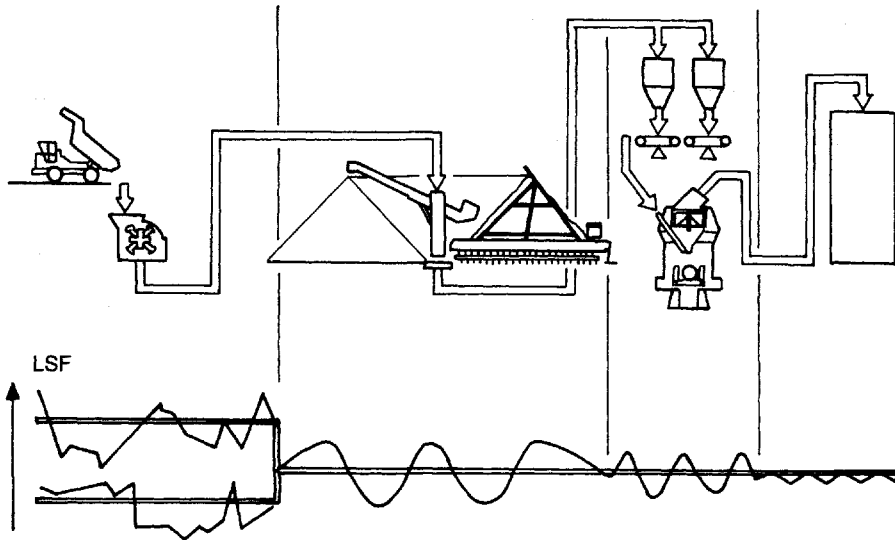


FIGURE 1.6 Homogeneity of raw material [12].

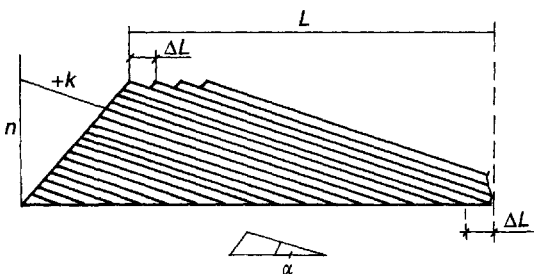


FIGURE 1.7 Chevcon method of stockpiling.

There are two methods of building blending beds: longitudinal or circular. The second is better because it overcomes the so-called 'end-cone problems'. It is difficult to keep the rate of reclaiming constant at the ends of the longitudinal pile and, especially when the reclaimer starts on the stockpile, the homogenizing effect is at first liable to be very unsatisfactory, because there will be a considerable segregation at the time of stacking. To avoid these problems, especially in longitudinal stacking, the so-called chevcon method is applied (Figure 1.7); the throw-off point of the stacker is varied by a radial distance ΔL in the course of each to and from cycle [13].

The effect of homogenization can be calculated using the following equation:

$$H = \frac{S_{\alpha}}{S_{\beta}}$$

where S_{α} is the standard deviation of input variations and S_{β} is the standard deviation of output variations.

For estimating the variations in output, the following equation is frequently used:

$$S_x = \frac{S_{\alpha}}{N^{1/2}}$$

where S_x is the standard deviation of the averages of slices and N is the number of layers.

In practice, there is no reason to use less than 50 or more than 500 layers (Figure 1.8)

Experience shows that with the current bed blending technology, the blending effects of up to 10 are attainable by qualitatively controlled build-up of the blending bed. For monitoring of the operation of blending beds, prompt gamma neutron activation analysis can be used which was elaborated and introduced in the cement industry in the 1980s by Gamma Metrics [14,15]. This method is designated for continuous analysis

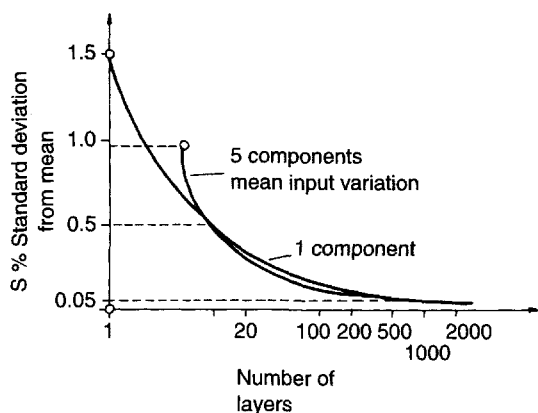


FIGURE 1.8 Blending effect as a function of the number of stacked layers of material.

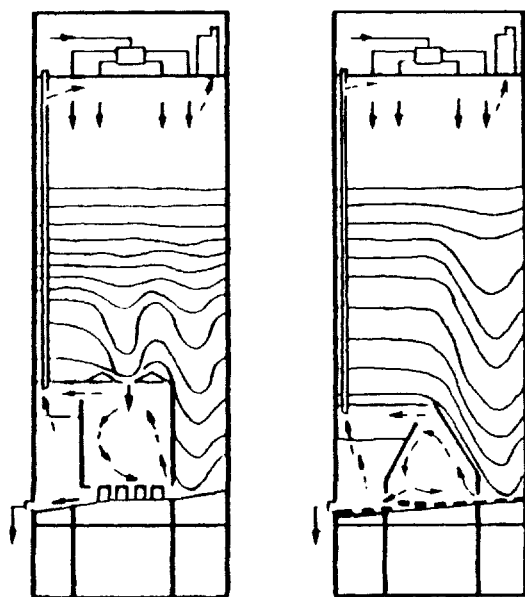


FIGURE 1.9 Two types of continuous homogenizing silos.

of the material stream of grain size up to 100 mm, for example on the belt conveyor.

There are several methods of raw meal homogenization [3]. Significant progress in pneumatic homogenization of raw meal has been made with continuous blending systems.

TABLE 1.3 Comparative data of various homogenizing systems [3]

Blending installation	Homogenization			
	Batchwise	Cascade	Continuous	
			One silo	Two silos
Blending factor	>20	>20	5–7	7–12
Capital cost (%)	180	185	100	115
Specific power, consumption (kWh/t)	0.5–0.7	1.2–1.5	0.2–0.6	0.3–1.0

There are two major types of blending silo designs: turbulence and controlled flow. In a turbulence silo, the material is tumbled about by the injection of high volume air through air-pads on the silo floor. In the controlled flow system, the silo is divided into a large number of flow streams which run parallel at different flow rates, and the meal is finally blended in a tank (Figure 1.9). The fluidizing air aerates only a small part of the silo bottom. It results in low air and power consumption. The homogenizing factor for the CF FL Smidth silo is larger than seven. Modern blending silos are generally of the continuous, controlled flow type. The data for different types of blending silos after Malzig and Thier [3] are presented in Table 1.3.

1.7 Clinker burning

The dry method became predominant in the cement industry because of the much lower heat consumption, a typical value being 3000 kJ/kg of clinker for dry and 5500 kJ/kg for wet method. This heat expenditure for the wet method can be lowered when the water content in a slurry is under 30 per cent and the well chosen chain zone with special lifters ensures a low gas outlet temperature, not higher than 200°C. In such conditions, heat consumption can be as low as 4800–5000 kJ/kg of clinker [16]. The fuel cost can be lowered further by the use of alternative fuels. More details about this problem will be given in the point dealing with the pollution control.

When the moisture of limestone in the deposit is high, for example about 24 per cent for chalk,

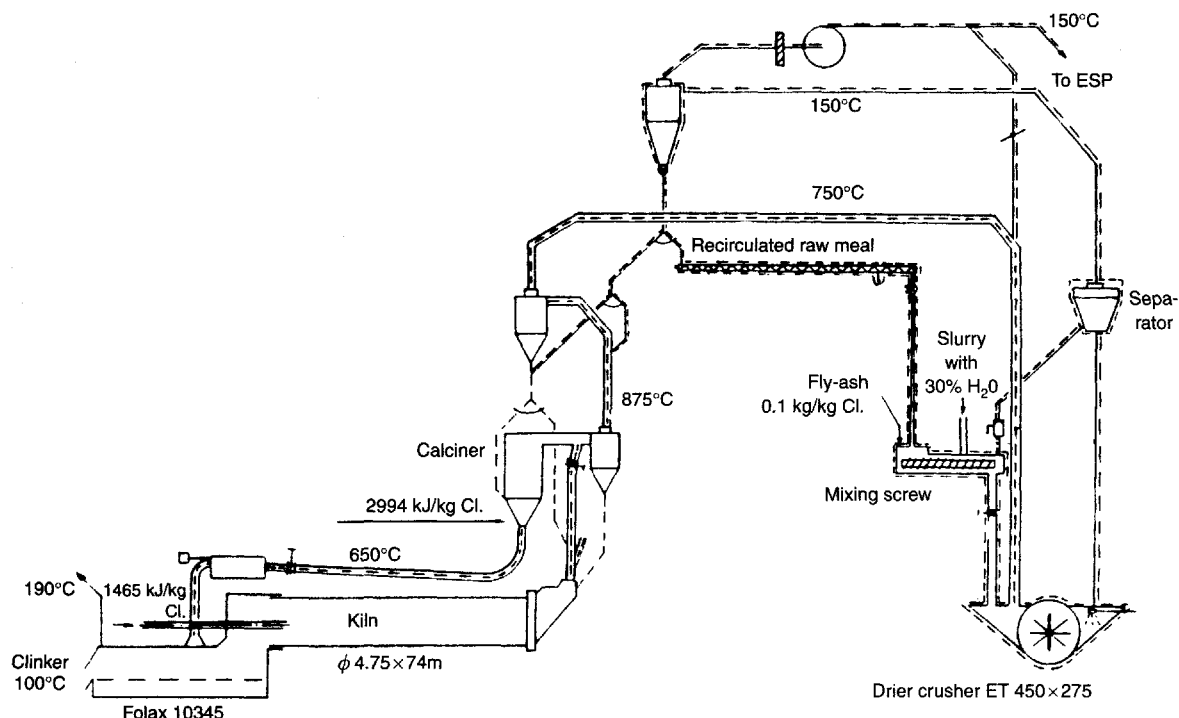


FIGURE 1.10 Flow sheet of kiln and drying departments. Only one of two identical preheater strings is shown [20].

the wet method become competitive with the dry process.

When the high humidity raw material is used, frequently the combined method of clinker production is applied. This technology consists in preparing the raw slurry in the same way as for the wet method, but then the slurry is injected into the drier-crusher and burned in the short kiln with a cyclone preheater [17] (Figure 1.10). The gas temperature is selected for the water content of the slurry through the adoption of appropriate cyclone stages (Figure 1.11). This technology was developed first in the Aalborg plant [17] and introduced successively in the Lagersdorf [18] and Rugby [19] plants. However, in the last two plants the slurry filtration in filter presses is applied and only the filter cake containing around 19 per cent of water is introduced to the drier-crusher.

A very original technology was developed by F. L. Smidth in the Chelm plant in Poland [18] the chalk and marl used in this plant are very homogenous and of stable composition, being

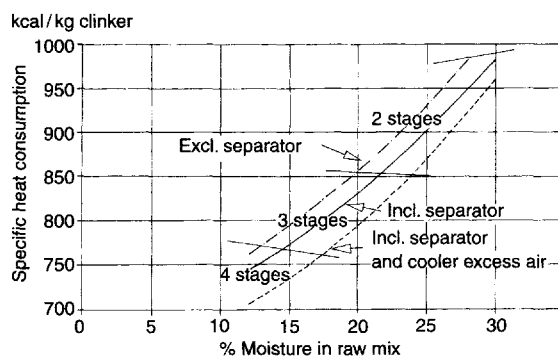


FIGURE 1.11 Drying capacity of compact kiln system with calciner [20].

simultaneously very soft [21]. The raw materials grinding process is totally eliminated and drier-crusher are fed directly by crushed raw materials (Figure 1.12). In this technology the splendid mixing behaviour of the cyclone preheater is utilized. This behaviour was firstly proved in the Rorhbach plant in Dotterhausen where limestone

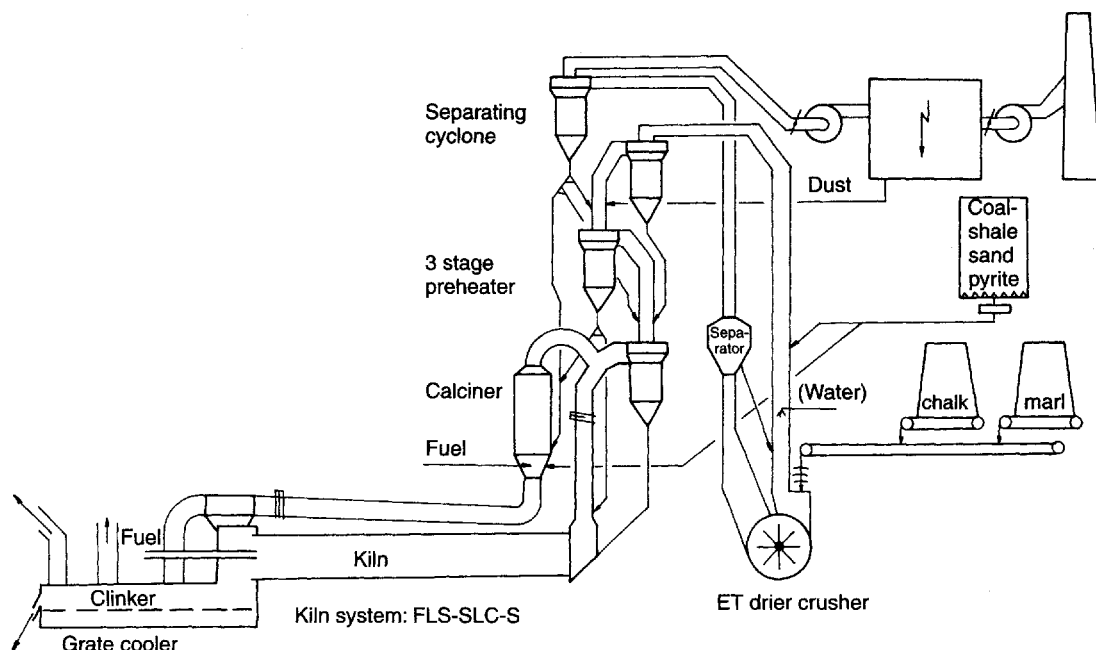


FIGURE 1.12 Semi-dry technology without raw material grinding, Chelm case.

from the preheater was mixed with shale ash in the last preheater stage. Thermal balances of different combined technology are compared in Table 1.4 [20,21,22]

The data in Table 1.4 comprise the heat consumption for the technology of filtration cake burning in the kiln with the Lepol grate preheater. This technology, that is, slurry filtration and cake nodulizing and burning in the Lepol kiln was very popular in France in the 1960s and 1970s, but totally disappeared in the 1980s. However, the dry method with granulation of raw mix and its burning in Lepol kilns does exist in France and the heat consumption is no higher than in the cyclone preheater kiln [23].

