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Chemistry and engineering of the clinkerization process — Incremental advances and lack of breakthroughs

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A R T I C L E I N F O

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A B S T R A C T

“Chemistry” and “process engineering” constitute the foundation of the clinkerization process but over the decades the engineering advances have been phenomenal to convert the chemical concepts into very large, fast reacting, energy-efficient and pollution-abated pyroprocessing systems.

Excepting the cooler design that still lags behind in attaining the desired cooling rate for clinker phases, notwithstanding several innovations for thermal efficiency, the rest of the engineering for the pyroprocessing system seems to be touching a plateau of efficiency parameters. However, the occurrence of volatile cycles and controls of process and quality are governed more by the systemic parameters than simple chemical behavior of the feed materials. The emission norms and the engineering control features are mostly in sync with each other, except the organic emissions of dioxins, furans, PCBs and PAHs, where more precise determination of their precursors is called for.

In respect of breakthroughs in new pyroprocessing technologies other than the conventional rotary kilns, the initiation of research dates back to eighties but the researches remain stalled perhaps in apprehension of non-viability. They need to be revived for efficiency and sustainability. The nano-cement technology should also be evaluated more intensely for its application potential.

The present keynote paper attempts to portray the present status of pyroprocessing and to define the areas of challenges lying ahead.

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1. Introduction

Over the last 190 years of existence of Portland cement the fundamentals of manufacturing chemistry have not undergone any significant changes, while considerable engineering advances have been made in the hardware and software of cement manufacture in order to achieve optimum cost and quality. These advances reflect in the following:

a) The capacity of a single kiln system has reached 12,000 tpd.
b) With automation, instrumentation and computer-aided controls, the man-hours per tonne of cement produced has come down to one or even less, thereby reducing the application of human discretion and increasing the dependence on electronic gadgets.
c) The variations in the hardware design cause differences in the chemical performance, thus necessitating precision in the hardware design.
d) The raw material characteristics and their impurities strongly influence the system performance, thus making it imperative for the hardware to be in sync with raw materials behavior.

In this backdrop, the present keynote treatise is an attempt to ascertain the recent incremental addition to our knowledge and understanding of the salient aspects of clinker manufacturing chemistry in the context of the advancements in process engineering at the operating plants. Although the basic intention was to track the progress from the 12th ICCC held in Montreal in 2007 to date, the present coverage had to start from earlier periods as the 12th Congress was overwhelmingly focused on sustainability issues of cement and concrete without any specific emphasis on “chemistry and engineering” of the traditional cement production process. Therefore for building up the theme in this paper, the raw materials preparation aspects have been touched upon for contextual requirement but the cement grinding technology which is essentially a physical process has been kept outside the purview of the paper for brevity. Effects and influences of the use of alternative raw materials and fuels on process and engineering have not been dealt with in this paper as these aspects are expected to be covered elsewhere.

2. Present perception of clinker chemistry and process technology

The major developments in cement chemistry in general and clinker manufacturing chemistry in particular over three decades from 1964 to 1989 can be perused in [1]. More specific manufacture related issues pertaining to raw materials preparation and clinkerization have been dealt with in fair details in [2–7]. Notwithstanding the widening knowledge base of materials chemistry from the engineers' perspective, the clinkerization process can still be represented in a simplified form by the reaction steps given in Fig. 1 [8]. It is evident from this summary diagram that the clinkerization phenomenon is strongly dependent on the reactivity (signifying the achievable rate of different reactions at respective temperatures within practical time limits) and burnability (signifying the overall measure of ease or difficulty of burning under practical operating conditions of raw mixes, which, in turn, depend on the intrinsic characteristics of the constituent raw materials). In this context one has to bear in mind that the burning process has several interdependent and interrelated controlling factors, as outlined in Fig. 2 [8]. Needless to mention that all the engineering advancements are based on the fundamentals that are best summarized as in the above two figures.

3. Prevalent practices and key issues of raw materials

3.1. Limestone

The process and the stoichiometric requirements have led to defining the broad chemical specification of limestone, the principal raw material for clinker production (Table 1). The reasons for specifying the limits of the constituents in Table 1 are known and have been dealt with in [2].

3.2. Preparation of raw mix and burnability features

3.2.1. Raw meal homogeneity

In general, as we all know, the raw milling is controlled for the stoichiometric requirements by the three important oxide ratios i.e. Lime Saturation Factor (LSF), Silica Modulus (SM) and Alumina Modulus (AM), which are known as modulii values in the industrial practice.

The homogenization of raw meal (which in effect is the ground raw mix) prior to pyroprocessing has always been a very important step in clinker manufacture. The most common homogenization system is the pneumatic one, which is based on air fluidization method. This system can either be discontinuous (or batch type) or continuous. The batch mode is adopted only in special cases where very high order of homogenization is required. It may have a blending factor of 20 or more. The most common practice is to have preblending of crushed limestone and continuous homogenization of ground raw mix. In plant practice the homogeneity is determined

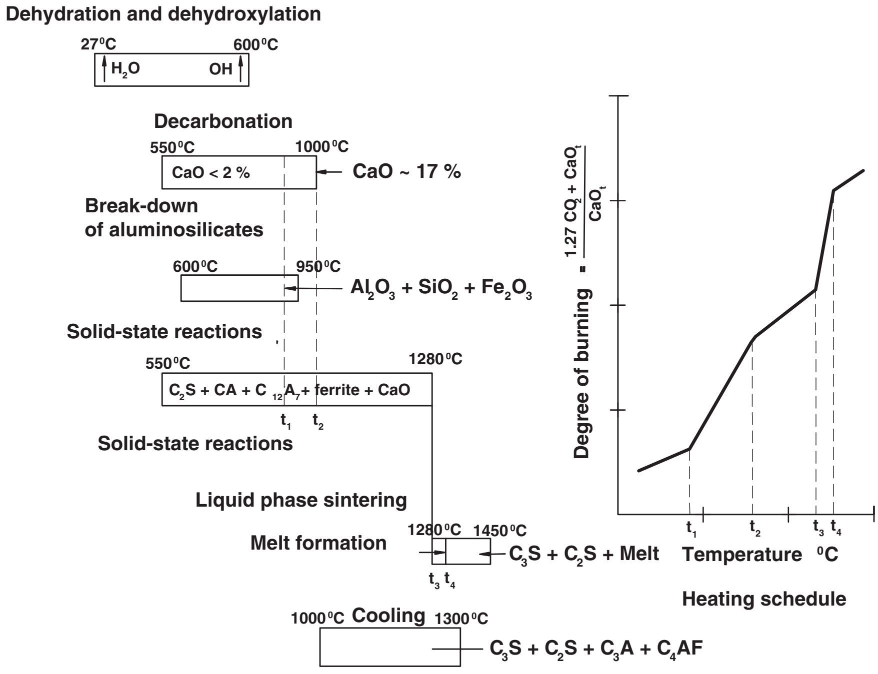


Fig. 1. Approximate reaction sequence in clinkerization at almost constant rate of heating [8].

on the basis of *n* numbers of hourly spot samples (normally 24 samples) and the targets are set as follows:

$S_{LSF} \le 1$per cent

$SCaCO_3 \le 0.2$per cent

$S_{SM} \le 0.1$

where S is the standard deviation.

In some plants the measure of homogeneity is carried out on the basis of four or eight hourly samples. These samples are analyzed for major oxides and these data are converted to potential C_3S or LSF. A kiln feed should typically have an estimated standard deviation of less than 3% C_3S or 1.2% LSF [9].

Although the homogeneity of kiln feed is expressed in terms of standard deviations of certain parameters, it should be borne in mind that it has a limitation in the sense that the standard deviations of any parameter do not distinguish between a steady trend and constant fluctuation.

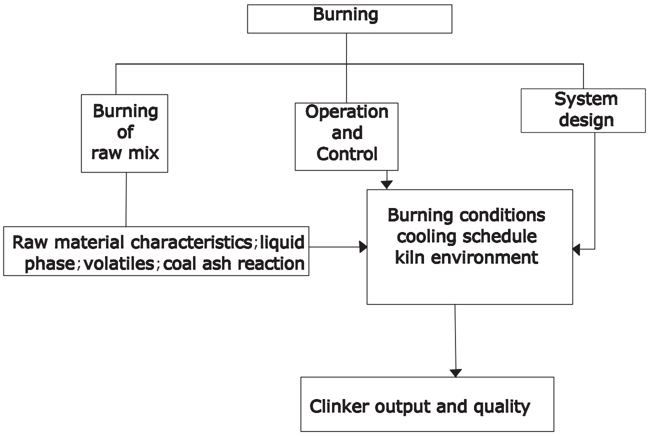


Fig. 2. Major factors controlling the burning operation [8].

3.2.2. Raw meal fineness

There are no rigid standards for raw meal fineness. It is determined empirically and should be as coarse as a given kiln system can tolerate. Typically, a raw meal is ground to about 15% residue on 88 μm sieve and correspondingly to 1.5–2.5% residue on 212 μm. But with improved burning systems and techniques residues as high as 30% on 88 μm and 6% on 212 μm are maintained in some plants with large preheater–precalciner kilns. It should be borne in mind that a narrow particle size distribution is optimally required as fines tend to increase dust loss by entrainment in exhaust gases, while coarse particles are harder to react in the kiln, resulting in high free lime or high fuel consumption.

From the considerations of burnability, it is highly beneficial to limit the top sizes of the following mineral phases in the raw meal as follows [9]:

• Silica minerals (e.g., quartz, chert, acid insoluble residue, etc.)	44 μm
• Shale particles	50 μm
• Silicate minerals (e.g., feldspar)	63 μm
• Carbonate minerals (e.g., calcite and dolomite)	125 μm

Table 1
Broad chemical specification of cement-grade run-of-mine limestone.

Constituents	Acceptable range for manufacture of ordinary Portland cement, wt.%	Limiting values taking into consideration other types of cement, scope of beneficiation or blending, wt.%
CaO	44–52	Minimum 40
MgO (max)	3.5	5
$SiO_2 + Al_2O_3 + Fe_2O_3$	To satisfy the LSF[a] and SM of raw mix	
Mn_2O_3	<0.5	<3.0
$R_2O(K_2O + Na_2O)$	<0.6	<1.0
Total S as SO_3	<0.6	<0.8
P_2O_5	<0.6	<1.0
Cl	<0.015	<0.05
Free SiO_2	<8.0	<10.0

[a] LSF = Lime Saturation Factor, SM = Silica Modulus.

It has often been claimed experimentally in the literature that every 1% increase of coarser quartz particles and every 1% increase of carbonate particles result in 0.93% and 0.51% increase in free lime respectively. Therefore, it may be advantageous to first characterize the particulate fineness on the 125 μm sieve and then acidify the mix and examine the coarse fractions (+44 μm) for their content of grains of concern. This may help to find out the ways and means of tackling hard burning characteristics of raw meals.

Another aspect in this context is worth mentioning. For all practical purposes it may be desirable to check if the +88 μm fractions of raw meals are lime-rich, relative to the total sample. For uniform and stable burning the raw meals should be ensured:

(a) to be consistently either lime-rich or silica-rich
(b) to have coarse mineral phases in the total raw meal distributed as follows:
  (i) Silica phases (>200 μm): not more than 0.5%
  (ii) Silica phases (90–200 μm): not more than 1.0%
  (iii) Silica phases (>45 μm): not more than 2.0%
  (iv) Carbonate phases (>125 μm): not more than 5%.

3.2.3. Chemico-mineralogical characteristics of raw meal

It is well known that the mineral phases present in raw meal also influence its burnability in some way. The more influencing features are recapitulated below [2]:

- Presence of ankerite [Ca(Mg, Fe)$(CO_3)_2$] or dolomite [Ca,Mg $(CO_3)_2$] causes an early release of lime in a reactive state, which may require reactive clays to enter into combination reactions.
- Presence of magnesia in the silicate form ensures the formation of small periclase crystals in clinker. Bigger crystals of periclase are likely to be present, when magnesia comes from the carbonate phase.
- Different forms of silica show different levels of reactivity as shown below:
  β-Quartz < Chalcedony < Opal
  < α-Cristobalite and α-Tridymite
  < Silica from silicates < Amorphous silica
- Ferruginous minerals like chlorite, glauconite, etc., release iron oxide in the ferrous state at early stages to give mineralizing effects.
- Alkali and sulfate bearing minerals result in the formation of volatile cycles during the burning process.