The dominating dry technology uses short kilns with cyclone preheaters. The kiln gases temperature is usually about 1100°C and the raw mix temperature about 800°C, with about 35 per cent calcination. The exit gas temperature is about 350°C for a four-stages preheater, but it can be lowered to 250°C for a six-stage preheater. The number of preheater stages is now only the question

TABLE 1.4 Thermal balances of combined methods [20–22]

Amount of heat (kJ/kg)	Semi-dry processes ^a		
	1 ^b	2 ^c	3 ^d
Heat of reaction	1671	1654	1750
Smoke gas loss	419	482	452
Evaporation of water	921	1570	1072
Surface heat loss	507	419	289
Cooler loss	586	419	176
Heat in filter-cake, air and fuel	84	84	–
Net fuel consumption	4020	4460	3739 ^e

^a 1: Filtration, drier-crusher for cake treatment, kiln with two-stage cyclone preheater; 2: drier-crusher feeding with slurry/cake (Aalborg); 3: cake granulated and burnt in kiln grate preheater.

^b Water content in kiln feed 18 per cent.

^c Water content in kiln feed 16 per cent.

^d Water content in kiln feed 21.7 per cent.

^e Total heat consumption [20].

of moisture content of the raw materials, because the gases from the kiln are used for raw meal drying. To avoid the necessity of an additional furnace for the raw mill, as a rule the four stages preheater is adopted, which ensures raw material drying of about 6 per cent humidity. In the past, the four-stage preheater was the most economical because of a high pressure drop in the cyclones. Now, new constructions of cyclones (Figure 1.13) give a lower pressure drop for six stages than before for four [24]. Simultaneously, the separation efficiency of these cyclones is also higher. The examples of typical heat balances of dry kilns are given in Table 1.5.

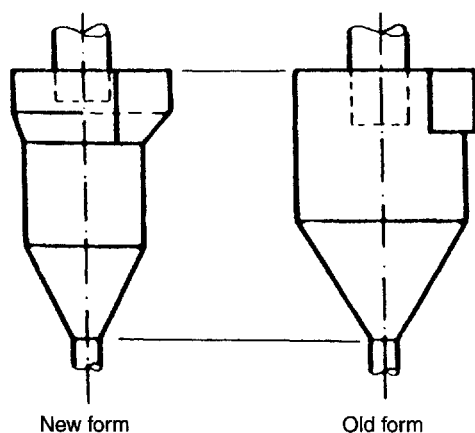


FIGURE 1.13 Comparison of new FLS cyclone with the old form.

A great development of dry kilns was the introduction of precalcination in the 1970s. This technology results in an important increase of kiln throughput by a factor of about 2.5. Two types of precalcining technology are used; with partial and with total calcination. In the first one the air for fuel combustion in the precalciner is introduced through the kiln, increasing the coefficient of air excess, and in the other a special pipe for tertiary air must be installed (Figure 1.14). To facilitate the correct choice of precalcining technology one can consult some relations found by Herchenbach [26] and presented in Figure 1.15.

The degree of calcination in the precalciner is not higher than 90–95 per cent. The unfinished calcining process constitutes a very convenient regulator preventing an excessive increase of the temperature in the precalciner. This protects against a too high temperature for the exit gases from the precalciner, and thereby, against the increase of the heat loss with the exit gases. At the same time, it protects from the possibility of a clinkering process starting in the calciner and leading to the formation of build-ups in the precalciner, which can block the inlet of the gases supplied from the kiln.

The combustion of the fuel in the precalciner is carried out flamelessly and the heat exchange, which is very intensive, takes place with 90 per cent by convection. These favourable conditions of heat exchange are the reason for a very short

TABLE 1.5 Heat balances of dry kilns with oil or coal fired calciners in kJ/kg of clinker [16,20,25]

Kiln size (m)	—	5.4 × 85	4.75 × 85 ^a	Last construction ^b
Preheater type	PASEC	RSP	FLS	FLS
Kiln output tpd	2440	3850	4200	—
Spec. cap. (t/m ³ × 24 h)	—	1.98	3.82	up to 5
Heat of clinkering	1792	1696	1796	1680
Dust in exit gases	—	38	40	—
Evaporation of water	12	29	12	— ^c
Exit gas	395 ^d	812	608	609
Cooler vent air	549 ^e	243	472	417
Clinker leaving, cooler	—	75	74	66
Radiation loss	212	210	216	273
Total	2960	3103	3218	3045

^a Oil firing; ^b 6 stage preheater, calciner, modern grate cooler; ^c in exit gas losses; ^d 5 stage preheater; ^e total losses of cooler and clinker.

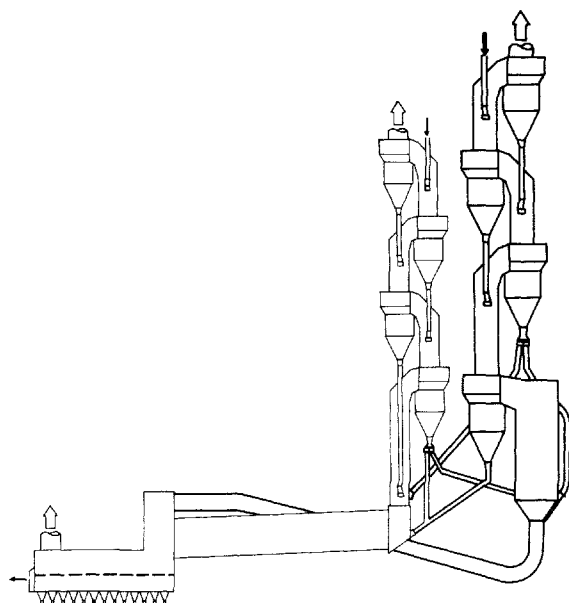


FIGURE 1.14 Conversion of SP kiln to an SLC system by FLS at Adelaide Brighton, Australia, the increase of production from 1800 to 4100 tpd [20].

time of calcination which is controlled by the rate of the chemical reactions.

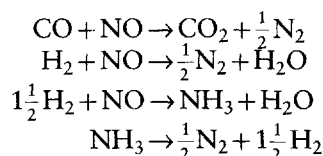
The latest achievement in burning technology is constituted by very short kilns with L/D ratio of about 10 [27–29]. These kilns ensure a very rapid clinker formation, which gives a very quick reactions run without recrystallization phenomena and, as a result, a higher hydraulic activity of the clinker is obtained.

These kilns are characterized by two supports, selfadjusting roller suspensions, a tangential tyre suspension system (Figure 1.16) and a kiln drive via supporting rollers. FL Smidth also introduced a new sealing system of kiln inlet and outlet ends, a so-called double-lamella seal, which allows a higher degree of vibration at the kiln ends. The volumetric load of these kilns is of the order of $5 \text{ t/m}^3 \times 24 \text{ h}$. FL Smidth mention further important advantages of these kilns, namely, the kiln alignment is not affected by foundation settlement [29]; also, the kiln shell ovality remains very low and the risk of kiln shell constriction is eliminated.

High volumetric loading of these kilns causes the drop in heat consumption due to a reduction of the heat losses from radiation from the kiln shell and preheater, but the main problem remains the heat losses with the exit gases.

The construction of precalciners also underwent a substantial development, especially in the view of limiting pollution problems. First of all, combustion of the fuel must be very good with very low CO level in the exit gases. For this aim, the retention time of fuel in the precalciner is increased through the elongation of this furnace. It found its expression in a large volume of calciners which operate with a volume rating of $7 \pm 2 \text{ t of clinker/m}^3 \times \text{day}$ which corresponds to the gas retention time of 2–3 s and a meal retention time of 6–12 s [30].

The lowering of NO_x emission is another important feature. For this aim, two zones in the calciner are created: a reducing zone in the lower part, and an oxidation zone in the upper part of the precalciner [30–32]. In the first zone, the following reactions occur:



These reactions are favoured by a high temperature and catalysed by the raw meal.

In the upper part, the remaining CO is oxidized to CO_2 , but because of the low temperature in the precalciner no additional oxidation of nitrogen will take place.

A very interesting example of a low CO and NO_x calciner is the ILC low- NO_x calciner of FL Smidth [31]. In the inlet of the calciner, the reduction zone is created where coal is introduced and the only oxygen available is the amount present in the rotary kiln gases. This favours NO_x reduction, according to the previously mentioned reactions. The high temperature that improves the efficiency of the first reaction is provided by splitting the raw meal between the oxidizing zone and the reduction zone. The temperature is controlled to $925\text{--}1050^\circ\text{C}$, or as high as possible without getting any encrustations in the kiln riser

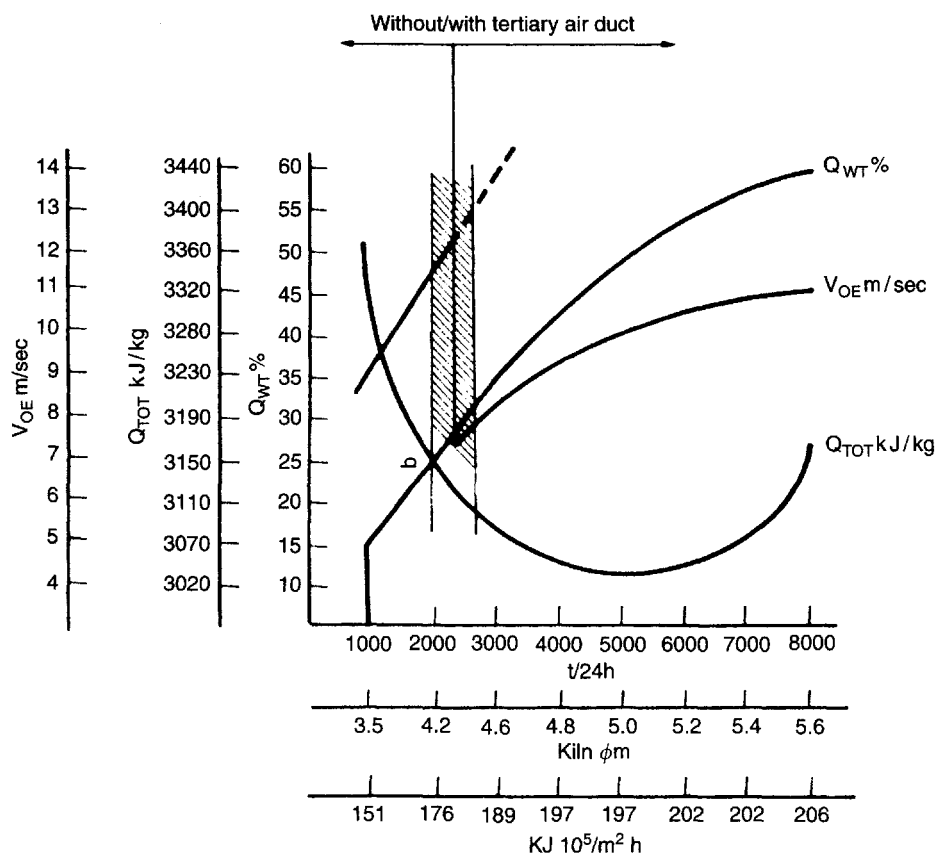


FIGURE 1.15 Relation between clinker production, kiln diameter, heat input in preheater, burning zone rating, gas velocity in kiln inlet and tertiary air control [26].

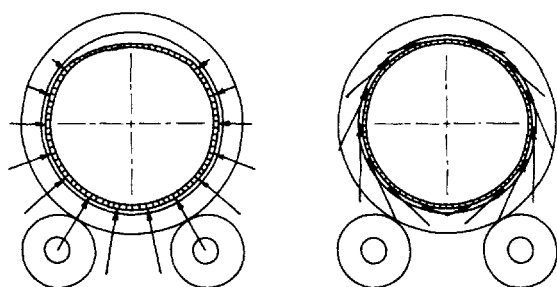


FIGURE 1.16 Plan view of FLS tangential tyre suspension system [29].

duct and reduction zone. Typically, 15–30 per cent of the raw meal should be fed to the reduction zone inlet (Figure 1.17). It is very important to assure the strongest possible reducing conditions

in order to favour the reactions of NO_x decomposition. In the ILC low- NO_x calciner, all the fuel is introduced to this zone before the tertiary air. The result of joint effects of all the decomposition reactions is the removal of approximately 70 per cent of the rotary kiln NO_x . The restriction in the middle of the calciner and the bend in the top are applied in order to improve the mixing, thus minimizing the CO emission and at the same time improving the fuel burnout. Even though after the reduction zone more than 3 per cent CO is in the gas, the concentration of the CO in the calciner exit gas will only be around 100–200 ppm, due to these facilities.

A very similar principle was adopted in the Pyrotop calciner of KHD Humboldt [30] (Figure 1.18). The kiln exit gases and tertiary air are

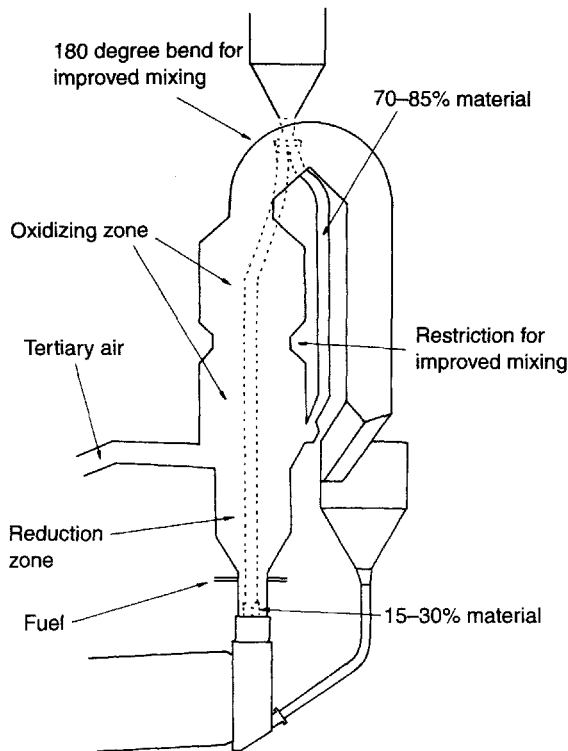


FIGURE 1.17 ILC low- NO_x calciner of FLS [31].

introduced into the calciner at an acute angle, which results in the slow mixing of the two flows. The fuel is burnt at two different locations and also the meal is admitted at two different points. The calciner is equipped with a new reaction chamber mounted at the location of the 180° elbow. It ensures a reliable mixing of the flow portions originating from the kiln waste-gas duct and from the tertiary air duct. Furthermore, a portion of the meal is discharged from the chamber and may either be recycled, that is, be routed back to the ascending calciner section, or directed to the calciner section running downward. A repeated deflection of gas/meal flow especially achieves an intensive mixing and thereby enhances combustion. The turbulent flow at the calciner outlet is a decisive prerequisite for good burning out of the fuel [30].

The construction of burners also underwent substantial changes and instead of very simple

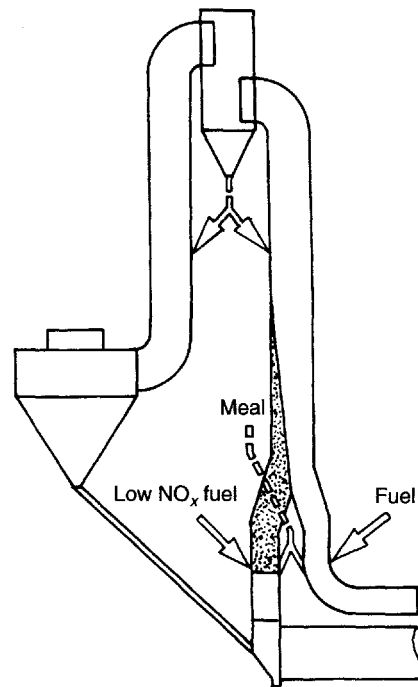


FIGURE 1.18 Pyrotop calciner of KHD Humboldt [30].

burners, the multi-channel burners were introduced [32–34]. Pillard was among the first people to develop this type of burner, which was adopted for a simultaneous use of several fuels [34]. The new constructions eliminate a very low fuel/air ratio, which was typical for old coal burners, and result in the higher combustion efficiency and a greater possibility for flame regulation. The volume and the shape of the flame may be changed by adjusting the ratio between the radial and axial air amount and velocity by adjusting the burner nozzle areas (Figure 1.19). Special constructions which diminish a NO_x formation in the flame, have been very popular recently [35].

1.8 Coolers

Clinker cooling is very important for heat consumption in the kiln and for cement quality. This process is conducted in the coolers. There are three types of coolers which are generally used: rotary coolers, planetary coolers and grate coolers (Table 1.6).

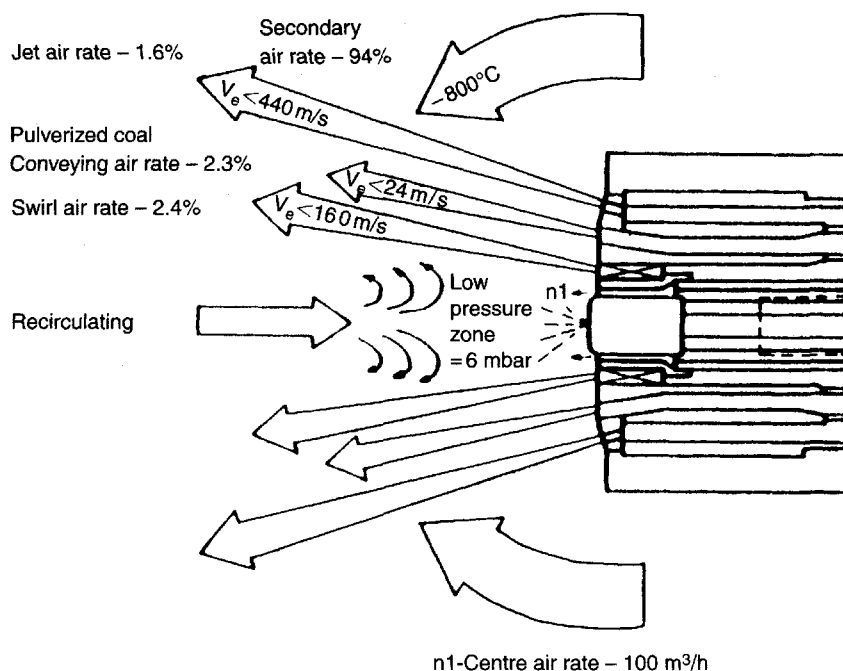


FIGURE 1.19 Multi-channel burner.

TABLE 1.6 Data of clinker coolers for dry kilns [40–43]

Cooler type	Rotary	Satellite ^a	Grate		
			SF	Coolax	Combined
Capacity (tpd)	up to 4500	up to 5000	Up to 5000	Up to 10,000	Up to 10,000
Power consumption (kWh/t)	4	2.5	5	7	6
Load/m ² × d	150 ^b	2 ^c	< 50	< 60	50
Clinker (°C)	160–210	120–200	65 ^e	65 ^e	80–110
Cooling air (nm ³ /kg)	0.85	0.85	1.78	1.97	2.0–2.2
Second air (°C)	800–870	700–750	1040	1000	840–900
Exit air (°C)	—	—	290	280	240–280
Exit air (nm ³ /kg)	—	—	0.97	1.13	1.1–1.3
Heat expenditure (kJ/kg)					
Secondary air	1006	922	1285 ^f	1246 ^f	1006
Clinker	168	126	66	66	67
Radiation	210	293	25	25	25
Exit air	—	—	368	423	377
Water chute	25	— ^d	—	—	—
Thermal efficiency	71	69	75	71	70

^a FLS Unax-cooler.^b Cross-sectional rating, inclination 4.5–5 per cent.^c Specific area rating.^d In hot climatic conditions, about 20 kJ/kg of clinker.^e Above ambient temperature.^f With tertiary air.

Grate coolers are most common because they ensure the lowest clinker temperature and highest kiln capacity [16,36]. Planetary coolers take second place – they are mounted on the kiln, and the air for cooling is provided by the kiln fan. Rotary coolers are seldom used. The superiority of grate coolers is finally caused by the convenience of tertiary air supply to the calciner.

The efficiency of rotary and planetary coolers is closely connected with the heat transfer, which is enhanced through a geometric configuration of the cooler and arrangement of internal fittings. A special system of elbows and different lifters, both for planetary and rotary coolers, has been developed by Magotteaux and Estanda [37,38].

Planetary and rotary coolers have a limited airflow, usually $0.85\text{--}0.95\text{ nm}^3/\text{kg}$ of clinker, depending on the fuel consumption of the kiln and regulated by the kiln ID fan. For these reasons, the clinker temperature exceeds 150°C and water injection is applied. On the contrary, the quantity of air in grate coolers, which is supplied by special fans, is much higher, up to $2.5\text{ nm}^3/\text{kg}$ of clinker and the clinker temperature is low, usually $50^\circ\text{C} +$ ambient temperature. However, the well-known problems with exit air must be resolved. The best solution is to use the exit air for drying raw materials, slag and coal. In some cases electrical energy is produced [39]. For dedusting of exit air, the electrofilter or gravel bed filter is used.

To diminish the quantity of cooling air different, variants of air recirculation have been employed and the exit air of low temperature, that is, 250°C , is reintroduced to the hot part of the cooler [39].

The grate cooler is frequently equipped with the roll crusher, which can work at a high temperature [41]. It is very important because the clinker cooling rate depends strongly on the grain size of this material.

The grate coolers regularly underwent developments in construction. The construction of the plates, and air supply directly to the plates in the so-called air-beam technology (Figure 1.20) have been recent achievements. The new plates have narrow air outlet slots, which ensure a sharp air

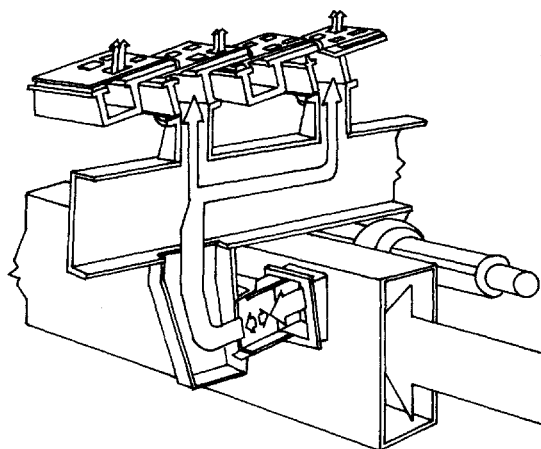


FIGURE 1.20 Aeration system for directly aerated troughed plates [41].

jet of about 40 m/s in the direction of clinker transport.

This solution permits the specific loading of the cooler to be raised, even the level to $100\text{ t/m}^2 \times \text{d}$ has been tested [41].

The Coolax of F. L. Smidth [40] is an example of a new cooler. In the heat recuperation zone, cooling air is supplied directly to the grate plates through a system of ducts and hollow beams instead of via an undergrate compartment as in conventional coolers. This system also eliminates the so-called ‘red river’ phenomena in the cooler. The principal Coolax features are:

- fuel savings of $130\text{--}170\text{ kJ/kg}$ of clinker;
- 30 per cent less cooling air and 40 per cent less air to be dedusted;
- smaller overall dimensions due to the high specific grate load-up to $60\text{ t/m}^2 \times 24\text{ h}$.

A very original construction was developed by Smidth and Fuller [42,44]. It is a so-called SF Cross-Bar Cooler in which the cooling process is separated from the conveying action. A large drag chain pulls the clinker over a stationary bed through which cooling air is blown. Each grate plate is equipped with a rectangular tower containing a weighed mechanical flow regulator, which acts as a barometric damper in a chimney (Figure 1.21). All these solutions enable a decrease of the cooling air

input to only $1.5\text{--}1.7\text{ nm}^3/\text{kg}$ of clinker. The heat losses are also diminished to 400 kJ/kg of clinker.

Environmental protection regulations limiting dust emission have led to developments in construction of the second degree coolers working in conjunction with a short grate cooler [45]. The latter supplies hot air to the kiln, and the clinker at approximately 500°C , after being crushed in a breaker, is fed to a static membrane g-cooler (Figure 1.22). In this cooler the clinker, descending slowly at the speed of $2\text{--}3\text{ cm/min}$, is cooled

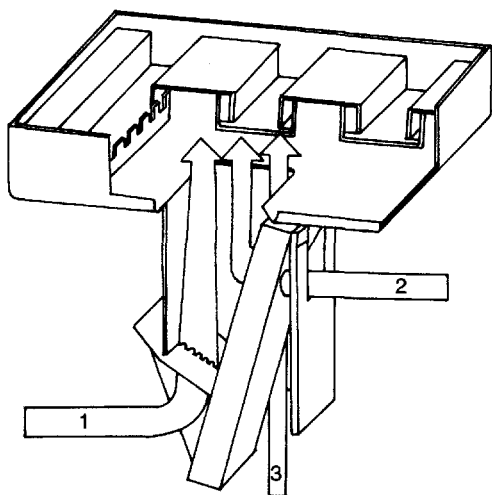


FIGURE 1.21 Aerating system for plates in SF Cross-Bar Cooler [42]. (1) air flow through holes in tongue; (2) air flow through idle hole; (3) air flow through gaps.

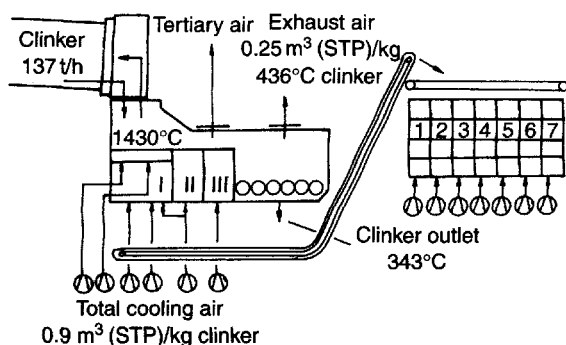


FIGURE 1.22 Short grate cooler used in combination with a gravitation cooler [45].

down to 100°C , heating the air flowing in the tubes up to $60\text{--}100^\circ\text{C}$. The specific capacity of this cooler amounts to $10\text{ t/m}^3 \times 24\text{ h}$. The specific power demand of the static cooler is about 1.2 kWh/t of clinker and of the whole installation is about 5 kWh/t . The g-cooler has been applied at the Robilante plant [46], for example.

1.9 Cement grinding

For cement grinding, ball mills are more frequently used. They have a rather high-energy consumption, typically 34 kWh/t for cement having a specific surface of $300\text{ m}^2/\text{kg}$. For good operational results, the level of ventilation, typically $0.3\text{--}0.5\text{ nm}^3/\text{kg}$ clinker and volumetric charge loading which is $25\text{--}30$ per cent for the first and $26\text{--}28$ per cent for the second compartment, are very important. The modern mills are two chamber mills with lifting liners in the first and classifying liners in the second compartment. The diaphragms play also a very important role. The new construction of Slegten-Magotteaux or Combidan of F. L. Smidth provide a good ratio of the mass of material to the mass of the balls and thus improve the effectiveness of grinding [43].

Much better results are achieved by the mills working in closed circuits which have lower energy consumption and higher capacity of 20 per cent in comparison with the same mill working in an open circuit. The efficiency of classifiers is also important. This is presented in Figure 1.23 [47].

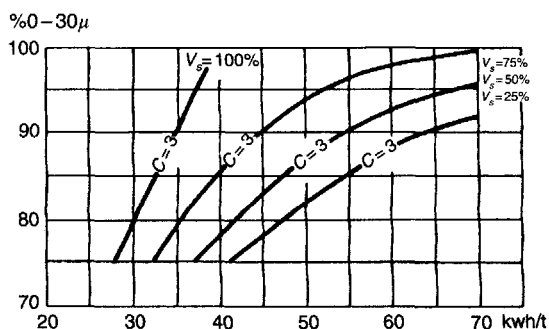


FIGURE 1.23 Influence of classifier performance on mill power consumption [47].

Ball mills have low efficiency, the majority of energy being transformed into heat. Significant progress in grinding technology has been due to the application of roller press for pregrinding or finish grinding [48]. The material between the rolls is submitted to a very high pressure ranging from 100 to 200 MPa. During the grinding process, partial breakdown of the grains occurs and there is a partial formation of incipient cracks in the interior of the grains. The material leaves the press in the form of agglomerates. When the roller press works in the closed circuit for finish grinding, a disintegrator must be used or a special separator must be installed to deglomerate the product. Frequently the roller press is applied for pregrinding with the ball mill as a second stage, thus the rise in capacity is of 30–60 per cent and 15–25 per cent for economy of energy [49]. Patzelt [49] gives, as an example, the installation of the roller press (dimensions 1.7×0.63 m) with a motor 2×575 kW which raised the raw mill throughput from 190 to 280 t/h that is, by about 47 per cent.

Regardless of the fact that special hard materials are used for the lining of the rollers, the shortcoming of this technology is relatively low reliability. It is due to the fact that the rollers are operating at a very high pressure. The maximum local pressures are near 350 MPa for clinker grinding [50]. It was the main reason for further development in the construction of special mills, and horizontal roller mills were produced. The so-called Horo-mill (Figure 1.24) was the first with a grinding pressure evidently lower, that is, 40–70 MPa. These mills are working in several cement plants in Europe, Turkey and Mexico [51,52], having a capacity up to 100 tph. The energy consumption of the mill alone is about 16 kWh/t. Another horizontal mill, the so-called Cemax, was developed by F. L. Smidth [53]. The Cemax grinds the material by compressing it between a ring and a roller. The energy consumption of the installation is about 25 kWh/t and is similar, both in the Horo-mill and in the Cemax.