3.2.4. Effect of raw milling systems

There are three main types of raw milling systems in vogue: ball mills, vertical roller mills (VRM) and hydraulic roll presses (HRP) often in combination with ball mills. A variant of roller mill in horizontal disposition (HRM) has recently come into commercial application. New grinding installations are primarily VRMs. Roll presses are used in upgrading existing ball mills for increased production or decreased specific power consumption. All raw grinding systems are close-circuited with separators (also known as classifiers) for efficient grinding. It should be borne in mind that the productivity of the raw milling systems depends on feed size to mill, grindability of the feed material, drying capacity of the system, product fineness required and the grinding power available.

Since now wider choices are available for grinding raw mixes, a comprehensive study has been conducted with raw mixes produced in two grinding systems — one consisting of a VRM modified with LV technology and another consisting of a HRP with V-separator in combination with a ball mill with a dynamic separator [10]. The objective was to compare their chemical, mineralogical, particle size and burnability characteristics. It was observed that, despite the significant differences in the engineering design of the two systems, the particle size and burnability characteristics varied within a very narrow range. For example, the residue of calcite particles on 125 μm sieve and that of quartz particles on 45 μm sieve were marginally lower in the raw mix ground in the hybrid HRP system. Although such minor differences reflected in the laboratory-based burnability test, there was no detectable effect of the two raw mixes on the overall kiln performance and productivity.

4. Clinkerization reactions

The clinkerization reactions, as we all know, take place at the pyroprocessing stage in a plant, which extends from the extraction of the kiln feed (or the raw meal) from the post-homogenization storage to the discharge of the clinker from the cooler for being conveyed to the clinker silo.

Barring the continuance of some old wet-process or semi dry process kilns in different countries, the new and modern plants almost exclusively operate dry-process 5-stage preheater–precalciner kiln systems with efficient grate coolers. Such kiln systems are also provided with multichannel burners having high flame momentum.

For all practical purposes this system has to take care of the following four major reaction steps:

a) Dissociation of limestone
b) Solid-state reactions.
c) Liquid-phase sintering
d) Reorganization of clinker microstructure through cooling.

The above chemical transformations and the corresponding processing parameters and the relevant equipment performance occur synergistically to the extent practically feasible.

4.1. Calcination of limestone

This important chemical process involving decarbonation or dissociation reaction is dependent on the physico-chemical characteristics of the limestone on one hand and preheater–precalciner system on the other. It is well known that the calcination rate and temperature are influenced by the partial pressure of carbon dioxide in the atmosphere, the concentration of carbon dioxide in the kiln gas stream and the presence of impurities and grain size of the calcite and quartz phases. The associated minerals and microstructure also influence the activation energy for dissociation of calcium carbonate. For a given set of limestone samples the activation energy for dissociation was observed to vary from 30 to 60 kcal/mol [8].

4.1.1. Carbonate dissociation and lime combination trends in raw mixes

In the author's laboratory an attempt was made to study the simultaneous trend for carbonate dissociation and lime combinability reaction for different raw mixes in the temperature range of 800 °C to 1000 °C by determining "undecomposed lime", "free lime" and "combined lime" in fired raw mixes and plotting these values in ternary diagrams. An illustration of these trends is given in Fig. 3 (a and b) for two different raw mixes with incorporation of three different mineralizers viz., sodium silicofluoride, fluorspar and gypsum. From the curves in Fig. 3 (a and b) it is evident that the interactions of the same mineralizers on 2 different raw mixes were quite different. The basic raw mixes without any mineralizer also showed appreciable difference in their behavior at the dissociation stage.

4.2. Preheater–precalciner systems for limestone calcination

It is well known that the advent of preheater and precalciner system has contributed significantly to improving the thermal efficiency of the energy-intensive process of clinkerization. Despite the differences in details, all suspension preheaters are designed and operated on the same principle of counter-current movement of cold material and hot gases. A suspension preheater system can have any number of stages, although for all practical purposes the number is restricted to 4–6 stages. The total preheater design has been

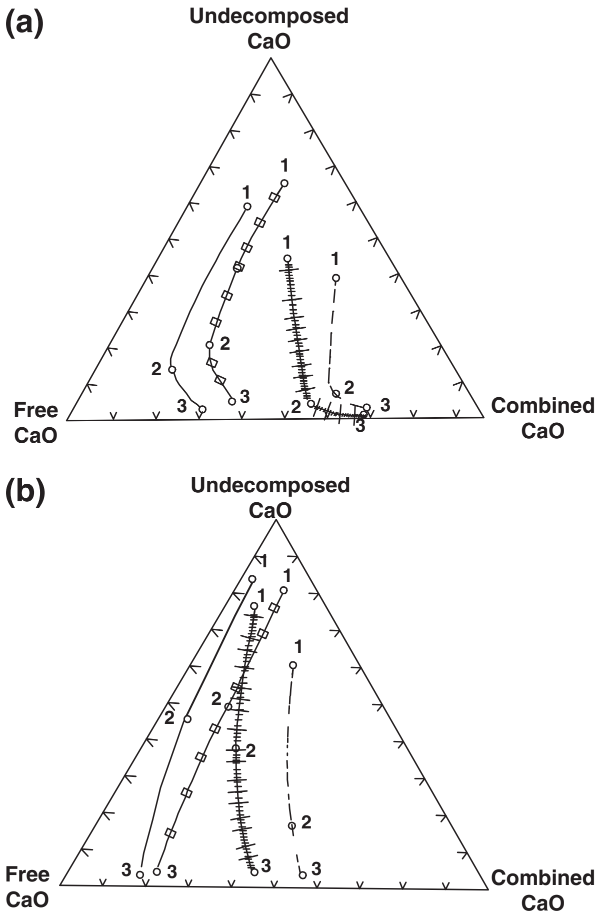


Fig. 3. Ternary plots of lime release in 2 different raw mixes.
Raw mix without mineraliser (———)
Raw mix with gypsum (–□–□–□–)
Raw mix with sodium silicofluoride (┼┼┼┼┼┼┼┼┼┼┼┼)
Raw mix with fluorspar (— — —)
1:800 C, 2:900 C, 3:1000 C

optimized and the cyclones for the various stages have been designed for specific duties, viz., higher separation efficiency for the top and bottom cyclones and lower pressure drops in the intermediate cyclones. Dust accumulation in the cyclones is reduced and the risk of material flashes is minimized.

The precalciner, being effectively the second firing stage, greatly expanded the systems capability. It became possible to generate and absorb over 60% of the total heat input in the calcination zone where the heat consumption was high due to the endothermicity of the decomposition reaction. Fuel combustion and to an even larger extent, the solids residence time depend on the gas flow regime. The calculated gas residence time varies in different designs from 1.4 to 1.7 s in systems with a separate precalciner vessel to 4–5 s in extended duct systems. Some precalciner vessels are designed with a swirling or cyclonic motion of the gas stream inside them, which gives the solids relatively longer residence time. The modern preheater–precalciner kiln systems are designed for at least 85% calcination as computed by the following equation [5]:

$$C = 100 \times 1 - \left[\frac{LOI_{\text{sample}} \times (100 - LOI_{\text{raw meal}})}{LOI_{\text{raw meal}} \times \left(100 - LOI_{\text{sample}}\right)}\right] \qquad (1)$$

Where

C = degree of calcination
LOI_{sample} = loss on ignition of the sample analysed
$LOI_{row\ meal}$ = loss on ignition of the raw meal.

One should bear in mind that it is the control of the calcination reaction that determines the stability of the kiln operation. From the experience gained with different types of precalciner kilns there appears to be a relationship between the variations in degree of calcination and the residence time of the material in the precalciner. The systems with shorter solids residence time tend to demonstrate wide fluctuations of calcination.

Another important aspect of precalciner operation is the temperature of the tertiary air. The higher the temperature, the lower the heat consumption and more stable is the kiln system. Thus, the precalciner kiln systems get strongly linked with the design and efficiency of the clinker coolers.

The basic configurations of precalciner systems are related to the flow of secondary air and tertiary air from the kiln and cooler respectively into the precalcining system (Fig. 4) [5]. It may be interesting to note that while the total flow calciner operates with combustion gas, impoverished in oxygen (10–14%), the tertiary air flow calciner operates with hot air containing 21% oxygen. The hybrid type starts the combustion under oxidizing condition but moves into a reducing state due to the mixing of the kiln combustion gases.

The nomenclatures frequently used to describe the above basic designs of precalciner systems are the following:

(i) AT (Air Through): precalciner or riser duct firing using combustion air drawn through the kiln.
(ii) AS (Air Separator): precalciner using tertiary air.

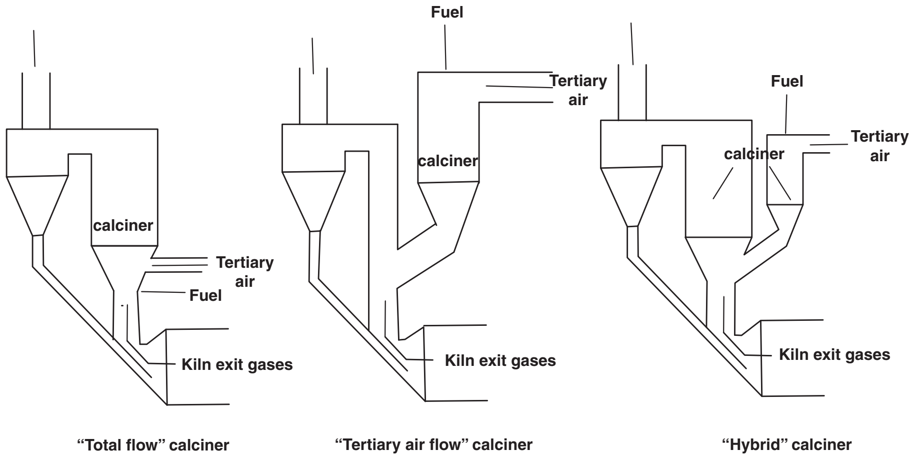


Fig. 4. Basic types of precalciners [5].

- (iii) ILC (In-line Calciner): AS calciner in which kiln exhaust gases and tertiary air are premixed before entering the calciner vessel.
- (iv) SLC (Separate Line Calciner): AS precalciner vessel in parallel with the kiln riser and fed only with gas from the tertiary duct.

The more widely used commercial systems include MFC (Mitsubishi Fluidised-Bed Calciner), RSP (Reinforced Suspension Preheater with Air Separate/Separate Line Calciner of Onoda design), SF (Suspension Preheater with Flash Furnace of Air separate/In-line Calciner of IHI design, etc.).

It is relevant to mention here that the plethora of design variation of preheater–precalciner systems is aimed towards achieving the following objectives:

- a) Meeting the contradictory demands of minimizing the temperature and oxygen levels and complete burn-out of fuel.
- b) Relief of the thermal load in the rotary kiln.
- c) Controllable degree of calcination.
- d) Abatement of NO_x emission.
- e) Use of alternative or hard-to-burn fuels.

So far as the above objectives are concerned, and more particularly the last one, the cement machinery industry has come out with calciner solutions for different fuel scenarios as shown in Fig. 5 [11].

It may be pertinent to recall that the heat of dissociation of $CaCO_3$ is 403 kcal/kg at 900 °C [12] which signifies the emphasis laid on the energy-efficient design of preheater–precalciner systems.

4.3. Kiln systems and clinkerization reactions

The permutation and combination of different preheater–precalciner configurations with even a single type of cooler, e.g., the grate cooler, can result in a wide range of pyroprocessing systems. It is possible to design and operate kiln systems having capacity of up to 12,000 tpd as shown in Fig. 6 [13].