The quality of cement from the Horo-mill, Cemax and roller press is also quite similar and

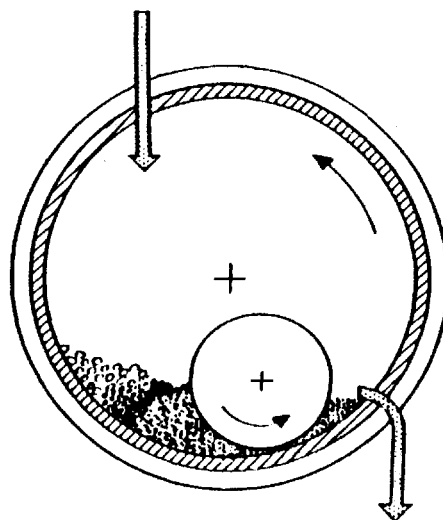


FIGURE 1.24 Principle of the Horo-mill.

comparable to the product of ball mills. A little higher water demand for the product of the roller press is noted.

Experience with roller mills used for cement grinding grows constantly. Ten years' experience in exploitation of a Pfeiffer roller mill in the Teutonia Zementwerk AG near Hanover has proved that these mills can be used for cement grinding [54]. The slag cement can be ground without preliminary slag drying. A specific power consumption by the grinding plant in the range 21–33 kWh/t can be attained. Thus the economy in energy, in comparison with ball mills, is between 25 and 45 per cent.

At the end of the 1970s, Loesche [55,56] started to develop new technologies in vertical roller mills, the so called 2+2 and 3+3 technology, which were applied with great success for cement and slag grinding. The main difference between the 2+2 mills and the conventional four-roller-mills for raw material grinding is that two differently sized pairs of rollers are used (Figure 1.25). The so-called s-rollers are used to prepare the material bed on the grinding table. These s-rollers are of light design and have a smaller diameter compared to the large grinding rollers, the so-called m-rollers. By means of

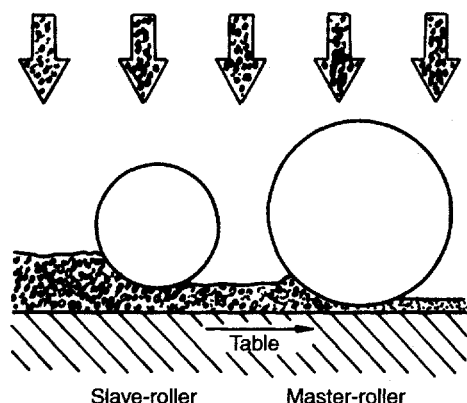


FIGURE 1.25 Diagrammatic representation of grinding bed preparation [55].

hydraulic attachments the small, light s-rollers are positioned at a certain height above the grinding table, where they slightly consolidate and deaerate the material bed.

After this preparation the material is properly nipped under the large and heavy grinding rollers of conventional design. The forces required for comminution underneath the m-rollers are created by means of hydraulic cylinders attached to the rocker arms of the m-rollers. All m-rollers are supported on individual stands, which are relocated on the mill foundation.

Furthermore, individual hydropneumatic spring systems for each roller provide a very smooth and almost vibration-free operation for the mill. The 2+2 system is available for capacities of up to 170tph OPC. In case of higher throughput the 3+3 system is used. Service lives of the roller shells, without any intermediate reworking, of more than 8000 h, have been achieved in cement mills in Japan and Korea and up to 15,000 h have been achieved for grinding track plates. The specific energy consumption for a complete cement grinding plant shown on Figure 1.26 is between 26 and 29 kWh/t for a finished product fineness, corresponding to Blaine's value of $3,300 \text{ cm}^2/\text{g}$. The comparison of energy consumption for grinding slag in a ball mill and Loesche mill is given in Table 1.7.

There is the Hon Chon of the Morning Star Co. cement plant in Vietnam, in which only roller mills are used and no ball mill is installed [57].

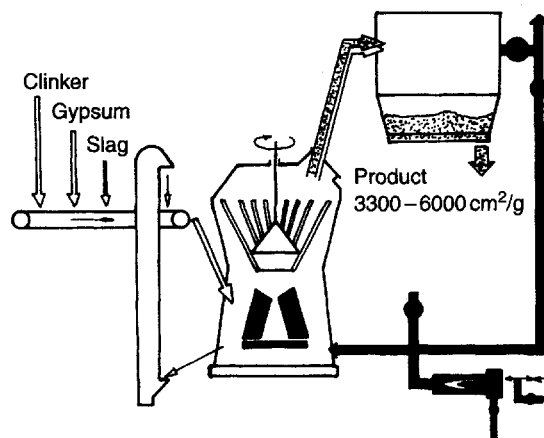


FIGURE 1.26 Cement grinding plant with roller mills [55].

TABLE 1.7 Power consumption for grinding of 60tph blast furnace slag with $4300 \text{ cm}^2/\text{g}$ [55]

	<i>Ball mill</i>	<i>Loesche mill</i>
Mill (kW)	4400	1560
Separator (kW)	100	70
Fan (kW)	180	550
Total (kW)	4680	2180
Specific consumption (kWh/t)	78.7	36.3

1.10 Automation

The process technology and mechanical equipment for cement production has become increasingly complex in recent years. Product quality and diversity, environmental protection, secondary fuels, and energy management require more sensitive plant management. These are the main reasons for the introduction of computers for process control and for information systems.

The classical structure of the process control and information systems is distinguished by a relatively clear pyramid hierarchy (Figure 1.27) [58]. There is a constant increase in information density which affects every level in the computer integrated manufacture pyramid. Hardware and software with appropriate functions are installed at different levels of the computer integrated manufacture pyramid and linked with one another

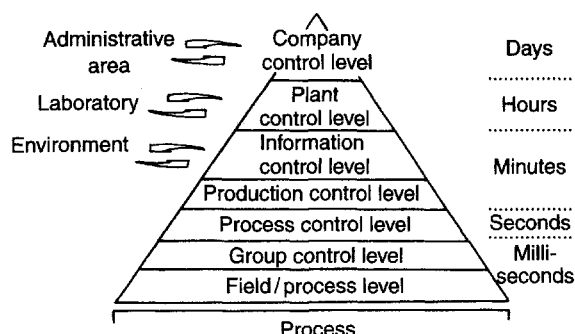


FIGURE 1.27 Structure of the process control and information systems (CIM pyramid) [58].

through communication buses to an integral process control and information system [58].

Nowadays, process control and information systems are not just a means of operating production plants; they are integrated parts of the plant and are essential for efficient, low-cost manufacture of quality products and for effective plant control and monitoring.

Many well-functioning computer-based systems for supervision, dialog and reporting have been introduced by different cement equipment producers as well as cement producers. Among others the HLC of Holderbank [59], TOPEXPERT of Ciments Français [60], SDR of FL Smidth [61], PRODUX of KHD and POLCID of Krupp-Polysius are the most popular ones [58].

The task of the higher-ranking process computer is to determine control inputs for the process and make them available for process control, to provide long-term storage of the process data and put them out as listings or diagrams, and also to make possible the dialogue between the operating personnel and decentralized processors with maximum convenience [62].

For many years, the automation concepts for raw meal preparation have been successfully introduced into cement manufacture. It was a very important step towards achieving a uniform kiln operation. But the problem of identifying a suitable microprocessor, based on the supervisory kiln control technique, took longer to resolve. Therefore, several methods were developed which were based on modelling of the operator actions

[62–64]. Basically, the technique involves expressing ill-defined or ‘fuzzy’ operator actions or commands in terms of precise mathematical logic. The fuzzy logic kiln control was applied to hundreds of kilns and the result fully proved its usefulness for automatic control of the burning process [65–67]. The introduction of automatic control of kilns saves thermal energy by 3 per cent, electrical energy by 2 per cent, results in production increase by 5 per cent, consumption of refractory lining diminution by 6–10 per cent and variance of clinker quality diminution of 4 per cent [60]. In case of mills the production increase is of up to 10 per cent, the decrease of energy consumption is 7 per cent, and, simultaneously, the quality variations are eliminated.

The actual breakthrough in the automation of rotary kilns and also the mills appeared with the introduction of new heuristic control methods, such as fuzzy logic, rule-based logic and online expert systems, coupled with the availability of powerful computers. In Europe alone there are now more than six suppliers of expert systems for cement kilns and ball mills [53].

In the last twenty years, new and very important measurement techniques were introduced. Perhaps the adoption of NO_x measurements to follow the temperature level in the sintering zone is most important [68]. Another very important tool in cement kiln control is the automatic supervision of protective coating thickness and hot spots on the kiln surface through kiln shell temperature measurements by the infrared technique. Several solutions of this problem are proposed by cement equipment producers [69]. Also the laser technique for cement fineness control or free lime control in clinker, which was introduced by Lafarge, is worthy of mention.

Laboratory automation has also become extremely important recently. Its particular function is to ensure that the data from raw materials and the products relevant to quality are continuously available to ensure a quality-driven process control. Full automation of laboratory functions is supplied by different producers. As an example, the Polysius system POLAB 3 can be mentioned which uses modular technology and includes two

completely separate sample preparation lines with five robots, including even the automatic fusion equipment [70]. The entire system normally comprises a representative sampling system, a plant for rapid sample transport, a sample processing system and analysis technology suited to the special features of the material samples, and reliable open- and closed-loop control equipment for ensuring and monitoring the quality [71].

For the raw materials, chemical composition control, very great progress can be achieved through prompt gamma neutron activation analysis [14,15] which was mentioned in point 3.

1.11 Environmental protection

The manufacture of cement necessarily involves interference with the environment, although the cement industry is doing its best to minimize the negative effects of this. The problem comprises the water discharge, solid waste, noise and air pollution. Water discharge should not be a concern beyond handling normal domestic waste and storm water run-off with its potential for leaching from stockpiles and spillage. Solid waste practically concerns kiln bricks. When chromium bricks are eliminated, the alumina bricks can be added to the raw material and magnesium bricks sent to the landfill. Air pollution has been the main problem for the cement industry and will be discussed in more detail.

For twenty years, a significant progress has been made within the cement industry in the field of air pollution protection. The dust emission problem is now practically solved and the new construction of electrostatic precipitators and fabric filters, operating with a compressed air (reverse-pulse) cleaning system [72], have ensured a very low emission level, typically under 50 mg/nm^3 of gases. However, for good electrostatic precipitator efficiency, the dew point of the gases is very important and for the dry method is always too low. It affects negatively the dust resistivity (Figure 1.28) Thus the conditioning towers in the gas circuit are installed and are in operation when the grinding/drying unit is not working.

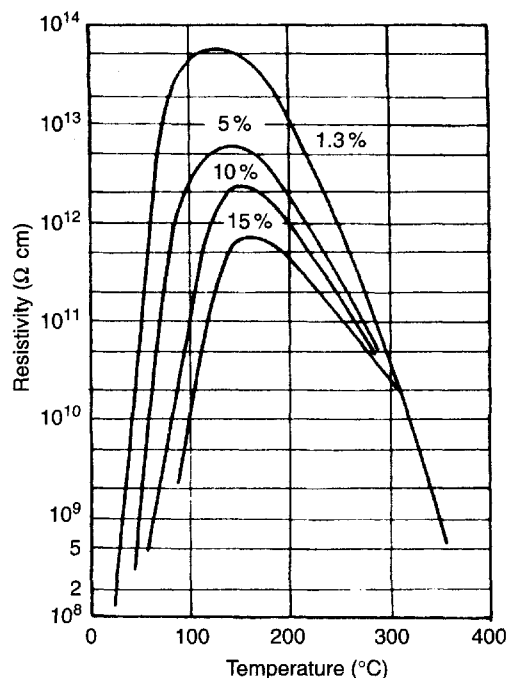


FIGURE 1.28 Resistivity of kiln dust as a function of temperature for different moisture levels of kiln gases (1.3, 5, 10 and 15 per cent).

Electrostatic precipitators underwent substantial modernization in 1990s and all modifications are reviewed in Peterson's paper [73]. Maybe the most important is the pulse energization system. By superimposing short-duration high voltage pulses on DC voltage, the charging of particles as well as the collecting efficiency of the precipitator are improved. The improvement factor of the precipitator performance is defined as a ratio between the dust migration velocity value w_k for pulse and for DC energization ascertained when both are adjusted to the optimum performance [74].

The w_k concept is useful since the required precipitator volume is inversely proportional to this value (Figure 1.29). Precipitator efficiency and the w_k migration velocity can be determined from the inlet and outlet dust concentration and gas volume flow rate:

$$w_k = \frac{Q}{A} \left\{ \ln \frac{100}{100 - \eta} \right\}^{1/k},$$

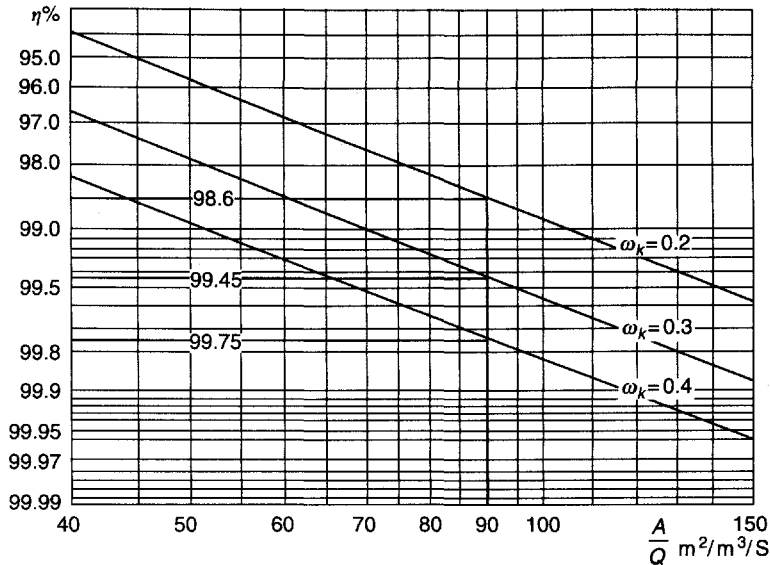


FIGURE 1.29 Electrofilter efficiency as a function of A/Q for three different values of w_k .

where w_k = particle migration velocity, m/s; Q = actual gas volume flow rate, m^3/s ; A = total collecting area, m^2 ; k = constant (0.5); η = collecting efficiency, %.

The efficiency as a function of A/Q is shown for three different values of w_k in Figure 1.28.