Another significant development in rotary kiln systems is the design of short two-support kilns with length-to-internal-diameter ratio of 10 to 14. This is considerably lower than the typical ratio of 16 to 18 of 3-support systems. Two-support kilns are larger in diameter than three-support kilns for the same production rate and volumetric loading and therefore have lower thermal loading than a traditional kiln (Fig. 7) [13].

The success of 2-support kilns has been accompanied with quite a few mechanical innovations like tangential tyre suspension, double-lamella seals, etc., which, for obvious reasons, are not being dealt with in this article. While these short kilns offer substantial economic and mechanical advantages, they meet all the process technology requirements for the clinkerization process, despite the fact that the average residence time in such kilns is of the order of 21 min or about half the time of conventional kilns. Depending on the burnability of raw materials and the clinker quality desired, the volumetric loading ranges from 4.5 to 5.3 tpd/m^3. The kiln diameter does not exceed 6 m to ensure reasonably long refractory lining life.

It is obvious that under plant conditions the entire pyroprocessing of raw meals is complete in about 20 min. There is hardly any reliable database available on such fast course of phase formation in short kilns after the nascent and reactive oxides are available from the calcination of carbonates and breakdown of aluminosilicates. However, it is expected that all the reactions known to occur at subsolidus temperatures in raw meal followed by the reactions in the presence of the melt phase would take place in the operating kiln systems. Of particular interest are the transient or intermediate phases that are formed and again resorbed in the melt phase, ultimately leading to the appearance of the final clinker phases. In the laboratory of the author an endeavor has been made to standardize an experimental approach to ascertain such appearance of intermediate subsolidus phases and their disappearance in the melt phase, which is described below.

4.3.1. Raw meal burnability evaluation by volume change on firing

Unlike the conventional approach of evaluating the burnability of raw mixes on the basis of free lime–temperature plots, an experimental approach has been standardized for assessing the lime combinability reactions by determining the volume change of raw mix pellets fired at different temperatures as detailed below:

- a) Preparation of homogenized raw mix or kiln feed including the likely incorporation of coal ash, maintaining the fineness as obtained in the plants as desired.
- b) Preparation of pellets of 3.3 × 1.5 cm size under a pressure of 500 kg/cm^2.
- c) Firing of pellets at temperatures ranging from 800 °C to 1400 °C.
- d) Removal of pellets at intervals of 100 °C in the above range of temperature, after a soaking of 30 min and immediate measurement of their firing shrinkage/expansion.
- e) Plotting of pellet volume change against temperature.
- f) Interpretation of the plots.

The plots are characteristic of the raw mixes as no two patterns are exactly alike. The identity of each pattern is observed through the entire temperature range. The initial expansion of the fired pellets indicates the solid state reactions forming the intermediate phases; the subsequent trend of shrinkage shows the appearance and quantity of the liquid phase and finally the compressive strength of the pellets at 1400 °C throws light on the expected granulometry of the clinker.

An illustration of a specific study is given in Fig. 8 (a and b). Two different raw mixes separately were subjected to the above test along with the incorporation of the same set of three mineralizers, e.g., sodium silicofluoride, fluorspar and gypsum as explained in the figure. Based on the volume change versus lime combinability plots as well

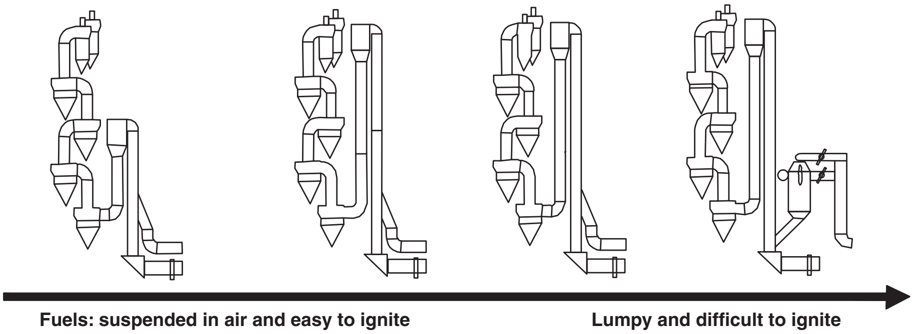


Fig. 5. Fuel compliant flash tube calciners of KHD design [11].

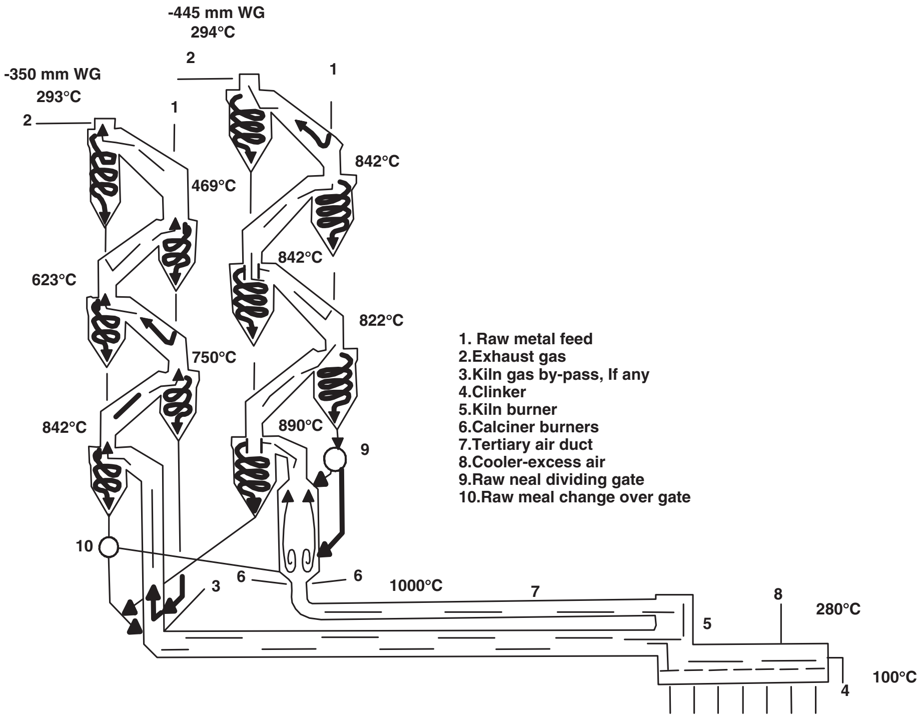


Fig. 6. A typical schematic representation of a modern large kiln system (FLS design) [13].

as the XRD scans of a few selected fired products, the following observations could be made:

- Expansion maxima are generally observed when the combined lime is more than 60% of the total lime available in the clinkers. Any shrinkage in this temperature range is indicative of vigorous formation of intermediate phases at the cost of delayed appearance of actual clinker phases.
- The magnitude of expansion maxima is an overall reflection of the total phase assemblage and not of the presence and absence of individual phases.
- Appearance of intermediate phases like $C_{12}A_7$, CA_2, CS, etc., generally promotes shrinkage and conversely high lime aluminates like C_3A and high lime silicates like C_2S result in expansion.
- Formation of CA_2 tends to result in higher shrinkage than $C_{12}A_7$.
- High expansion at higher levels of combined lime, when preceded by some amount of shrinkage, indicates incipient appearance of a melt phase.

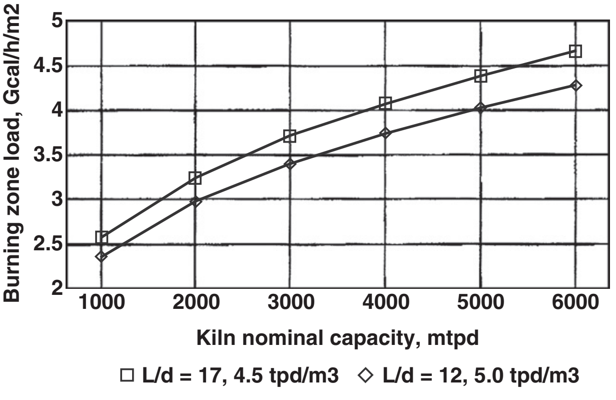


Fig. 7. Comparison of burning zone thermal loads of traditional kiln ($L/D_I = 17$) and of short kiln ($L/D_I = 12$) [13].

In the temperature range beyond the occurrence of expansion maxima, there is invariably an intense shrinkage. The total shrinkage value of each raw mix is taken as the value obtained at 1400 °C from the maximum expansion point prior to this temperature. This set of data indicates the relative effect of the liquid phase formed for each blend within this temperature range. Further, when the strength of the pellets is determined for the products fired at 1400 °C, an idea is obtained regarding the expected granulometry of the clinker. Whenever required, correlation is also attempted between the mineralizing constituents and reaction products by determining the mineralizer constituents like F, SO_3 etc. in reaction products showing maximum expansion or shrinkage or both.

It is obvious from the above illustration that the thermal behavior of raw meals can be appreciably variable but, interestingly, the kiln operation primarily with the control of feed and fuel takes care of such variations. This is where one finds strong discordance between the laboratory studies and clinkerization under plant conditions.

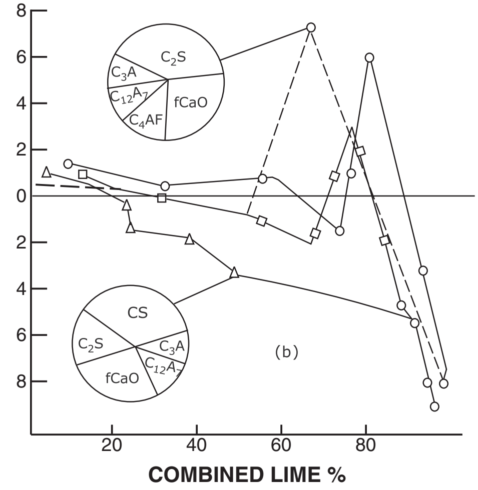
4.3.2. Relatively recent laboratory studies on clinker phase formation

Studies on the effect of minor constituents on the clinker phase formation have continued to engage the attention of the scientists in many parts of the world. The influence of foreign oxides on the lattice parameters and reactivity of pure clinker phases was reported in [14]. It was shown that the change in reactivity by doping oxides was not directly linked with the intensity of changes in the lattice parameters. It was more a function of the kind and concentration of doped foreign oxide, e.g., MgO, Al_2O_3 and Fe_2O_3 in the C_3S phase and Fe_2O_3, SiO_2 and Na_2O in the C_3A phase.

Another study on the effect of phosphorous and fluorine on the formation of alite-rich clinker led to the conclusion that the alite polymorph changed from monoclinic (M_3) to rhombohedral and there was improvement in cement strength [15].

Significant attention has been paid to reascertaining the influence of alkalis and sulfates on the phase characteristics [16,17]. It was observed that as the sulfate content increased, the C_3S/C_2S ratio decreased. At 2.5% sulfate content there was no formation of C_3S. Sulfur was preferentially incorporated in the C_2S phase along with

(a) Raw mix 1



(b) Raw mix 2

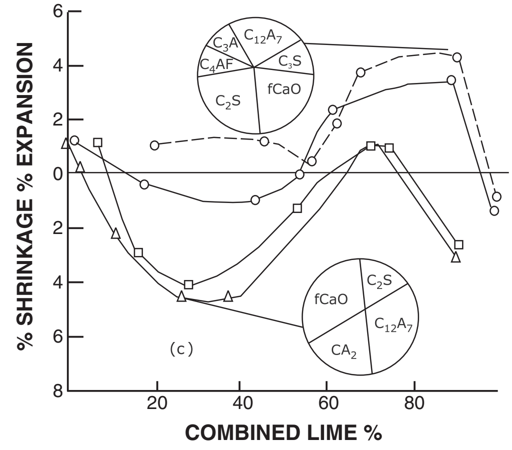


Fig. 8. Curves showing the relationship between volume change of two different raw mixes in the temperature (800–1400)°C.