In pulse energization the discharge current can be regulated independently of the precipitator voltage by variation of the pulse repetition frequency and the pulse height (Figure 1.30). This makes it possible to reduce the discharge current to the threshold limit for the back corona with high resistivity dust without reducing the precipitator voltage.

The gaseous emission comprises NO_x and SO_2 , and in the case of alternative fuels, dioxins and furans. The nitrogen oxides are formed mainly in the burning zone and are mostly thermal NO_x [75]. The typical level of NO_x for a cement rotary kiln is 1000–1500 ppm in which 90 per cent is thermal NO_x . There is also a fairly stable 200–250 ppm background contribution of NO_x associated with fuel nitrogen and this is generated at relatively low temperatures within the flame itself. In the kilns with calciners, the NO_x content becomes considerably lower because of the low burning temperature in the calciner. Also, the spe-

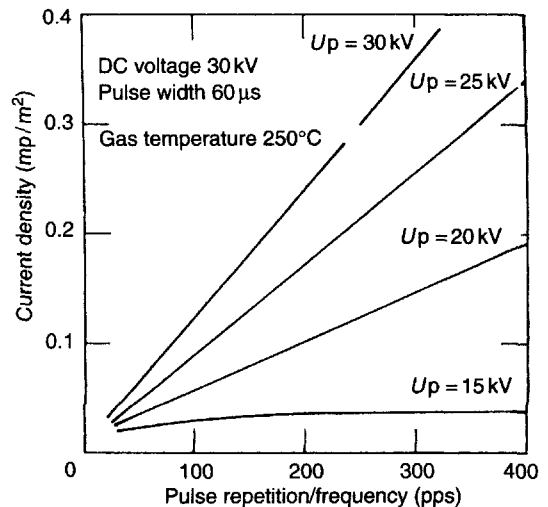


FIGURE 1.30 Current density as a function of repetition frequency for different U_p values.

cial $deNO_x$ calciners are used which were described earlier. In the case of these calciners only 0.35 g/kg of clinker comes from the kiln and around 0.7 g NO_2 from the calciner, so that only around 1.05 g NO_2/kg of clinker is emitted, which is a little lower than 500 $mg NO_2/nm^3$ (10 per cent

of oxygen level). Because there is no ascertainable elimination of NO_x in conditioning towers or grinding/drying plants, when the decrease of NO_x in exit gases is indispensable, a very promising method is a non-catalytic decomposition of NO with NH_3 [76]. The selective reaction of NH_3 with NO takes place in the presence of oxygen, preferably at temperatures of about 950°C . Kreft [77] determined the best location of NH_3 injection to the cyclone preheater (Figure 1.31).

The emission of sulphur usually presents no problems. Additionally, the emission of SO_2 can be reduced by passing the gas through a grinding mill or conditioning tower. The cement burning process and grinding process thus function as ideal desulphurizing systems in which more than 90% of SO_2 is retained [72]. However, in some cases, when sulphides are present in raw material, the problem must be specially solved, because sulphur is combusted in the preheater and SO_2 leaves the kiln with the exit gases [78]. Bonn and Hasler [78] present the opinion that only absorption in a circulating fluidized bed can promise sufficient lowering of the SO_2 . In the fluidized bed the exhaust gas is brought into contact with water to lower the temperature down to the dew-point range, then with a mixture of raw meal and slaked lime, the SO_2 is combined as sulphite and the product is fed back to the kiln, though in limited quantities. A very efficient desulphurization system is also in use at the Aalborg cement plant [79].

Polysius implemented an innovative system, called POLVITEC, which solved the problem of high SO_2 and NO_x emission and simultaneously

provided the preconditions for environmentally acceptable utilization of sewage slurry as a fuel [80]. The system comprises an activated coke-packed bed filter in combination with an ammonia liquid injection into a kiln inlet. The pollutants contained in the kiln exhaust gases, including sulphur dioxide, ammonium compounds, heavy metals, hydrocarbons and residual dust from the upstream electrostatic precipitator are collected in the activated coke-packed bed filter. The gas passes the filter in the cross-current mode. The activated coke moves vertically through the housing. Collecting the replacement of activated coke takes place discontinuously in small steps. The exhausted activated coke is used as a fuel in the kiln.

Cement kilns are very promising reactors which effectively burn even hazardous waste. Because of the high flame temperature, the air excess cement kiln presents excellent conditions for burning of the most difficult organic compounds, that is PCB and PAH, so all hazardous wastes are destroyed and neutralized [81]. Simultaneously, a strongly basic medium in cement kilns absorbs the heavy metals and the immobilization is of the order of 99.99 per cent [82]. As long practice has shown, the emission of toxic substances and heavy metals from the cement kiln is as a rule lower than in the case of classic fuels [82]. However, the quantity of noxious components in the alternative fuels must not exceed the threshold quantity, which is shown in Table 1.8 [82].

The use of alternative fuels has been developed especially in France where the share of these fuels reached 52.4 per cent in 1994 [83]. The different

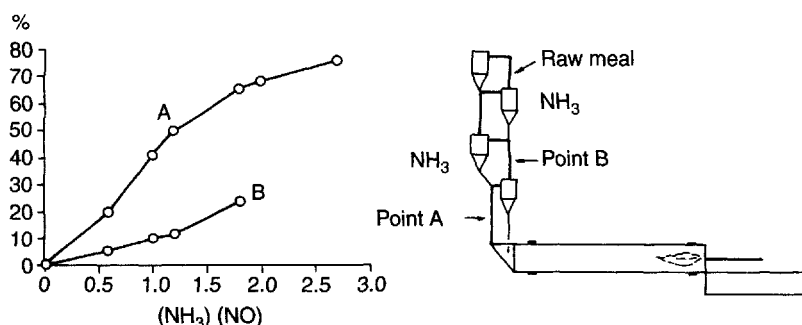


FIGURE 1.31 Reduction of NO_x for two location of feeding points in the suspension preheater.

TABLE 1.8 Pitch acceptability limits [82] in mg/kg of fuel

Chlorinated organic substances	<100
PAH	<50
PCB	<50
Metals	
Hg	<2.5
Hg + Tl + Cd	<20
Total	<1000

combustible wastes which are used as fuels are: petroleum coke, used lubricants, oils, paints, organic solvents, tar, waste-containing cyanides, pesticides, sundry organic and inorganic and others. The most popular alternative fuel for a long time has been old tyres.

1.12 Acknowledgements

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Composition of cement phases

Herbert Pöllmann

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2.1 Introduction

Cement components are usually described by their phase relations out of phase diagram determinations. Basically, the most important cement phases can be shown in the phase diagram $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (Figure 2.1) with additional MgO and Fe_2O_3 and some minor, but also important components. Different hydraulic and latent hydraulic materials are shown in Figure 2.2. The stability fields of the phases can be given by these diagrams, but due to the multicomponent system, it is often difficult to describe solid solutions,

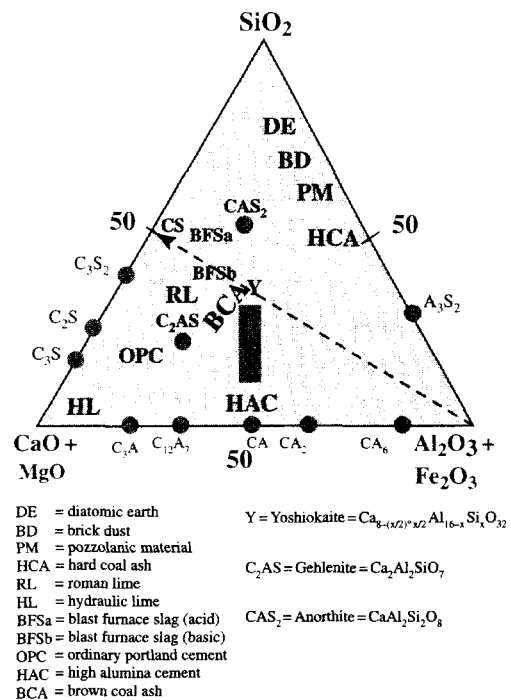


FIGURE 2.1 Hydraulic and latent hydraulic materials in the system $(\text{CaO} + \text{MgO})-(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)-\text{SiO}_2$.

phase transitions, phase stabilization and true element contents. For that, often isoplethic or isothermal sections are used to show the details. For these already quite well-known phase diagrams, the phase boundaries, melting points,

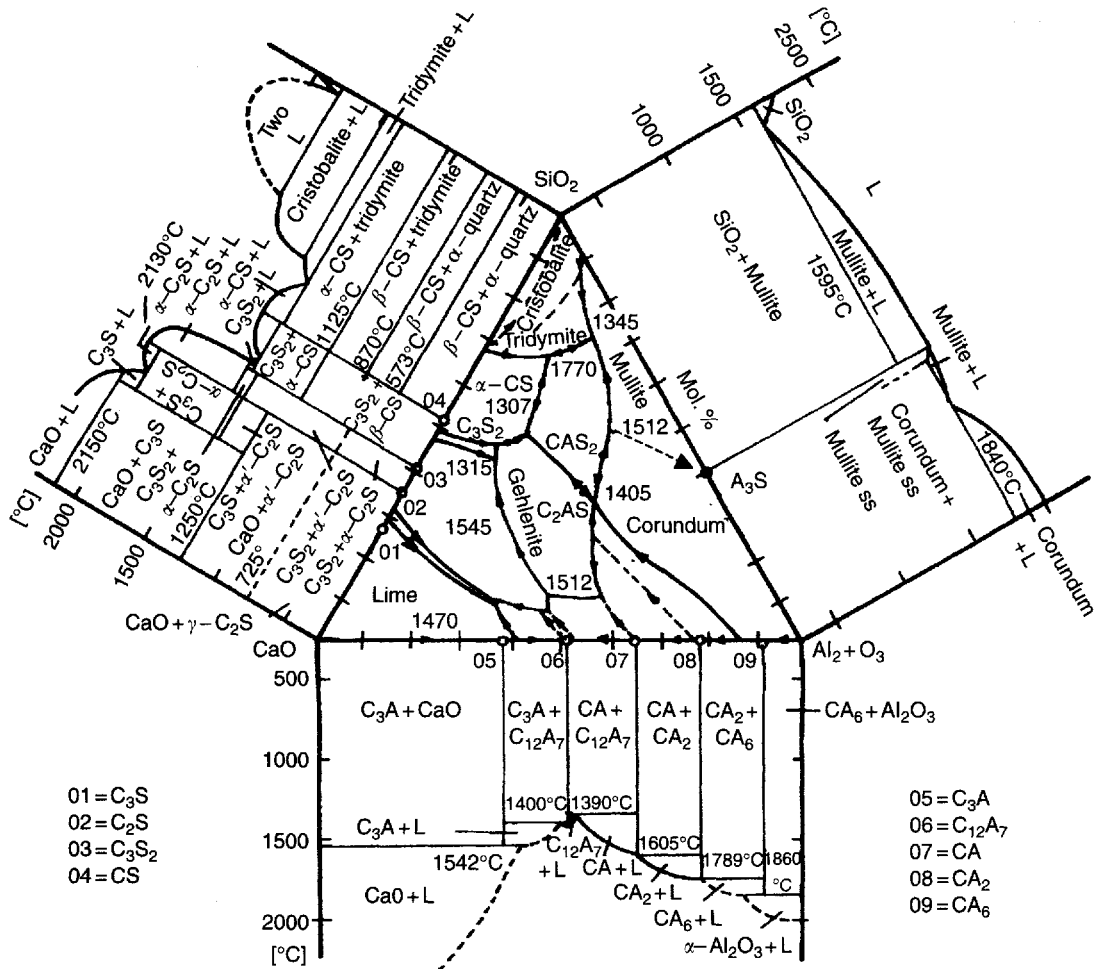


FIGURE 2.2 The ternary phase diagram $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ showing the three binary phase diagrams $\text{CaO}-\text{SiO}_2$, $\text{CaO}-\text{Al}_2\text{O}_3$ and $\text{Al}_2\text{O}_3-\text{SiO}_2$ (Bowen, N. L. and Greig, J. W. 1924; Greig, J. W. 1927; Phillips, B. and Muan, A. 1959; Rankin, G. A. and Wright 1915; Roy, D. M. 1958; Welch, J. H. and Gutt, W. 1959).

transition points and stability regions can be given in detail. In a "cement system" characterization of compositional changes, solid solutions and the additional knowledge of the influence of minor contents of elements as a function of temperature can lead to differences in non-equilibrium systems. The existence of non-equilibrium conditions can often be seen by zoned crystals in cement clinkers. The complex phase composition of cement minerals is also now increasingly influenced by the use of alternative fuels, waste compounds and fluxing agents which can cause phase

changes or formation of new phases. Besides, for phase diagrams which are based on pure components, the *in situ* determination of compositions of phases is possible by using micro-techniques such as microdiffractometry, EPMA or EDX analysis. The varying chemical contents and impurities, the crystallographic changes of clinker minerals coming from different sources, kilns and production techniques can be measured and shown directly.

Due to these varying conditions, the equilibrium mineralogical calculations such as Bogue or

modified Bogue are increasingly replaced by direct quantification methods to describe the real phase assemblages quantitatively. As microscopic techniques are mainly used to determine quality and quantity of clinker minerals at moderate times, the X-ray Rietveld technique can be developed for different clinkers even as a completely automated method for quality control. The quantification results can be obtained in at least 10–20 min after a proper installation of the control files. Phase compositions, crystal chemistry and crystallographic parameters of all phases must therefore be known.

The next steps will therefore provide direct determination methods qualitatively and quantitatively. A comparison of the advantages and disadvantages of microscopy, X-ray methods and Bogue calculations are summarized in Table 2.1. Small amounts of additional phases which can occur due to increasingly used impure raw and secondary materials cannot be found directly by X-ray methods, but must also be identified by different additional methods. Despite the knowledge of phase formation and crystallization conditions derived from phase diagrams, a description and investigation of clinkers and phase formation requires different methods:

1. Bogue calculation of theoretical phase contents including modified Bogue.
2. Direct X-ray analysis.
3. Rietveld analysis.
4. Chemical methods like free-lime determination.
5. X-ray fluorescence.
6. Electron microprobe analysis for small-sized samples and individual chemical information.
7. Optical methods like reflected-light microscopy, powder mounts and thin sections.
8. Scanning electron microscopy with fluorescence, secondary and back-scattered images.
9. Selective dissolution methods for enrichment of phases.
10. Thermoanalytical methods for alkali phases and carbonization effects.
11. Spectroscopic methods.
12. EPMA, ESR, ICP, AAS.

2.2 Simple oxides, elements and their potential role in cement chemistry

The role of simple oxides in cement chemistry is dominated by the free lime content which is measured in cement plants for quality control. High free lime contents can be an indication that burning conditions or homogenization are not successfully adapted. Low-burnt clinkers can have increased content of free lime. With grinding and transport of fine ground material, often carbonization can take place. This must be taken into account when free lime determinations are made routinely after some time, because lower free lime contents are measured. Free lime and free magnesia contents of clinkers are restricted due to the hydration of phase on-expansion reactions which can occur in the final product.

Other oxides like SiO_2 can be due to coarse quartz in the raw meal or due to incomplete homogenization. Corrective additives like iron-containing compounds can lead to the formation of iron spinels like magnetite or magnesium containing spinels. Spinel may occur due to reactions of metals²⁺ and metals³⁺.

Other iron oxides like wüstite were identified when reducing conditions occurred in the clinker. The incorporation of Fe^{2+} in alite can lead to a destabilization of alite. With increasing reducing conditions, even native iron was found in clinkers.

Free titanium dioxide is normally not found in clinkers, but can be found when increased amounts of painting residues are added and incomplete homogenization takes place.

In Figures 2.3 and 2.4, free lime and an iron-rich spinel coming from reducing conditions are shown. Some details for these phases are summarized in Table 2.2.

2.3 Calcium silicates (C_xS_y)

The system of CaO-SiO_2 was investigated by Welch and Gutt (1959), Philips and Muan (1958) and Roy (1958). Four binary phases exist within the system which are increasingly hydraulic with increasing C/S-ratio. The different modifications

TABLE 2.1 Comparison of Bogue, microscopy and X-ray techniques for phase determinations (Pöllmann *et al.* 1997)

	<i>Preparation</i>	<i>Measurement</i>	<i>Calculation</i>	<i>Precision</i>	<i>Advantage</i>	<i>Disadvantage</i>
Microscopy	crushing; embedding in epoxy resin; polishing; surface etching (high personnel expense; no automatization; time consumption 2 days)	visual investigation; point counting of >10,000 points; description of the microstructure (well educated and trained personnel necessary; high time consumption (1 days); no automatization)	calculation of vol% into mass% (table calculator)	Standard deviation of about 2%	quantification and microstructure simultaneously; information on clinker genesis and on crystal shape and size	high time consumption; high preparation effort; well trained worker necessary; no automatization possible
Rietveld refinement	grinding; sample preparation (low personnel and equipment effort; automatization; time consumption ca. 20 min)	PC-controlled XRD (high equipment effort; automatization possible; time consumption ca. 1 h)	quantification with a PC program; automatic calculation within 1 min;	absolute error of 1 mass%	exact results on phase composition no texture effects; standardless; additional information on minor phases (like MgO);	rel. high measuring time; only quantification data
Bogue calculation	grinding; powder/glas pellets preparation (low personnel and equipment effort; automatization possible; time consumption ca. 20 min)	XRF analysis; wet analysis of volatile compounds and of free lime (XRF automatically; measurement time ca. 5 min; wet analysis needs high personnel and time effort)	normative phase quantification from chemical analysis (automatic calculation)	depends on the phase composition	fast and automatic analysis; within defined phase composition good quantification results	only normative phase; quantification; wet analysis necessary for exact quantification

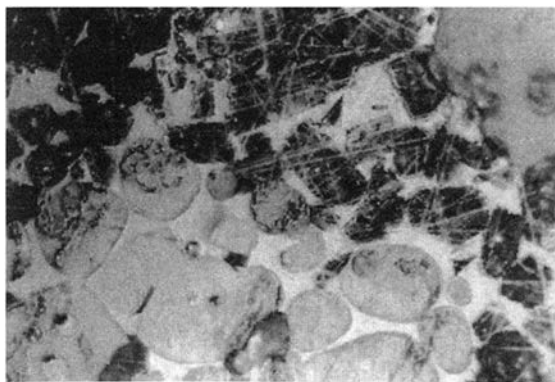


FIGURE 2.3 Reflected light microscopy nest of free lime (magnification $800\times$).

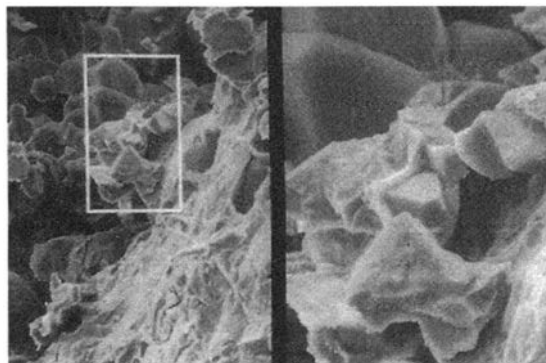


FIGURE 2.4 Iron-rich octahedra of spinel closely related to magnetite surrounded by interstitial phase (Octahedra $10\mu\text{m}$).

of CS are not hydraulic. C_3S_2 (Rankinite) is also not hydraulic and does not occur in Portland cements. C_3S and C_2S are the main hydraulic phases, undergoing several phase transformations. The complex solid solutions of C_3S and C_2S are named 'alite' and 'belite'. Important data on calcium silicates are summarized in Table 2.3.

2.3.1 C_3S – alite

C_3S , a highly hydraulic compound occurs in amounts of 50–90 per cent in Portland cements. C_3S is formed above 1250°C by a reaction of C_2S and C and can be metastably obtained by rapid cooling of the mixtures. The formation of C_3S and its polymorphs is highly influenced by other ions present, so high SO_3 contents even can suppress alite-formation which otherwise can be partly avoided by the presence of fluorine-ions. C_3S undergoes several phase transformations which are summarized in Figure 2.5. The high temperature polymorph R melts congruently at 2070°C . The polymorphs are all structurally similar with only small distortions, therefore they can be described by pseudohexagonal unit cells. By Rietveld refinement, mainly monoclinic polymorphs can be identified in clinkers. A stabilization of polymorphs can be obtained by incorporation of foreign ions in alite-lattice. Due to foreign ions and stabilization of C_2S , only small amounts of alkalis are incorporated in C_3S ; instead alkalis are incorpo-

rated in belite. At 1500°C up to 1.4 per cent K_2O , 1.4 per cent Na_2O and 1.2 per cent Li_2O can be taken up, but in commercial clinkers, normally less alkalis are incorporated. The incorporation of 2.2 per cent MgO and 1 per cent Al_2O_3 and 1.1 per cent Fe_2O_3 at 1550°C was described. ZnO can be incorporated up to 5 per cent, Cr_2O_3 1.4 per cent and Ga_2O_3 up to 1.4 per cent. A combined incorporation stabilizes triclinic and monoclinic polymorphs. A combined addition of Al_2O_3 and Fe_2O_3 leads to an influence on each other on incorporation. A fluorine-stabilized C_3S was described by a formula $\text{Ca}_{6-0.5x}\text{Si}_2\text{O}_{10-x}\text{F}_x$. The incorporation of small amounts of Fe^{2+} in C_3S under reducing conditions leads to a destabilization and formation of belite and calcium-ferrite, but can also lead to increased free lime contents.

A diagram of varying contents of MgO and SO_3 showing the stabilization of different M_3 and M_1 modifications in industrial clinkers was determined by Maki. A zonal structure of alite is obtained due to lower cooling (less foreign ions), and the size of alite crystals is influenced by residence time in the furnace.

Due to rapid cooling, often a zonation of alite crystals can be found caused by M_1 and M_3 modifications or varying chemical compositions. The chemical variations and varying reactivities are not well established yet, but it seems to be clear that the inner cores of the crystals contain increased contents of foreign ions. The determination and

TABLE 2.2 Simple oxides and elements occurring in cements

Chemistry	Mineral name	Melting Point * in °C	Space group	Lattice parameters (Å)						JCPDS-No	Occurrence and properties
				a_o	b_o	c_o	α	β	γ		
CaO	Lime	2570	Fm3m	4,811	—	—	—	—	—	37-1497	free lime
MgO	Periclase	2800	Fm3m	4,211	—	—	—	—	—	45-946	free periclase
SiO ₂	α -Quartz*	573	P3 ₂ 2	4,913	—	5,405	—	—	—	46-1045	coarse quartz in raw meal, insufficient homogenization
SiO ₂	Tridymite* _{2H}	870	P6 ₃ /mm2	5,046	—	8,236	—	—	—	18-1169 and others	HAC From rotary kiln production
SiO ₂	Cristobalite*	1470 1723	P4 ₁ 4 ₁ 2	4,973 —	— —	6,924 —	— —	— —	— —	39-1425	high alumina cements
TiO ₂	Rutile	1830	P4 ₂ /mnm	4,593	—	2,959	—	—	—	21-1276	
Al ₂ O ₃	Corundum	2072	R3c	4,759	—	12,99	—	—	—	46-1212	Al-rich HAC
Fe ₂ O ₃	Hematite	1565	R3c	5,036	—	13,75	—	—	—	33-664	
FeO	Wustite	1369	Fm3m	4,293	—	—	—	—	—	46-1312	HAC from rotary kiln
Fe ₃ O ₄	Magnetite	1594	Fd3m	8,396	—	—	—	—	—	19-629	production
MgAl ₂ O ₄	Spinel _{ss}	2105	Fd3m	8,083	—	—	—	—	—	21-1152	reducing kiln conditions
MgFe ₂ O ₄	Magnesio-ferrite _{ss}	1750	Fd3m	8,375	—	—	—	—	—	17-464	
Fe	Native iron	1535	Im3m	8,866	—	—	—	—	—	6-696	reactions with refractories strong reducing condition

*Transformation point.

SS = Solid solution; 2H = Ramsdell symbols.

TABLE 2.3 CS in cements and their properties

Chemistry	Mineral name	Melting Point	Space group	Lattice parameters (Å)						JCPDS-No	Occurrence and proper
				a_o	b_o	c_o	α	β	γ		
Para $\text{CaO} \cdot \text{SiO}_2$	Wollastonite-1A*	1126	C1	10,10	11,05	7,30	99,53	100,56	83,44	42-547	not occurring in cementitious systems
α - $\text{CaO} \cdot \text{SiO}_2$	Wollastonite-2M	1545	P2 ₁ /a	15,43	7,07	—	95,38	—	43-1460		
$3\text{CaO} \cdot 2\text{SiO}_2$	Rankinite	1465	P2 ₁ /a	10,61	8,91	7,85	—	120,00	—	22-539	mainly known from slays
α_L - $2\text{CaO} \cdot \text{SiO}_2$	Bredigite ($\text{Ca}_{14}\text{Mg}(\text{SiO}_4)_8$)	2130	Pmnn	10,904	18,38	6,75	—			36-399	
		650					—		—		
β - $2\text{CaO} \cdot \text{SiO}_2$	Larnite*		P2 ₁ /n	9,31	6,76	5,51	—	94,46	—	33-302	belite-phase belite-phase dusting, not hydraulic alite phase in cement
γ - $2\text{CaO} \cdot \text{SiO}_2$	Skannonite		Pcmn	5,08	6,76	11,22		—	—	31-297	
$-3\text{CaO} \cdot \text{SiO}_2$	R Harturrite	2070	R3m	7,15	—	25,56				16-406	
$-3\text{CaO} \cdot \text{SiO}_2$	*M _{III}	1060									
$-3\text{CaO} \cdot \text{SiO}_2$	*M _{II}	1050	P	12,23	7,03	24,96		90,10	—	42-551	
$-3\text{CaO} \cdot \text{SiO}_2$	*M _I	990									
$-3\text{CaO} \cdot \text{SiO}_2$	*T _{III}	980	P1	14,08	14,21	25,10	90,10	90,22	120,00	31-301	
$-3\text{CaO} \cdot \text{SiO}_2$	*T _{II}	920									
$-3\text{CaO} \cdot \text{SiO}_2$	*T _I	600									

*Phase transition.

quantification of the C_3S modifications by X-ray diffractometry is increasingly simplified by using the structural models and calculations of Rietveld methods.

A comparison of X-ray diagrams of high temperature R-phase to monoclinic phase is shown in Figure 2.6. The crystalline structural model is given in Figure 2.9 and the SEM micrographs of single pseudo-hexagonal shaped C_3S is given in Figures 2.7 and 2.8.

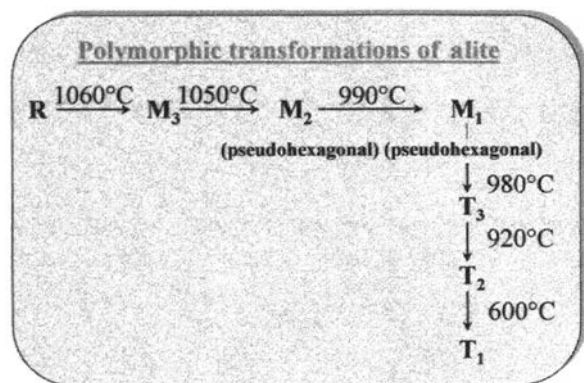


FIGURE 2.5 Polymorphic phase transformations of C_3S .

The crystalline structure was determined by Maki. A triclinic structure determination was done by Golovastikov (1975). Monoclinic alites show pseudotrigonal symmetry, in clinker often M_1 or M_3 and mixtures of both in zoned crystals are quite common (Kato 1978; Maki 1982).

The structure is composed of SiO_4 -tetrahedra which are linked by calcium ions. Calcium is coordinated by eight oxygens (1978, 1982).

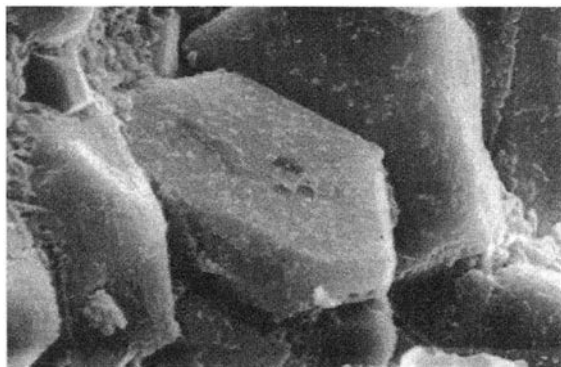


FIGURE 2.7 SEM micrograph of pseudo-hexagonal alite crystals showing slight surface coatings from starting hydration.