Raw mix without mineraliser (————)
Raw mix with gypsum (–⊟–⊟–⊟–)
Raw mix with sodium solicoflouride (ǂǂǂǂǂǂǂǂǂǂ)
Raw mix with flouspar (— — ——)
1:800 °C, 2:900 °C, 3:1000 °C

increased inclusion of aluminum and iron. The addition of sodium oxide caused the orthorhombic C_3A to appear.

A specific study has been reported on the phase assemblage of high-belite clinker containing alkali and sulfate in the quaternary system $CaO–SiO_2–Al_2O_3–Fe_2O_3$ [18]. It was seen that an active belite clinker with one per cent potassium oxide plus one per cent sodium oxide added to the raw mix contained 8.5% β-C_2S, 21.2% $\alpha'_H - C_2S$, 24.1% $\alpha - C_2S$ and 18.9% total C_3S, 17.3% C_2A and 18.0% C_4AF. In the absence of alkalis the belite phase essentially stabilized the β-polymorph. With combined addition the alkali oxides helped stabilize the high-temperature polymorphs.

The crystal structure of low-magnesium alite has been deciphered with the help of Rietveld quantitative phase analysis [19]. As a part of this study the laboratory and commercial clinkers were studied by synchrotron X-ray powder diffraction and the Rietveld method. It was observed that the alite refined volumes (V/Z) might be useful to predict the magnesia content of a clinker and the alite type. Thus a refined V/Z value between 121.0 and 121.3 A^3 should contain up to 1.0% MgO and the alite polymorph would be T_3 type. If the value is smaller than ~119.8 A^3, the clinker might contain more than ~2.1% MgO and the alite polymorph would turn out to be M_3 type. However, the application of these results to commercial materials would certainly call for some caution because of the simultaneous influence of the foreign ions.

4.3.3. Coolers and reactions during the clinker cooling

Cooling is an integral and essential process of clinkerization. It generally occurs in two steps:

(a) inside the kiln between the burning zone and the kiln discharge end;
(b) inside the cooler.

In the first step the clinker is cooled from the burning zone temperature to about 1200 °C–1250 °C and in the second step the cooling process continues to about 100 °C.

The clinker coolers are necessary not only for freezing the final clinker phase assemblage and microstructure but also for preheating the combustion air and making the clinker transportable. Needless to mention that, although the reciprocating grate coolers were developed to overcome the deficiencies of rotary and planetary coolers as far back as 1951, this is the system that has become suitable to-day with further mechanical improvements to match clinker capacities of 12,000 tpd production.

Keeping in mind the requirements of transport efficiency and uniform aeration, a large number of mechanical improvements have been effected in the grate coolers even after the switch-over from traveling grates to reciprocating grates. These improvements include grate design, air flow regulators, sealing devices, etc. The IKN Pendulum Cooler, the Pyrofloor clinker cooler of KHD, the Polytrack clinker cooler of Polysius, the SF Cross Bar clinker cooler of FL Schmidt, etc. are some of the improved variants that are in operation in the cement industry.

A special mention may be made of a new Revolving Disc Cooler (RDC) designed and developed by CemProTec (Fig. 9) [19]. It is a revolving cooler installed below the discharged end of the kiln and is provided with a Clinker Distribution System (CDS) above a slowly rotating disc. Smart Blade Grate system that is used in other models of coolers as well, forms the RDC grate surface. A number of aerated compartments underneath the rotating disc provide cooling air to the Smart Blade Grate System and also to the clinker bed. A special removing device discharges the clinker onto a Roller Crusher, located at the outer diameter of RDC. The diameter of RDC is synchronized with kiln diameter and kiln capacity. The total residence time in this cooler is estimated at 30 min, which is somewhat lower than a reciprocating grate cooler (~45 min).

The effect of cooling conditions on clinker quality is well known but the correlation of clinker quality with specific cooling schedule has proved difficult due to interactive effects of many parameters. It appears that slow cooling up to, say, 1200 °C with rapid cooling to the discharge

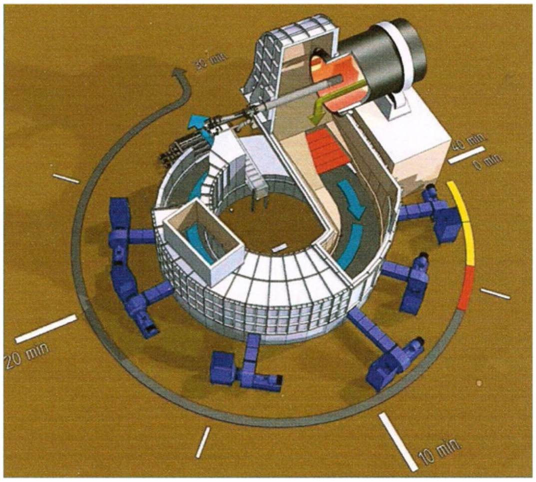


Fig. 9. Revolving disc cooler of CemProTec design [16].

temperature is expected to maximize the formation of alite, calcium aluminate and alumino-ferrite phases. With slow cooling in the range of 1200° to 1000 °C often there is a tendency for decomposition of alite with release of free lime. It may also alter the polymorphic form of belite. In addition, it results in coarsely crystallized clinker with poor grindability. The slow cooling, as is well known, may result in the crystallization of coarse periclase grains, if the clinker has high magnesia content.

In view of these observations it is evident that the total effect of cooling is the result of cooling inside and outside the kiln. As a result, the differences in the cooling schedule obtained in different types of coolers assume a lower degree of significance in modifying the clinker quality. In fact it has been proven in practice that no significant difference in the quality characteristics of clinker is detected when different types of coolers are used [20].

The process importance of the cooler design is in practice, more for heat recuperation than clinker quality. As already mentioned earlier, an important aspect of precalciner operation is the temperature of the tertiary air for both fuel economy and kiln stability. This demands that the cooler design and operation should ensure a consistently high efficiency. It may be borne in mind that small differences in cooler throat, kiln hood, tertiary air off-take, secondary air temperature and velocity can have an enormous effect on the air flow patterns for combustion of fuel.

4.3.4. Kiln burners and combustion

The kiln burner technology has undergone substantial improvements and burners with multiple channels for air and fuel flow are being universally used. The multiple channels provide flexibility in changing the flame shape and its intensity by the control of air flow in the axial and swirl channels, air velocities and adjustment of burner position. Three-channel and five-channel burners are in operation. While the three-channel solid fuel burners have the provision of feeding additionally a gaseous or a liquid fuel, the five channel burners are designed for simultaneous firing of three fuels in proportioned quantities [21].

Further improvement in burner technology has been reported in [11]. The essence of the new burner design is a sandwich concept, in which the fuels are captured between two air streams and exposed to high oxygen accessibility and turbulence. As an aid for need-based flame shaping the outer jet streams can be directed in different angles, forming either a convergent or a divergent or a rotational flow pattern. For this purpose the jet nozzles are individually mounted on air supply tubes, which can be rotated over 360° (Fig. 10) [11].

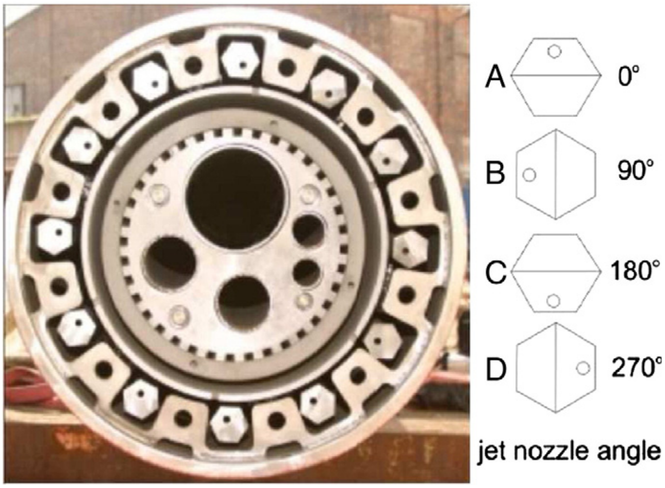


Fig. 10. Rotational jet nozzles [12].

5. Volatile cycles

A comprehensive review on the role of volatiles in cement manufacture and use was presented in [22]. Although this review was made in the nineteen eighties, no radically new addition of knowledge and data in the last three decades has come to light so as to alter the concept and practices in cement plants. The volatiles encountered in the kiln feed, fuel, process water and certain mineralizers include compounds of potassium, sodium, sulfur, chloride, fluorine and zinc. While the first four are more widely encountered in practice, the last two elements come into picture mostly when special raw materials or mineralizers are used.

The system volatility is a function of the primary volatility of the constituents. The condensation-evaporating cycles can be conceived to be functions of such system volatility and the associated factors (see Fig. 11) [23]. A bypass becomes necessary particularly when the feed chemistry is unfavorable with the molar ratio of alkalis-to-sulfate being much removed from unity, the chloride-to-sulfate ratio exceeding unity or the chloride content being more than 0.015%.

As a guide, the acceptable concentration limits of volatile constituents as percentage of clinker in the kiln riser duct are [5]:

R_2O <3–5%

SO_3 <3–5%

Cl^- <1.2–1.6%.

The coating condition to be expected in the event of simultaneous presence of Cl^- and SO_3 in hot meal is diagrammatically shown in Fig. 12 [24].

The factors such as higher gas velocity, higher burning zone temperature, higher concentration of carbon dioxide in the kiln atmosphere, etc, are known to promote volatility of alkalis. The reducing conditions increase the volatility of sulfur.

For all practical purposes the alkali sulfates are important in the condensation process; other species such as the alkali hydroxides or elemental alkalis are not observed to condense but they are of great importance in mediating the vapor transport processes [7].

The continuous increase of alternative fuel consumption in recent years has led to considerable increase of chlorine input into the kiln system, the operational consequences of which are widely known. In order to avoid these problems, the design and application of a new chlorine bypass system REDUCHLOR has been reported in [24]. The bypass ratio was only 5% of the kiln inlet gases (1100 °C, −3 mbar) due to very high volatility of chlorine. But it required to be mixed with almost 500% of cooling air and 340% of raw mill exhaust gases to cool down the kiln gases to 200 °C. The gas mixture was compressed by a quenching fan via a pipe into a quenching chamber, which happened to be a special feature of the system. Another important engineering feature was a dust handling system that could tackle the problematic pneumatic transport of high-chlorine bypass dust. The guarantee features of such a bypass system are shown in Fig. 13 [24].

5.1. Modeling the volatile cycles

The Research Institute for the Cement Industry in Dusseldorf has attempted to develop a model for the circulating sulfur, chlorine and alkali systems in the clinker burning process [25]. The approach was made to first work out models of different plant components, viz., cyclone preheater, calciner, bypass, rotary kiln and grate cooler. They were mathematically linked with one another, ultimately leading to the modeling of the steady-state condition of the entire rotary kiln plant. Fig. 14 [25] shows the comparison of measured and calculated levels of circulating compounds in different parts of the kiln system. The model calculations for the circulating sulfur, chlorine and alkali

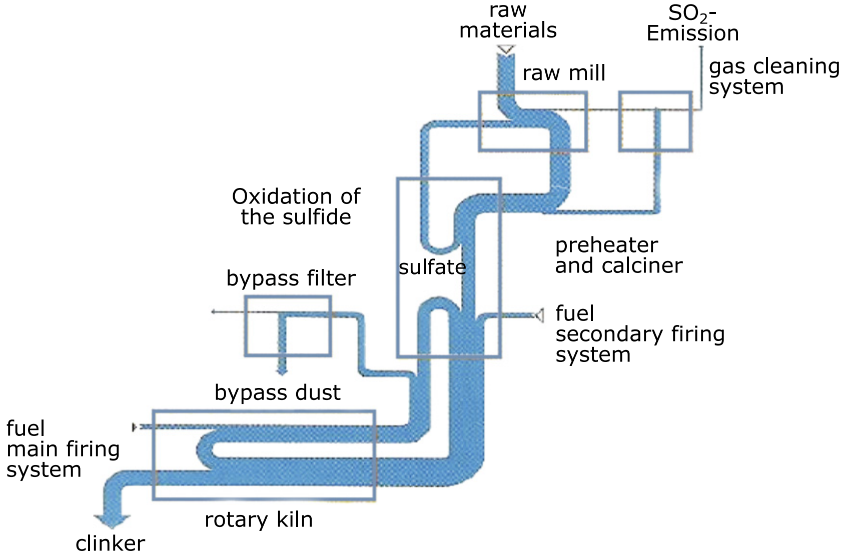


Fig. 11. A typical sulfur cycle in a preheater–precalciner kiln [23].

constituents were in fair agreement with the plant measurements in most of the situations, although there were differences at some points.