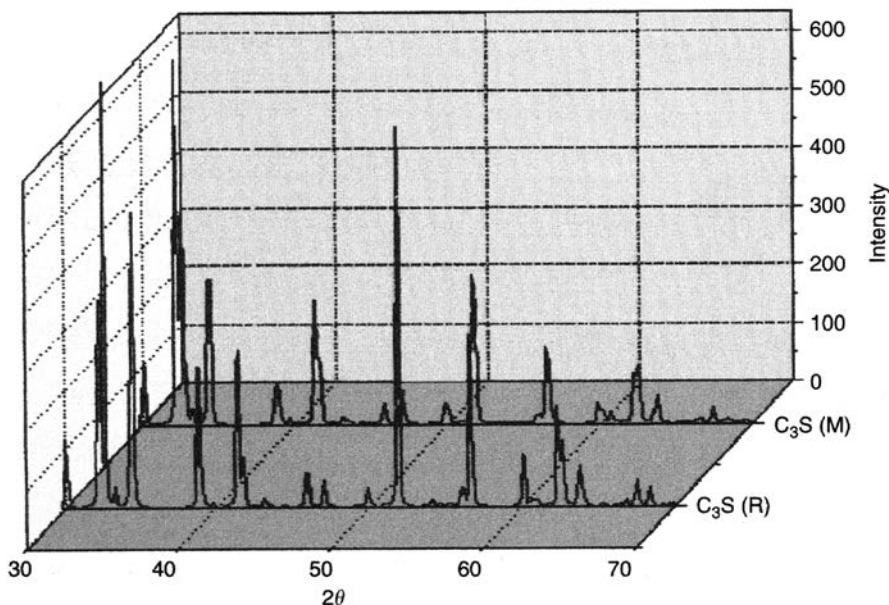


FIGURE 2.6 Comparison of X-ray powder data ($CuK\alpha$) diagrams for rhombohedral high temperature C_3S and monoclinic C_3S .

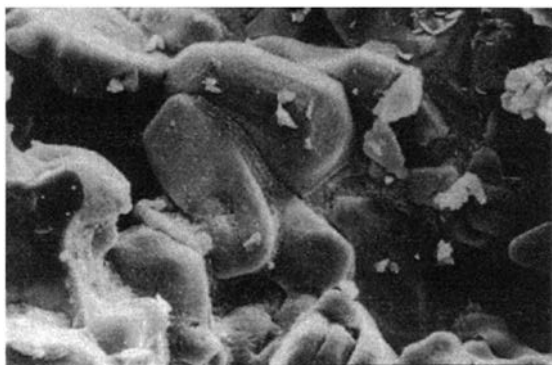


FIGURE 2.8 SEM micrograph of alite crystals separated by interstitial phase.

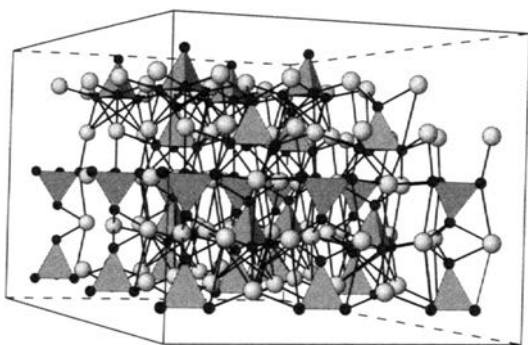


FIGURE 2.9 Crystal structure of C₃S.

2.3.2 C₂S – belite

C₂S mainly occurs in an amount of 10–40 per cent in OPCs. In special cements like belitic cements, low energy cements and slag materials, different modifications of C₂S may occur.

C₂S undergoes several phase transformations in the temperature range (Figure 2.10). The phase transformation to γ -C₂S is known as ‘dusting’ due to an enormous volume change. γ -C₂S is barely hydraulic. β -C₂S can be obtained by quenching or crystallochemical doping. In cements, often α - or β -polymorphs occur. These phase transformations cause the twin lamellae which can be seen in the optical microscope. The different C₂S-modifications can be stabilized at room temperature with doping by B, P, Mg, alkalis, Ba, Sr preferen-

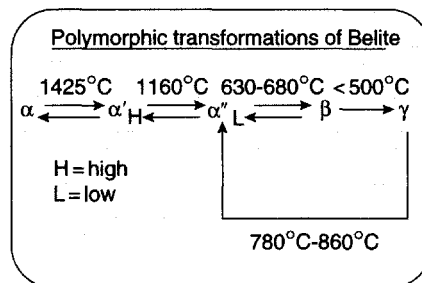


FIGURE 2.10 Polymorphic transformations of Belite.

tially. Mainly, rather large or small ions have stabilizing effects. It is quite obvious that belite is capable of incorporating larger amounts of foreign ions than alite. The stabilization of highly reactive α -polymorphs by foreign ions using alkalis is used in technical applications. Optically, four different types can be distinguished (F. P. Sorrentino 1998). Activated belite can be obtained by rapid cooling, lattice distortions by solid solutions, crystal size, crystallochemical changes and chemical shift of bonding energies. A comparison of X-ray powder diffractograms of three different polymorphs is shown in Figure 2.11.

In OPC clinkers, different belite origins coming from different sources can occur:

1. Primary belite formed by reaction of lime and silicon sources.
2. Secondary belite formed by the decomposition reaction of Alite according $C_3S \Rightarrow C_2S + C$ and forming small crystals on the rims of alite crystals.
3. Tertiary belite due to the recrystallization of the interstitial phase coming from the decomposition and decreased solid solution of SiO₂ in C₃A-phases.

Some compositions of belites in different clinkers were given by (F. P. Sorrentino) (1998):

OPC	(Ca _{1.97} Na _{0.01} K _{0.02})(Mg _{0.02} Fe _{0.02})(Al _{0.07} Si _{0.92} S _{0.01})O ₄
white cement	(Ca _{1.97} K _{0.02})(Mg _{0.01} Fe _{0.01})(Al _{0.08} Si _{0.90} S _{0.02})O ₄

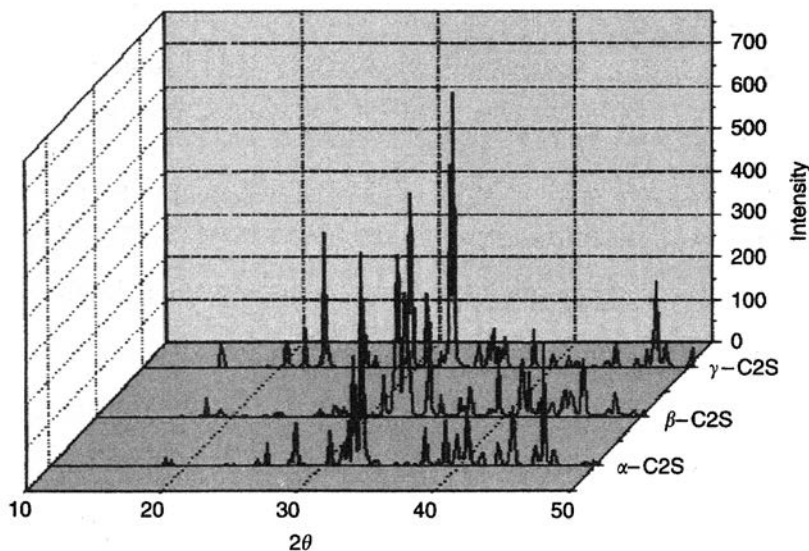


FIGURE 2.11 Comparison of X-ray powder data (CuK α) diagrams for different polymorphic phases of C₂S.

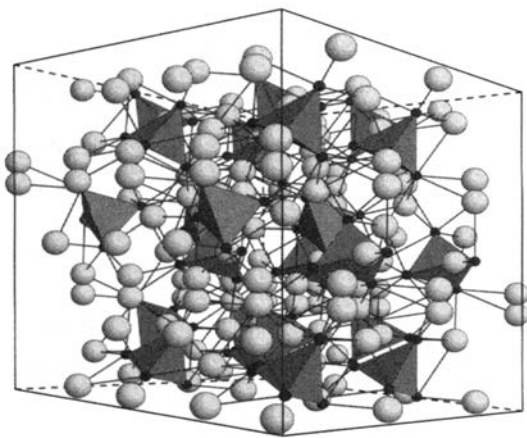
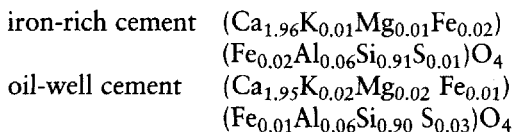


FIGURE 2.12 Crystal structure of C₂S.



The attempts to form active belitic cements by doping C₂S or rapid cooling are increasingly interesting because of lowered temperature requirements and also because of the possibilities of using other lower-quality raw materials for

cement production. The stabilization of β -C₂S by excess CaO and of γ -C₂S by excess SiO₂ was reported. Bredigite is now known as an one phase with a composition of Ca₁₄Mg(SiO₄)₈. Bredigite was formerly believed to be similar to α -C₂S but contrary to belite modifications, it is not hydraulic at room temperatures.

The structural model of these phases and their polyhedral links of SiO₄-tetrahedra linked by calcium is shown in Figure 2.12

1. α -C₂S, β -C₂S, γ -C₂S

A comparison of selected X-ray diagrams is summarized in Figure 2.11. The crystal structure models of α -C₂S is given in Figure 2.12. Optical and SEM micrographs are given on Figures 2.13–2.16.

2.4 Aluminum silicates, calcium aluminium silicates, their properties and occurrence in cements

Aluminum silicates and calcium aluminum silicates do not play an important role in OPC production, but metakaolinite and mullite can occur as decomposition products of clay materials in raw meal composition. Calcium aluminum silicates as gehlenite and anorthite typically occur in

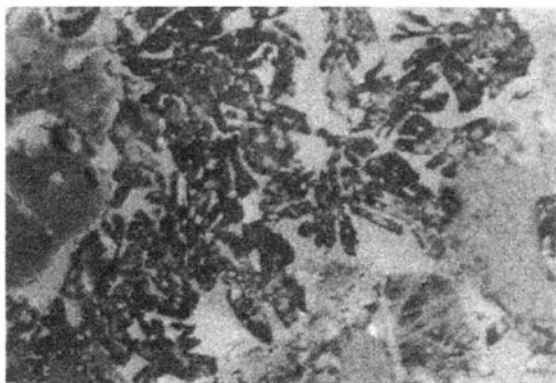


FIGURE 2.13 Optical reflected microscopical ragged belite crystals (magnification 700 $\times$).

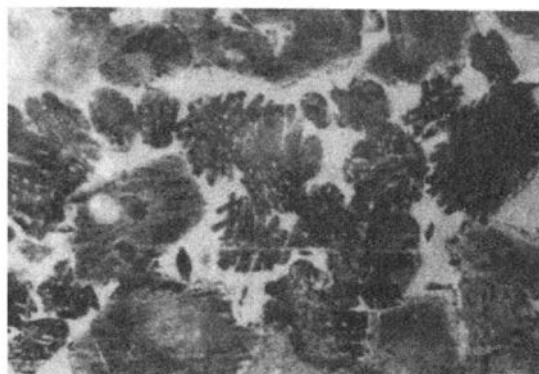


FIGURE 2.14 Optical reflected microscopical ragged belite crystals (magnification 700 $\times$).

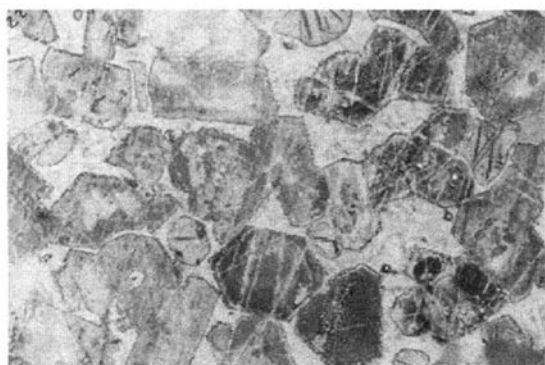


FIGURE 2.15 Reflected-light microscopy, belite aggregates (magnification 700 $\times$).

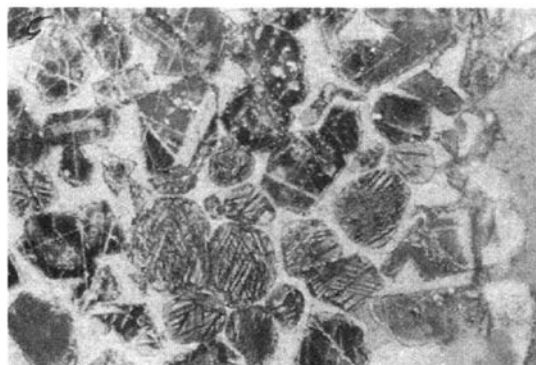


FIGURE 2.16 Reflected-light microscopy, belites with typical lamellae structure (magnification 700 $\times$).

slags and ashes from different sources. Gehlenite is also a typical mineral for high-alumina cements containing increased contents of silicon. Yoshioakaite is a metastable mineral showing some compositional variation within a nephelite-similar structure. Compositional variations within the calcium aluminum silicates with glassy structure occur in glass cements. Table 2.4 summarizes the most important data on some of the phases.

2.5 Calcium aluminates

In the system $\text{CaO-Al}_2\text{O}_3$ (Rankin and Wright 1915) four binary and one pseudobinary compounds exist (see Table 2.5).

C_3A is the most abundant Al-containing phase in OPC, but CA is the most important for high-alumina cements. Due to the Ca/Al-ratio, also CA_2 and CA_6 can occur in special HACs. C_{12}A_7 is not a pure compound in the system $\text{CaO-Al}_2\text{O}_3$, but instead, must be given by the formula $\text{C}_{11}\text{A}_7 \cdot \text{Ca}(\text{OH})_2$. $\text{Ca}(\text{OH})_2$ can be replaced by CaF_2 , CaCl_2 and others.

2.5.1 Tricalcium aluminate – C_3A

Several polymorphs as a function of Na, Fe and S-content were synthesized by Lee, F. C., Banda, H. M. and Glasser, F. P. (1982). The cubic pure C_3A crystallizes in $\text{Pa}3$, but cubic C_3A doped with alkalis seems to crystallize in $\text{P}2_13$.