The model was based on energy and material balances for the kiln plant that had been divided into about 1000 balance locations. The most important chemical reactions calculated in these locations are the calcination of the limestone, the clinker phase formation and the combustion of fuel. Most of the process engineering principles concerned the circulating dust systems, which included the repeated mixing and separation of gas and dust in the cyclone stages and the entrainment of dust in the kiln and the cooler. The particle size distribution of the clinker in the cooler, which can have a significant influence on energy consumption, was also taken into account. The heat engineering equations for radiation, convection and conduction were taken from the reference books.

As a possible application of the modeling one may illustrate the following situation. It is known that energy used in the kiln for vaporization of alkali chlorides is released again in the lower part of the preheater during condensation. Depending on the inputs, this can result in the formation of substantial circulating systems having significant effects on the local energy balances. This kind of displacement of heat from the kiln to preheater or precalciner could be measured in this model. The model could also be extended to the design studies for the clinker burning process and could obviously be used as a supporting tool for solving operational problems.

6. Emission chemistry and technological solutions

In modern dry process cement plants the emissions can be best described under the following categories:

6.1. Inorganic gases and solids

i) Carbon dioxide emitted from the carbonate and fuels accounts for the major share of the kiln exhaust gases.
ii) Dust emitted from the process is generally limited to less than 30 mg/m^3 of gases by employing dust arresting facilities.
iii) Nitrogen oxides (NO_x) directly related to high flame temperature (1850°–2000 °C) consists of 95% nitrogen monoxide (NO) and about 5% of nitrogen dioxide. Since most of NO gets oxidized to NO_2 under atmospheric conditions, emissions are reported as NO_2 per cubic meter of exhaust gases. Fuel NO_x might be added from the precalciner fuels. The total range of emissions are reported in the range of 300 to 2000 mg/Nm^3. Without reduction measures the process-related NO_x contents in the exhaust gases

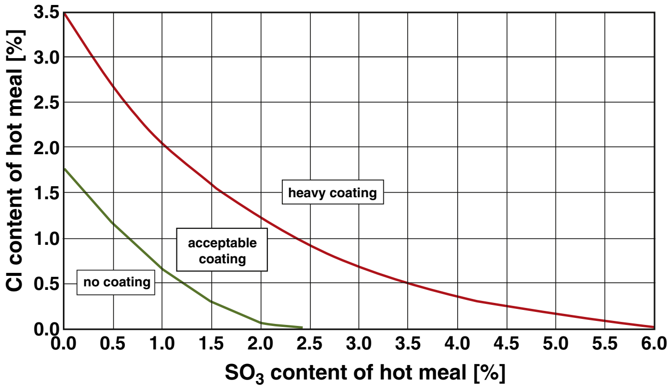


Fig. 12. Coating condition as related to the presence of sulfate and chloride [24].

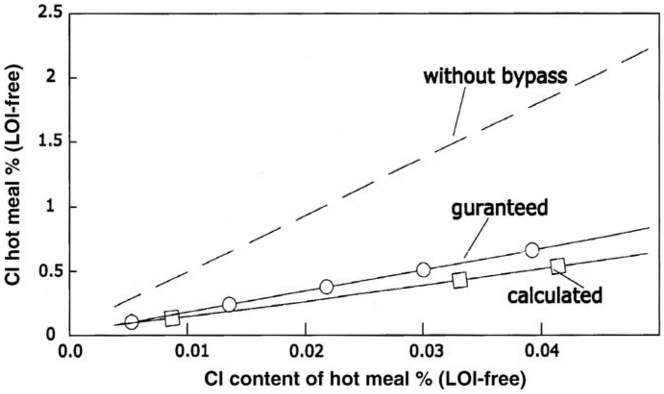
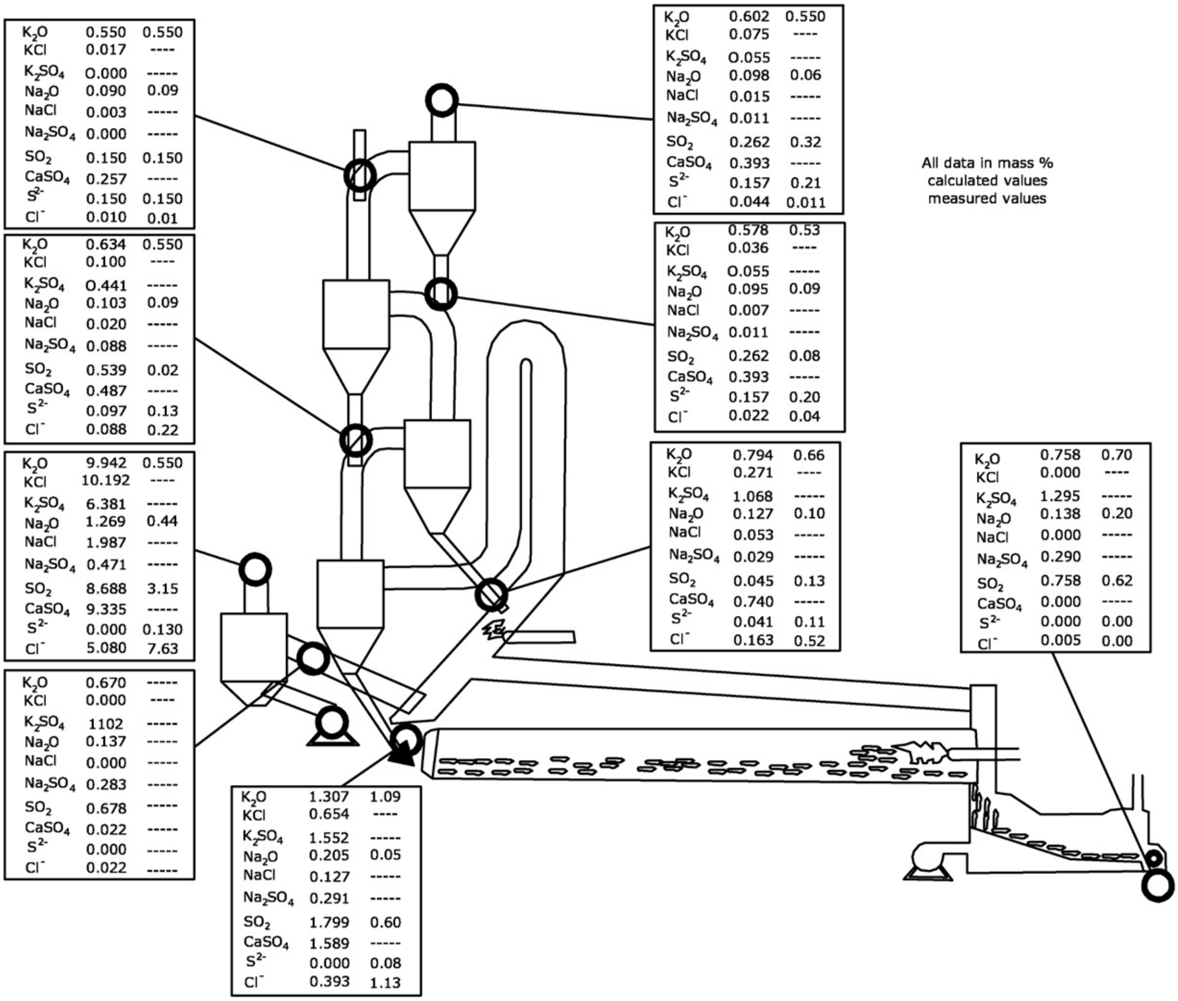


Fig. 13. The guaranteed level of Cl in hot meal with bypass [24].



K_2O	0.550	0.550
KCl	0.017	----
K_2SO_4	0.000	-----
Na_2O	0.090	0.09
NaCl	0.003	-----
Na_2SO_4	0.000	-----
SO_2	0.150	0.150
$CaSO_4$	0.257	-----
S^{2-}	0.150	0.150
Cl^-	0.010	0.01

K_2O	0.634	0.550
KCl	0.100	----
K_2SO_4	0.441	-----
Na_2O	0.103	0.09
NaCl	0.020	-----
Na_2SO_4	0.088	-----
SO_2	0.539	0.02
$CaSO_4$	0.487	-----
S^{2-}	0.097	0.13
Cl^-	0.088	0.22

K_2O	9.942	0.550
KCl	10.192	----
K_2SO_4	6.381	-----
Na_2O	1.269	0.44
NaCl	1.987	-----
Na_2SO_4	0.471	-----
SO_2	8.688	3.15
$CaSO_4$	9.335	-----
S^{2-}	0.000	0.130
Cl^-	5.080	7.63

K_2O	0.670	-----
KCl	0.000	----
K_2SO_4	1102	-----
Na_2O	0.137	-----
NaCl	0.000	-----
Na_2SO_4	0.283	-----
SO_2	0.678	-----
$CaSO_4$	0.022	-----
S^{2-}	0.000	-----
Cl^-	0.022	-----

K_2O	0.602	0.550
KCl	0.075	----
K_2SO_4	0.055	-----
Na_2O	0.098	0.06
NaCl	0.015	-----
Na_2SO_4	0.011	-----
SO_2	0.262	0.32
$CaSO_4$	0.393	-----
S^{2-}	0.157	0.21
Cl^-	0.044	0.011

K_2O	0.578	0.53
KCl	0.036	----
K_2SO_4	0.055	-----
Na_2O	0.095	0.09
NaCl	0.007	-----
Na_2SO_4	0.011	-----
SO_2	0.262	0.08
$CaSO_4$	0.393	-----
S^{2-}	0.157	0.20
Cl^-	0.022	0.04

K_2O	0.794	0.66
KCl	0.271	----
K_2SO_4	1.068	-----
Na_2O	0.127	0.10
NaCl	0.053	-----
Na_2SO_4	0.029	-----
SO_2	0.045	0.13
$CaSO_4$	0.740	-----
S^{2-}	0.041	0.11
Cl^-	0.163	0.52

All data in mass %
calculated values
measured values

K_2O	0.758	0.70
KCl	0.000	----
K_2SO_4	1.295	-----
Na_2O	0.138	0.20
NaCl	0.000	-----
Na_2SO_4	0.290	-----
SO_2	0.758	0.62
$CaSO_4$	0.000	-----
S^{2-}	0.000	0.00
Cl^-	0.005	0.00

K_2O	1.307	1.09
KCl	0.654	----
K_2SO_4	1.552	-----
Na_2O	0.205	0.05
NaCl	0.127	-----
Na_2SO_4	0.291	-----
SO_2	1.799	0.60
$CaSO_4$	1.589	-----
S^{2-}	0.000	0.08
Cl^-	0.393	1.13

Fig. 14. Comparison of measured and calculated levels of circulating compounds in the feed material, hot meals, clinker and bypass dust [25].

would in most cases considerably exceed the specifications (see Table 2). The reduction measures like water cooling of main flame, use of low NO_x burners or low NO_x calciners (creating reducing zones) are effective to a limited extent. But appreciable reductions can be achieved with selective Non-Catalytic Reduction (SNCR) with ammonia or urea in suitable temperature windows [19].

Table 2
Some examples of emission norms of cement plants [27].