TABLE 2.4 Aluminum silicates and calcium aluminium silicates, their properties and occurrence in cements

Chemistry	Mineral name	Melting point	Space group	Lattice parameters (Å)						JCPDS-No	Occurrence and properties
				a_o	b_o	c_o	α	β	γ		
A_3S_2	Mullite	1810	Pbam	7.55	7.69	2.88	—	—	—	15-776	slags, ceramics
C_2AS	Gehlenite	1593	P42 ₁ m	7.69	—	5.07	—	—	—	35-755	HAC's rich in SiO ₂
CAS_2	Anorthite	1553	P1	8.18	12.87	14.18	93.17	115.91	91.20	41-1486	slags
$Ca(Al,Si)_2O_4$	Yoshiokaite		P3	9.94	—	8.25	—	—	—	46-1336	glass cements and glass slags
AS_2	Metakaolinite		amorphous	—	—	—	—	—	—	—	dehydrated China clay

TABLE 2.5 Calcium aluminates in cements and their properties

Chemistry	Mineral name	Melting point	Space group	Lattice parameters (Å)						JCPDS-No	Occurrence and properties
				a_o	b_o	c_o	α	β	γ		
$3CaO \cdot Al_2O_3$		1540	Pa3	15.26	—	—	—	—	38-1429	OPC	
$CaO \cdot Al_2O_3$		1600	P2 ₁ /2	8.70	8.09	15.21	—	90.14	—	23-1036	HAC
$CaO \cdot 2Al_2O_3$	Grossite	1790	C2/c	12.44	8.91	5.45	—	107.0	—	46-1475	HAC
$CaO \cdot 6Al_2O_3$	Hibonite-5A	1860	P6 ₃ /mmc	5.56	—	21.91	—	—	—	38-470	HAC
$(C_{11}A_7 \cdot Ca(OH)_2)$	Mayenite	(1400)	I43d	11.98	—	—	—	—	—	9-413	HAC
$3CaO \cdot Al_2O_3$ (3.8% Na ₂ O)			Pbca	10.875	15.105						OPC
$3CaO \cdot Al_2O_3$ (5.7% Na ₂ O)			P2 ₁ /a	10.877	15.135		90.1				OPC
$3CaO \cdot Al_2O_3$ (4% Na ₂ O)				10.851	15.109		—	—			high-temperature phase
							—	—	(T > 450°C)		

Different stabilized cubic, orthorhombic and monoclinic lattice parameters are given by Moranville-Regourd and Boikova. The crystal structure is composed of $(\text{AlO}_4)^{5-}$ -tetrahedra linked to $(\text{Al}_6\text{O}_{18})^{18-}$ -rings which are connected by the Ca^{2+} -ions. For solid solutions with alkalis 2 Na^+ replace Ca^{2+} . Therefore a Na^+ -ion takes the place of the Ca^{2+} and the second is located in the centre of the $(\text{Al}_6\text{O}_{18})^{18-}$ -rings. Metastable forms of C_3A (proto- C_3A) were synthesized by crystallization of highly undercooled melts with increased contents of Fe_2O_3 and SiO_2 (Lee, Bandd and Glasser 1982). The crystal structure of an orthorhombic complex solid solution with the composition $\text{Ca}_{0.8375}\text{Na}_{0.875}[\text{Al}_{5.175}\text{Fe}_{0.45}\text{Si}_{0.375}\text{O}_{18}]$ was determined by Takeuchi, Nishi and Maki (1980).

The orthorhombic and monoclinic solid solutions of C_3A can be transformed at high temperatures ($T > 450^\circ\text{C}$) into tetragonal (pseudoorthorhombic) polymorphs (Meissner 1986).

The Na-doped tricalcium aluminates seem to show decreased reactivity. The ranges of solid solutions and the symmetry changes can be given by:

0–1.9%	Na_2O	cubic
1.9–3.7%	Na_2O	cubic + orthorhombic
3.7–4.6%	Na_2O	orthorhombic
4.6–5.9%	Na_2O	monoclinic

These contents of sodium can be increased significantly in the presence of other foreign ions.

The existence of a NC_8A_3 can probably only be confirmed in the case when Si is present and rapid cooling of melts is occurring. A similar compound containing potassium can also be obtained preferentially when additionally iron and silicon-ions are present. A tetragonal KC_8A_3 was synthesized by Adams.

C_3A crystallizes in a cubic lattice, but due to incorporation of foreign ions, mainly alkalis and SiO_2 , the symmetry changes to orthorhombic and monoclinic point groups. A detailed structure schemata is given in Figure 2.17. SEM micrographs of tricalciumaluminate are shown in Figures 2.18 and 2.19. X-ray data examples of tricalciumaluminate and sodium containing phases are given in Figure 20.

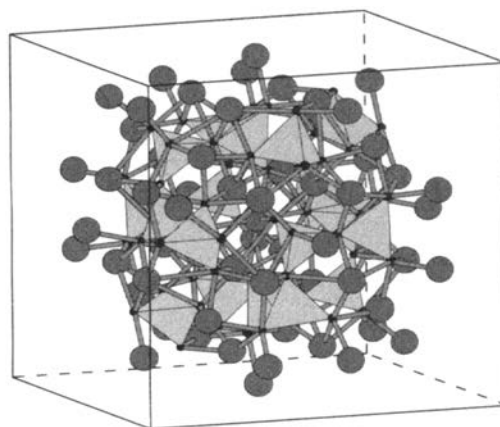


FIGURE 2.17 Crystal structure of tricalcium-aluminate.

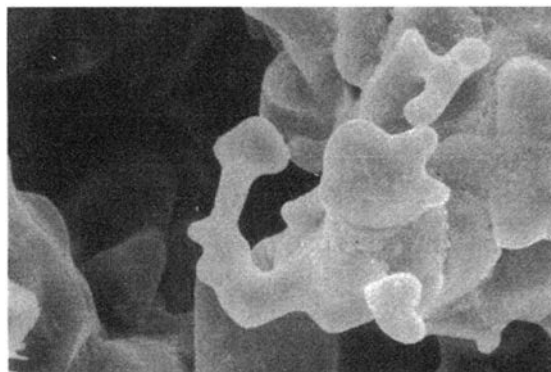


FIGURE 2.18 Molten calcium aluminate phase – SEM micrograph of molten interstitial phase, mainly aluminate.

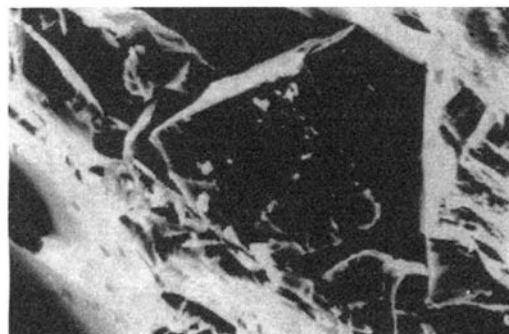


FIGURE 2.19 Cubic tricalcium aluminate – SEM micrograph of cubic C_3A -crystal edge.

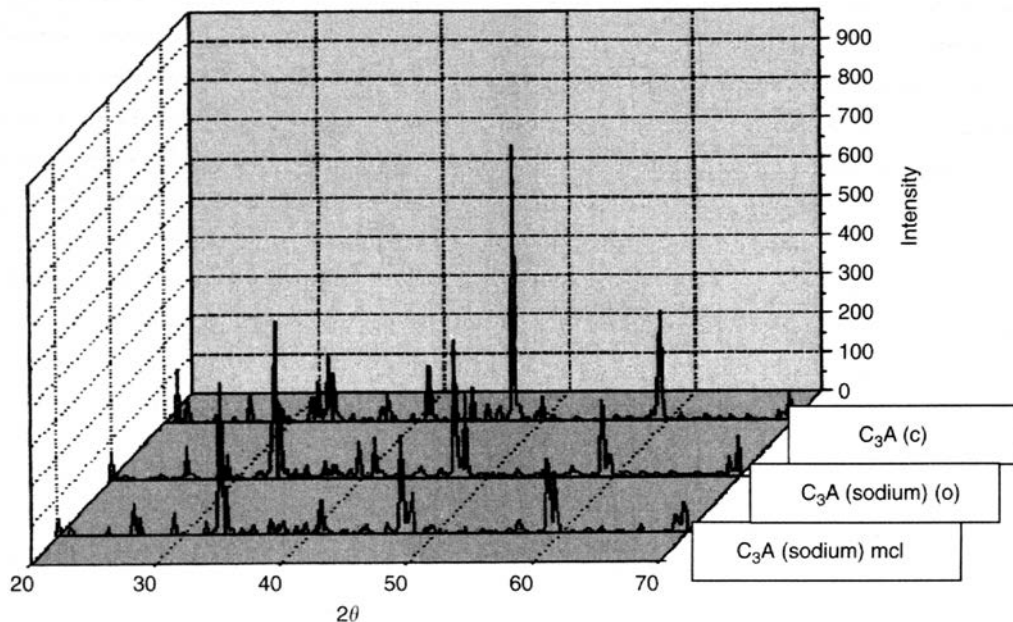


FIGURE 2.20 X-ray diagrams of typical cubic, orthorhombic and monoclinic tricalciumaluminate with different sodium contents.

2.5.2 Other calcium aluminates

Monocalcium aluminate is the main phase of HAC and crystallizes in a monoclinic point group. The hydroxide in $C_{11}A_7 \cdot Ca(OH)_2$ can be replaced by F_2 , Cl_2 and others. These phases can play quite an important role in special cements like early hydrating cements. The fixation of halogenide ions is also very important in the combination of burning raw meals with chlorine or fluorine-bearing waste materials. In OPCs, the calcium content is too high, so that these phases cannot be found. Mayenite can also be formed as an additional constituent in high-alumina cements. CA_2 and CA_6 can occur in aluminum-rich high-alumina cements.

2.6 Calcium aluminium ferrites

Iron is mainly fixed under oxidizing conditions in the calcium aluminum ferrite phase. The composition of the ferrite phase can be described by a limited solid solution between C_2F and C_6A_2F

with $C_4A_xF_{(1-x)}$, $0 < x < 0.7$ (Table 2.6). According to Büssem, the crystal structure of C_4AF is composed of layers of $(Al,Fe)O_6$ -octahedra and $(Al,Fe)O_4$ -tetrahedra linked along joint edges. In the open spaces in-between, the calcium atoms are located. A natural mineral was named 'brownmillerite'. Due to the occupation of iron and aluminum in tetrahedral and octahedral sites within the solid solution, a change of space group from Pcmn to Ibm2 takes place at a composition $Ca_4Fe_{4-2x}Al_{2x}O_{10}$ ($x < 1.14$) (Colville and Geller). Preferentially, aluminum occupies the tetrahedral sites. Mn^{3+} and Cr^{3+} also can be incorporated in brownmillerite. C_4AMn was synthesized by Puertas, F.; Blanco Varela, M. and Dominguez, R. (1990). The crystal structure is shown in Figure 2.21. According to Mayerhofer, brownmillerite shows preferential orientation in $(0k0)$ -direction. With decreasing Al-content of the solid solution, lattice parameter b_0 mainly decreases. But, due to the increased uptake of silicon and magnesium at elevated temperatures and varying cooling rates, lattice parameters of calcium aluminium ferrites are also

TABLE 2.6 Calcium ferrites and calcium aluminum ferrates occurring in cements

Chemistry	Mineral name	Melting Point* (°C)	Space group	Lattice parameters (Å)						JCPDS-No	Occurrence and properties
				a_o	b_o	c_o	α	β	γ		
C ₄ AF	brownmillerite	1410	Pcmn	5.57	14.52	5.35	—	—	—	30-226	members of ss.-series
Ca ₂ Al _{1,38} F _{0,62} O ₅			Ibm2	5.51	14.48	5.31	—	—	—	42-1469	ferrite phase in OPC
C ₂ F	srebrodolskite	1450	Pnma	5.42	14.75	5.60	—	—	—	38-408	end member of ss series
CF		1210	tetr.	5.33	—	7.58	—	—	—	41-753	minor phase
CF ₂		1205	C2	10.41	6.01	31.65	—	96.5	—	39-1033	in HAC
C ₄ AMA				5.465	14.904	5.244	—	—	—	42-105	synthetic laboratory product

affected. In quenched laboratory samples, peak-broadening of X-ray peaks is rather common. The intensities of peaks within the solid solution is influenced by the site occupancies of aluminum and iron (Mayerhofer 1996; Walenta 1997) (Figure 2.22).

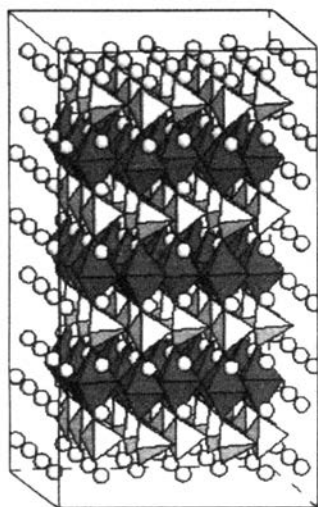
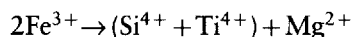


FIGURE 2.21 Crystal structure of C₄AF showing tetrahedral and octahedral coordination of (Al,Fe)O₆ and (Al,Fe)O₄ with Ca-ions.

In typical clinkers, the uptake of magnesium, titanium and silicon takes place, and can be given by the following equation:



with a Si/Ti ratio = 3 : 1 (Harrison *et al.*) The composition of these ferrite phases typically lies within the range: Ca₄Al₂Fe_{1.2}Mg_{0.4}Si_{0.3}Ti_{0.1}O₁₀.

The composition in iron-rich cements can vary from the composition given above. The influence of varying burning conditions and reducing atmosphere on the aluminum/iron ratio was shown by Sieber *et al.* Due to increased silicon solution at high temperatures, some exsolution can occur at lower temperatures forming the tertiary belite in the interstitial phase. Titanium forms in high-alumina cements phases like perovskite or C-f-T with similar structure to perovskite but with Fe²⁺ (Motzet and Pöllmann 1998). OPCs normally have only low titanium contents which may increase when addition of wastes like painting dusts are added in fabrication. Then, TiO₂-phases or ilmenite may additionally occur.

Reducing conditions can lead to the formation of Fe²⁺. This leads to increased formation of

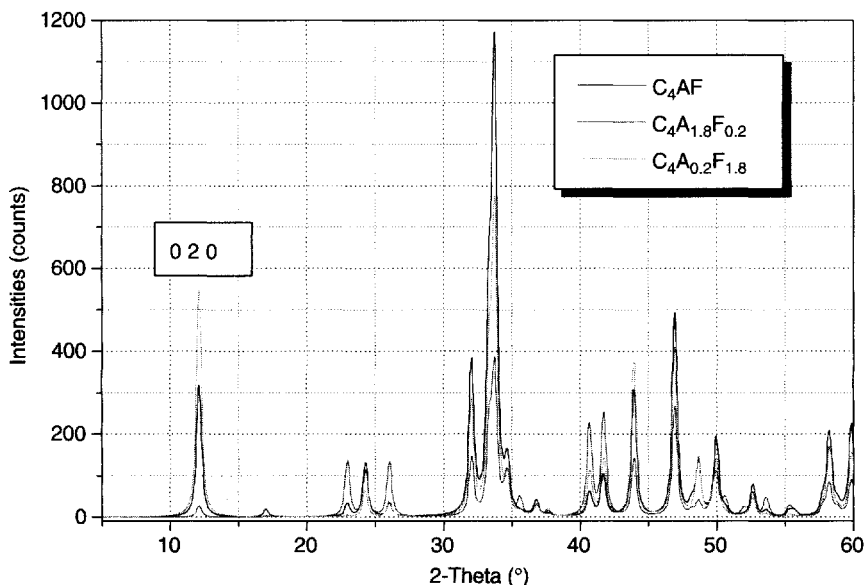


FIGURE 2.22 X-ray diagrams of ferrate phase showing different aluminum/iron contents.