Emission component and measurement units (24 h average values)	World bank	EU Waste Incineration Directive	USA (w/o waste firing)
NO_x (mg NO_2/Nm^3 at 10% O_2)	600	500 (800 for existing plants)	500 (new) (variable for existing)
SO_2 (mg NO_2/Nm^3 at 10% O_2)	400	Negotiable	Negotiable
Dust (mg/Nm^3)	50	30	25
CO (mg/Nm^3)		Negotiable	Negotiable
TOC (mg/Nm^3)		Negotiable	77.1
Dioxins and furans (ng/Nm^3 at 10% O_2)		0.1	0.16
Heavy metals			
Hg (mg/Nm^3 at 10% O_2)		0.05	
Cd + TI (mg/Nm^3 at 10% O_2)		0.05	
Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V (mg/Nm^3 at 10% O_2)		0.5	
HCl (mg/Nm^3 at 10% O_2)		10	
HF (mg/Nm^3 at 10% O_2)		1	

iv) Sulfur dioxide emissions from the rotary kiln systems are often attributable to the sulfides contained in the raw material generally in the form of pyrite or marcasite which oxidizes to form SO_3 at the temperatures between 370° and 420 °C. The sulfur input from the fuels is completely converted to SO_2 during the combustion process. Depending on the inputs from the raw materials and fuel, in most situations the SO_2 content in the exhaust gases remains below 300 mg/Nm^3. But in situations where high sulfur fuels are used the value may go up to 3000 mg/Nm^3 or beyond.

The reduction technique is the well known desulfurization process with hydrated lime but it generally becomes effective when the SO_2 content in the exhaust gases are below 700 mg/Nm^3, beyond which one may have to take recourse to wet sulfur scrubber technology.

It may also be pertinent to recall that the SO_2 in the kiln gases also has the opportunity of reacting with alkalis to form alkali sulfates which get entrapped as a clinker phase under oxidizing conditions in the kiln.

v) Minor emissions of CO and organically bound carbon during the clinker burning process are caused by the small quantities of organic constituents present in the raw materials which during preheating become oxidized to form CO and CO_2. In this process small quantities of total organic carbon are also formed. These are apparently not directly related to combustion processes and no practical preventive measures are taken under normal circumstances.

6.2. Organic emissions

i) Dioxins and furans are the organic pollutants having carcinogenic and mutagenic potentials. They form when there are organic precursors present in the fuels and in the flue gases. Polyvinyl chloride, chlorotoluenes, chlorophenols and sodium chloride are recognized as precursors of dioxins and furans. Formation of the latter compounds is catalytically accelerated by raw meal or cement kiln dust and is promoted in the temperature range of 290°–790 °C with furans becoming predominant above 700 °C. The range of emissions varies from non-detectable values to less than 0.1 mg/Nm^3. Rarely values of 2–3 mg/Nm^3 have been noticed.

   Control of dioxin and furans formation is possible by reducing the flue gas temperature below 260 °C. The number of stages in the preheater design is therefore of significance in this context. Further the systems should be so configured that the exit temperature of gases from the preheater can be sufficiently reduced by the use of water spray, particularly when the raw mill is not running.

ii) The emission behavior of polychlorinated biphenyls (PCB) is similar to that of dioxins and furans. The polycyclic aromatic hydrocarbons (PAHs) in the exhaust gases usually appear with predominance of naphthalene (>90%). Emissions owe their origin, as mentioned earlier, essentially to the presence of organic constituents in the raw materials, as the contributions of such constituents from the fuels get destroyed in the rotary kiln firing.

iii) BTEX — the acronym popularly used for Benzene, Toluene, Ethylbenzene and Xylene are formed during the thermal decomposition of organic raw material constituents in the preheater and when present in the exhaust gases, they appear in a characteristic ratio. Not much measurement details and formation conditions are available in the literature. The range of emission of benzene is reportedly 1–2 mg/Nm^3, higher values being extremely rare.

   For all the above organic pollutants, no abatement techniques of practical significance are known, except limiting the inputs through raw materials.

6.3. Inorganic acids

i) Chlorides available from the raw materials and fuels generally enter into the formation of volatile cycles described earlier. Thus gaseous inorganic chloride compounds are generally not emitted with the exhaust gases, unless the inputs exceed the carrying capacity of the pyroprocessing system. Even under such conditions the range of emission remains below 10 mg/Nm^3. No direct HCl abatement technique is readily available but it is claimed by the equipment suppliers that the wet sulfur scrubbers can reduce HCl emissions as well.

ii) When fluorine is present in rotary kilns, 90–95% of it is bound in the clinker and the remainder goes with the dust in the stable form of CaF_2. Ultrafine dust fractions that escape the measuring gas filter may give an impression of low contents of gaseous fluorine compounds in the exhaust gases.

6.4. Heavy and trace metals

A fairly detailed status report on the effects of minor elements in cement manufacturing is given in [26]. Narrowing down our focus here on only heavy and trace elements and relying on the observed plant behavior, one may summarize the following observations:

a) In the clinkerization process arsenic, nickel and vanadium remain non-volatile and become entrapped in clinker.

b) Lead and cadmium preferentially react with excess chlorides and sulfates and form volatile cycles between kiln and preheater. Ultimately they remain entrapped in clinker.

c) Thallium forms a chloride phase and condenses in the upper zone of the preheater (450°–500 °C). Consequently a cycle is formed between preheater and raw mill drying section.

d) Mercury and its compounds are not precipitated in the kiln and the preheater and escape with the exhaust gases.

On the whole the heavy and trace element emission levels are low under normal circumstances.

The prevalent limits of emissions of different constituents in the dry-process preheater–precalciner kiln systems are given in Table 2. Throughout the world there is a focus on controlling emissions from cement plants, although they vary significantly from country to country and are strongly influenced by the local considerations.

6.5. Advances in chromium reduction

Portland cements can have total chromium levels between 100 and 300 ppm. In the oxidizing and alkaline burning conditions of the kiln, Cr (VI) may form. Chromium (VI) compounds are classified as extremely toxic because of their high oxidation potential and their ability to penetrate human tissue. They have a high solubility in water and thus can easily come into contact with the skin during manual handling of wet mortar and concrete, causing skin troubles. Portland cement clinker typically has a water-soluble Cr (VI) level of up to 30 ppm, with majority lying between 5 and 15 ppm. In view of this, there is an EU directive since 2005 which restricts the marketing and use of cement and cement-based preparations where they contain, when hydrated, more than 0.0002% (2 ppm) Cr (VI) of the dry weight of cement.

Hence it has become imperative to look at the three options for reducing chromium level in clinker:

a) selection of raw materials
b) avoidance of use of magchrome refractory bricks
c) use of special reducing agents.

So far as the last step is concerned, the reducing agent commonly used is ferrous sulfate prior to bagging and shipping of cement. Although this compound serves the purpose, it has the disadvantage of low shelf-life and need for higher dosage which affects the hydration behavior of cement.

As an alternative various companies have tried to synthesize stannous sulfate which is reported to be more effective at lower dosages when used at the cement grinding stage [28].

The leaching mechanism of hexavalent chromium from treated soil has been reported in [29], in which the method of determining Cr (VI) in cement and clinker has been dealt with. According to these authors it was estimated that the contents of Cr (VI) in cement samples were about 50–80% of total chromia present in different valency states.

7. Advanced techniques of process control

For the last 25 years the structure of control systems for cement plants has been based on the Distributed Control System (DCS) in which Programmable Logic Controllers (PLCs) are dispersed throughout the process system, each to control a certain section of the process. The entire system may be networked for communication and monitoring. The fully developed DCS comprises SCADA (Supervisory Control And Data Acquisition) software plus HMIs (Human Machine Interfaces) which are usually PCs. A typical architecture of a SCADA system for a cement manufacturing process consisting of input/output signal hardware, controllers, HMI, networks, communications database server and software is shown in Fig. 15 [9].

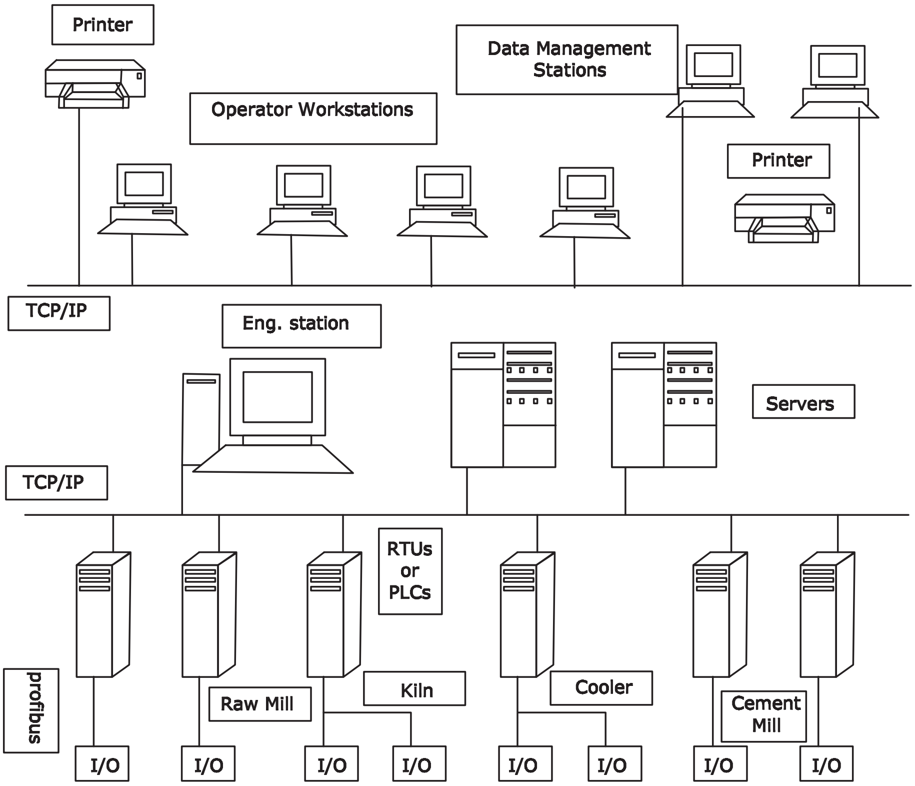


Fig. 15. A typical architecture of a SCADA system for the cement manufacturing process [9].

The process conditions for each production section are monitored and the resulting signals transmitted by wire or optical cable to each RTU (Remote Terminal Unit) or PLC via I/O (input/output) devices. The control signal generated from the RTU or PLC then returns through I/O to each executive device. The RTU or PLC performs PID control loop functions, data compiling and formatting, manages alarm logic and interlocking control. The communication between HMI, Master Station and controllers uses an open communication protocol such as Ethernet or TCP/IP.

Various Expert Systems are available for process optimization. ABB's Expert Optimiser is widely popular followed by FL Smidth Automation's ECS/Process Expert. The emerging new systems include Pavillion's Pavillion8 MPC and Powitec's Pit Navigator. In the meantime Lafarge has developed its own captive system LUCIE Polysius continues to supply its Polexpert KCE/MCE as part of their turnkey contracts [30].

On the technology front the kiln optimization is still ruled by fuzzy/rule based control. The mill control seems to continue with the rule based fuzzy. The latest versions of MPC are also trying to get established.

The key issue in process control still remains linked up with the introduction of novel soft sensors. Powitec's ‘Predictor’ and FLSA's new RGB Camera software are examples of such soft sensors that are likely to play an increasing role in the application of technology. Without the good quality soft sensor for product quality the real advancement of process control cannot be achieved.

7.1. On-line quality control techniques

The quality parameters required to be attained for Portland clinker and cement are fairly well established and the presently practised process control measures are geared towards achieving those parameters. But many of those measures like chemical analysis based Bogue computation of clinker or cement phases are indirect in nature and some quality control techniques are off-line and do not yield real-time values. Hence, there has been a persistent effort in the industry to develop and implement on-line systems.

One such effort is on-line x-ray diffractometry (XRD). This provides the basis for a new level of control, where the controlled parameter is the clinker mineralogy including percentages of alite, belite, ferrite, aluminate, free lime, alkali sulfate, periclase, etc. Furthermore, by monitoring the various polymorphic forms and crystal symmetry of clinker phases the kiln operation can be adjusted through calciner parameters, kiln speed, burners, coolers, etc. to ensure production at the optimum cost and quality.

The system offered by FCT ACTech COSMA [31,32] operates on the basis of continuous sampling and sample preparation. The ground sample passed through COSMA is approximately 70 kg of powder per day, continuously returned to the process by pneumatic transport. The instrument uses, as claimed, a patented full area detector and it also employs Rietveld refinement of patterns. The unit automatically updates the analysis of the process stream every minute. With frequent analysis comes the trend setting of the results and the ability to control processes on-line.

7.1.1. Clinker quality control

Over the years cross belt analyzers have become very popular for controlling the proportioning of raw materials. However their set points need frequent adjustment to allow for changes in the process. By using the on-line XRD analyzer, it is possible to apply feedback control to adjust the raw materials set points in real time (Fig. 16) [32]. In addition, the unit measures free lime in real time (Fig. 17) [32]. This result can be transmitted to the plant's automatic kiln control system (Fuzzy, Lucie, Linkman, etc.) to accurately control the burning zone conditions.

7.1.2. Cement quality control

By using an on-line XRD analyzer in a cement milling circuit (Fig. 18) [32] any variations in the quality of gypsum or additives like limestone are automatically taken care of. The dehydration of gypsum

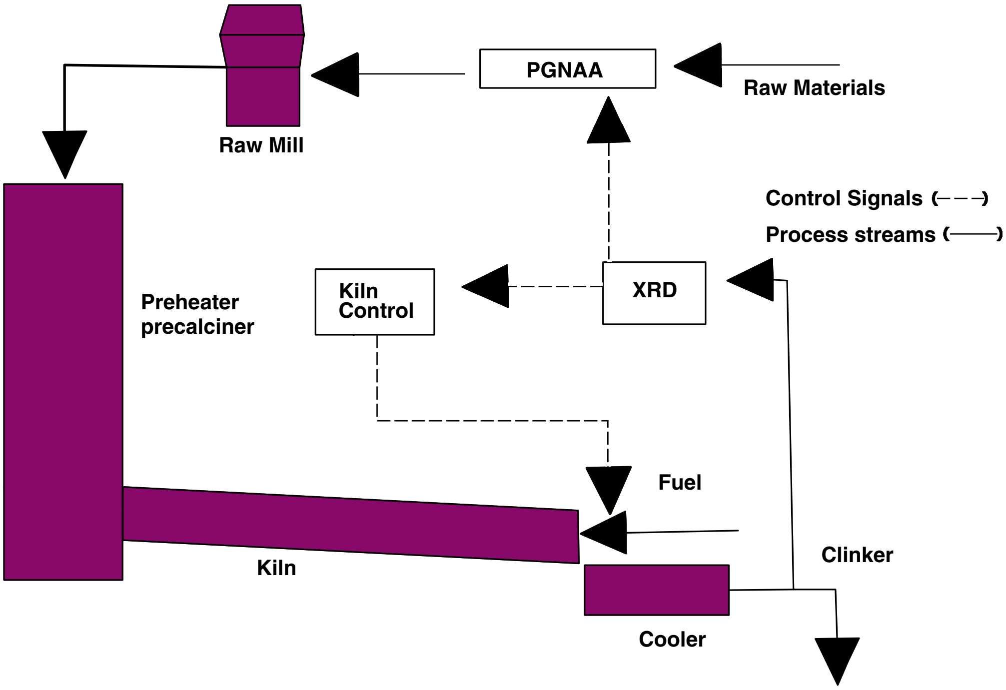


Fig. 16. An illustrate flow sheet for on-line XRD for clinker quality control [32].

during grinding can also be detected and the mill temperature can be controlled through proper ventilation or water spraying in ball mills.

Thus, continuous monitoring of the mineralogy of cement and clinker opens up the possibility of more precise process control.

8. New processes for making clinker/cement

The long history of Portland cement and clinker manufacture has seen many breakthroughs and many incremental improvements. But the basic rotary kiln technology for pyroprocessing has so far stood the test of time quite firmly. The same technology has been effectively adopted for manufacture of all modified Portland cements such as calcium sulfoaluminate belite cement [33]. Hence the effort here is to focus on a selected few radically new non-rotary kiln technologies that have some potential for process breakthroughs.

8.1. Fluidized bed clinkerization

A historical account of the development of fluidized bed clinkerization process was presented in [34], starting from the Pyzel process followed by Fuller Company's pioneering attempt and finally continued by the Japanese pilot plant trials separately by IHI-Chichibu and Kawasaki-Sumitomo companies. Subsequently, however, Kawasaki Heavy Industries pursued their own further development to scale up the process by designing, constructing and operating 2 tpd, 20 tpd and 200 tpd plants. The system configuration is shown in Fig. 19 [35]. It was claimed that the system could take various coals from low calorific value to low volatiles, could offer 10–25% better thermal efficiency, 10–25% reduction in CO_2 emission and 40% or more reduction in NO_x emission, 10–30% saving in construction cost, and 70% reduction in space. The scale up data for the commercial plants developed then are given in Table 3. Apparently the scaling up of the process beyond 3000 tpd was found problematic and in terms of the specific heat consumption the system did not offer any significant improvement over the rotary kiln systems. As a result, there is hardly any adoption of this new technology at the present times. The scope of further development and exploitation of this technology remains.

8.2. Alinite cement

Alinite cement was developed in the former Soviet Union but this technology could not be widely exploited due to the apprehension of

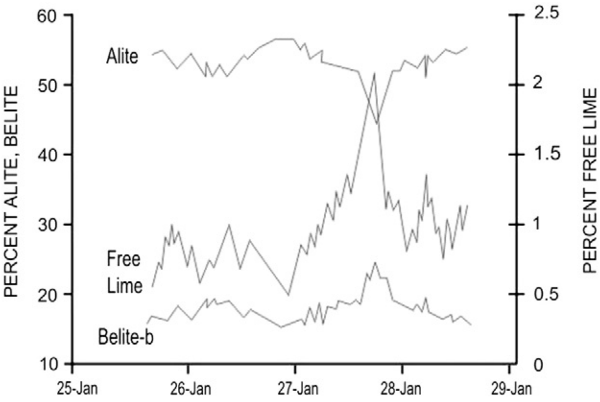


Fig. 17. Online XRD traces of clinker phases [32].

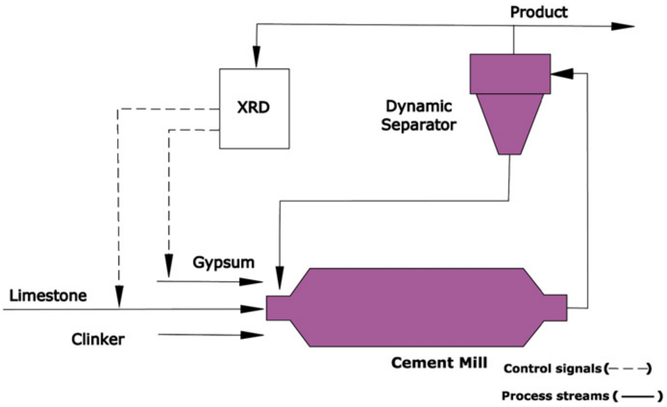


Fig. 18. An illustrative flow sheet for on-line XRD for cement quality control [32].

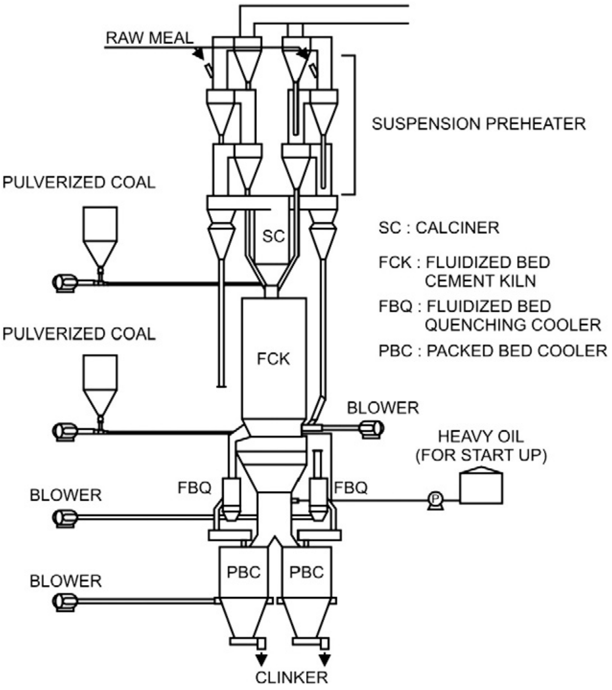


Fig. 19. A schematic diagram of the fluidized bed pyroprocessing system of KHI design [35].

rebar corrosion by Cl released from the hydrated phases. But since the burning temperature of alinite clinker is low (1000°–1200 °C) and the chlorine-containing waste including incinerated ash of municipal refuse might be used as a raw material for the cement, attention has been reverted to this technology for development of "eco-cement" [36]. From the industry sources it is learnt that Taiheiyo Cement Corporation in Japan has taken lead in utilizing the alinite cement technology for utilizing chlorine bearing incineration ash by putting up first a pilot plant with a capacity of 20,000 tonnes per annum in Tahara city, Aichi Prefecture, and then two larger units — one with a capacity of 110,000 tonnes of cement per year in Ichihara city and another of 130,000 tonnes in Hinode city. It is reported that the environmental problems and equipment corrosion issues accompanying the use of high-chlorine material in the process have been duly addressed. The composition and property details of eco-cements are furnished in Table 4.

In this context it may be relevant to mention about the research work reported in [37] on the application of the vortex reactor to the manufacturing of alinite cement, subsequent status of which, however, is not known.

8.3. Sol–gel process

A sol–gel process was attempted by the author and his team to produce clinker by two alternative routes as depicted in Fig. 20 [38].

Table 3
Projected scale-up data for the commercial plants.

Parameters	Unit	200 tpd	1000 tpd	3000 tpd
Heat consumption	Kcal/kg cl	771	713	690
Power consumption	KWh/t cl	43.0	41.5	37.2
Fluidized bed kiln dia	m	2.5	5.7	9.7
Fluidized bed quenching cooler dia	m	0.7	1.6	1.9
Packed bed cooler dia	m	3.1	7.0	8.6
Tower size				
Width	m	10	17	26
Length	m	8	16	26
Height	m	51.5	63	72

Table 4
Typical chemical and mineralogical compositions of eco-cement [36].

	Ordinary type	Rapid hardening type A	Rapid hardening type B
Chemical composition (%)			
SiO_2	22.6	18.4	18.6
Al_2O_3	4.1	12.1	13.1
Fe_2O_3	2.7	1.5	2.5
CaO	59.9	63.1	62.4
MgO	2.2	1.5	1.0
Cl	4.0	2.0	0.5
Mineralogical composition (%)			
Alinite	70.0	58.0	–
Belite	23.0	18.0	9.0
Calcium chloroaluminate	2.0	20.0	25.0
Alite	–	–	60.0
Ferrite	2.0	–	4.0

The basic technical feasibility of producing β-C_2S in the lime-silica system was established. The effect of dopants like boron oxide, sulfate, magnesia and fluoride was seen in the crystal size and the hydraulic reactivity and not in any polymorphic transformation of the calcium silicate. However, dopants like alumina and fluoride in combination appeared to help in the formation of C_3S at temperatures much lower than its known threshold temperature of stability (1280 °C). In all the experiments the molar C/S ratio ranged from 2.26 to 2.38. A white cement of very high reflectance and high compressive strength levels could be produced by this technology in the system C–A–S–Fl at a temperature of 1200 °C. The technology appeared feasible also for making colored clinker with suitable chromophors.

8.4. Microwave heating

Synthesis of clinkers for Ordinary Portland Cement, white and colored cements by microwave processing was reported in [39]. The experiments were conducted in a 900 W 2.45 GHZ multimode cavity

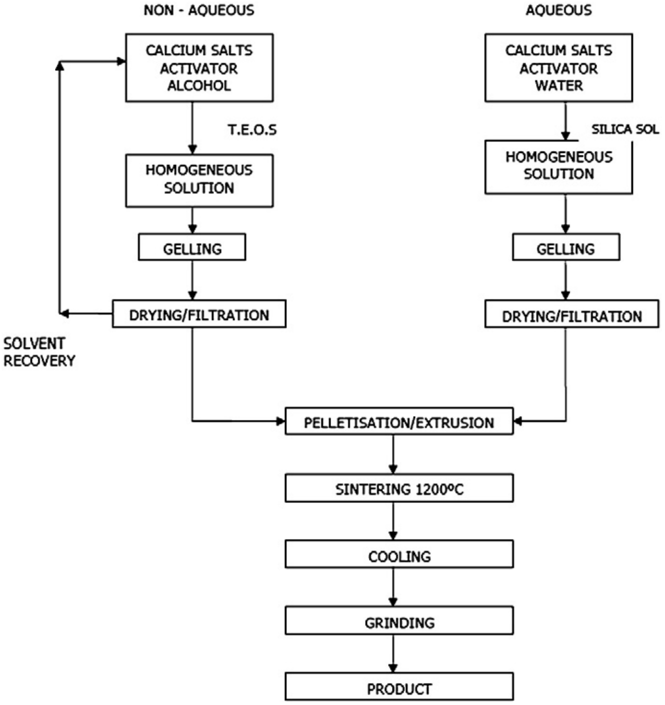


Fig. 20. Sol–gel process scheme for manufacture of cementitious materials [38].

with a turntable to rotate a sintering packet in which the sample was loaded. A single pellet sintering was carried out.

The results showed that the microwave processing enhanced the clinkering reaction to certain extent on both ordinary and white cements. This effect was maintained by the lower temperature of clinkerization as compared to the parallel runs of the same raw meals in conventional fast heating electric furnace. The clinkering temperature was found to be lower by almost 100 °C. The XRD patterns revealed that the clinker phase formation was quite normal (Fig. 21) [39]. The iron oxide in the ordinary Portland cement raw meal and amorphous silica in the white cement sample seemed to be responsible for the microwave enhancing effects.

Some recent studies on microwave clinkerization with different types of succeptors used in the system have been reported in [40]. The microwave heating patterns showed the heating time 1/8 of the electric furnace time for activated carbon, 1/4 for petcoke and 1/3 for natural coal. The crystal sizes of the clinker phases were smaller in microwave heating. The β–γ conversion of C_2S was observed to be more common during the cooling process in microwave heating.

8.5. Electron beam or radiation process

A systematic experimental approach to apply radiation energy for clinker making was reported from the former Soviet Union in nineteen seventies and eighties [41].

In the radiation synthesis of clinker, the pyroprocessing was effected by a high-energy beam of accelerated electrons. After conducting a series of experiments, it was established that at an absorbed power dose of 20–40 Mrad/s, the clinkerization process could be completed in a few seconds or in case of less powerful flux of electrons, within a few tens of seconds. It was also shown that the process was completed at a temperature 200 °C lower than the normal temperatures required for clinkerization in rotary kiln. The schematic view of the experimental set-up is given in Fig. 22 [41].

The Ordinary Portland Cement Clinker synthesized by radiation was observed to be black and porous. Alite crystals were mostly acicular in shape and only a few crystals showed platy habits. Belite displayed both round and anhedral structure. The liquid formation was observed to be insignificant. Mass percentage of alite grains showed a linear relationship with compressive strength at all ages (Fig. 23) [41]. The technology obviously had some merits of being

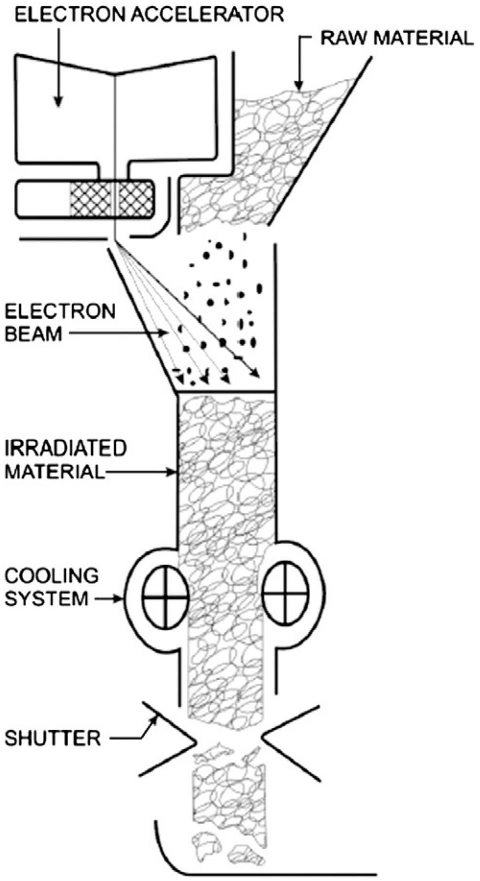


Fig. 22. A schematic diagram of the radiation synthesis process of clinkerization [41].

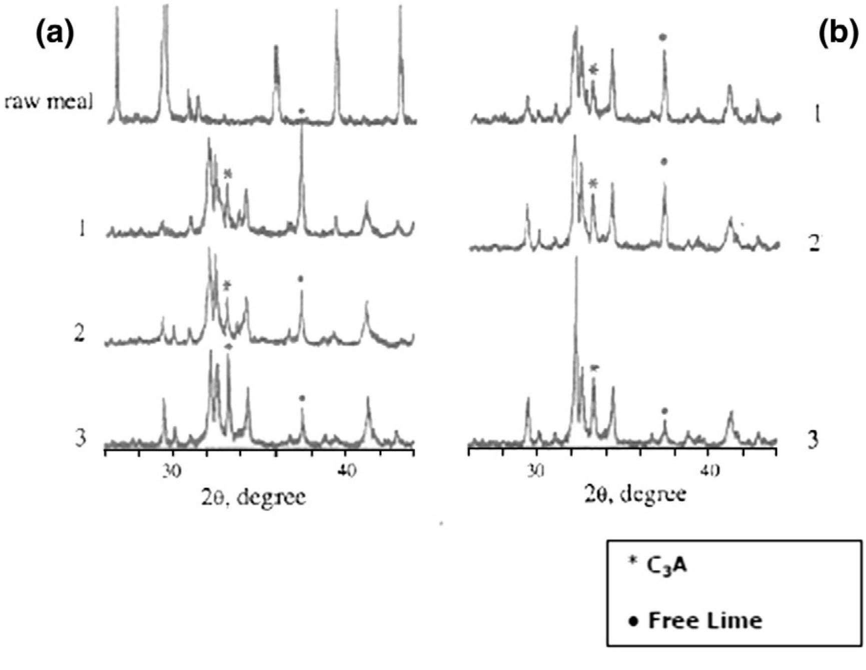


Fig. 21. Comparison of XRD patterns of a raw meal fired in conventional electric furnace (a) and microwave heating device (b) at three temperatures [38] 1 — 1300, 2 — 1350, and 3 — 1400 °C with 10 min sintering time in MW.

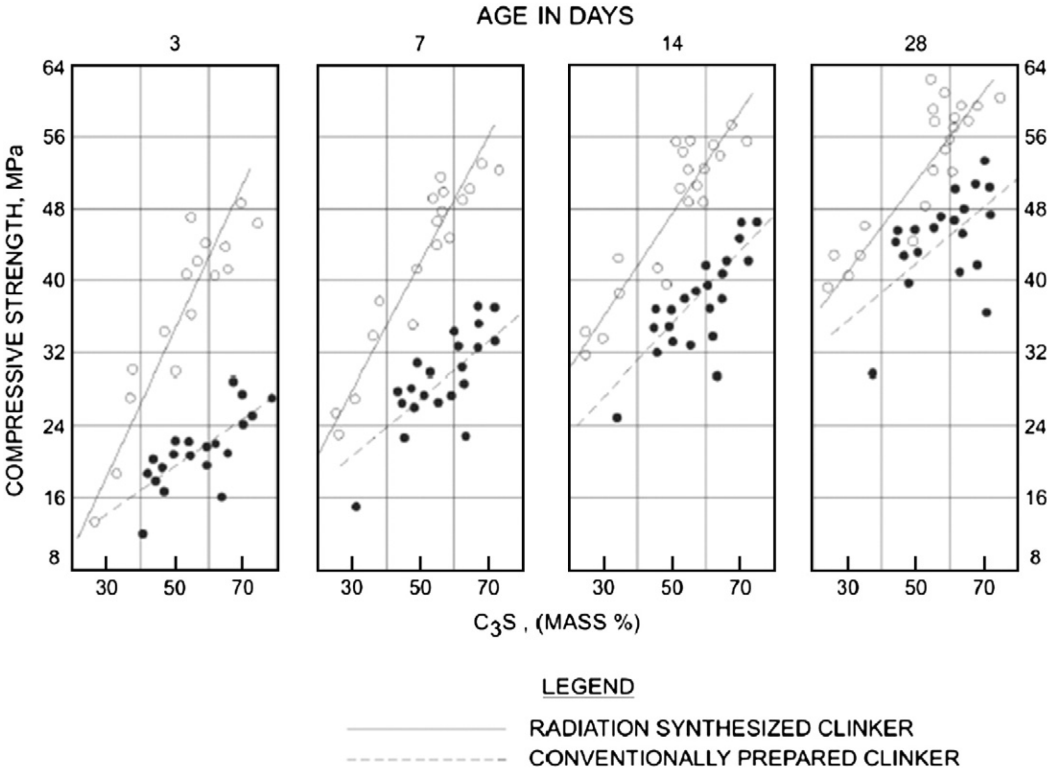


Fig. 23. Comparison of compressive strength versus C_3S relationship of a radiation synthesized clinker and a conventionally prepared clinker of the same composition [41].

pollution free and less energy consuming, although the problems inherent with the use of radiation process cannot be ignored.

8.6. Nanocement technology

One of the most promising achievements in recent times is the development of nanocement additives with the help of High-Energy Mills. A computer-controlled commercial Simolayer milling device (CM 20), which operates at 500 rpm with a ball-to-powder ratio of 1/46, has been reportedly used to produce nanocement products: Fine Cement (FC) with 24.0% nanoparticles and Ultra Fine Cement (UFC) with 39.0% particles below one micron. The particles, however, maintained their crystallinity as seen from their XRD patterns [42].

Three mix designs were attempted to decipher the activation effect of FC in concretes containing OPC Type II, 10 mm limestone aggregate, river sand, superplasticiser and FC. In all the three mixes 30.0% of OPC was substituted by FC and a control sample without FC was prepared for comparison. The results are given in Table 5.

It appears that the high-energy milled nanocement additives have certain activation capabilities in mortars and concrete, the economic feasibility of which needs to be established.

Table 5
Strength parameters of concrete mixes containing FC [42].

Parameter	Mix 1		Mix 2		Mix 3	
	Control	With FC	Control	With FC	Control	With FC
OPC, kg/m^3	246	172.2	296	207.2	450	31.5
FC, kg/m^3	–	73.8	–	88.8	–	13.5
Compressive strength MPa						
1 – day	6	19	112	32	23	49
7 – day	20	35	25	52	50	73
28 – day	31	47	30	56	59	81
60 – day	34	54	37	67	75	97

9. Concluding remarks

Although “chemistry” and “engineering” are the main props on which rests the basic process of clinkerization and cement production, over the years the advances in “engineering” have overtaken the endeavors of unravellling the intricacies of fundamental chemical reactions and phase transformations in the manufacturing process. As a result, plants of gigantic clinkerization capacities, such as 12,000 tonnes per day from a single kiln system, have been set up.

Such an engineering feat has succeeded, despite the problems of high variability and impurity contents of natural raw materials, wide variety of fuels used including alternative and refuse derived ones, pressures of energy conservation and protection of environment including overall sustainability.

The marvel of engineering conversion of process chemistry is reflected in the design and operation of large pyroprocessing systems consisting of 5/6 stage preheaters with low pressure drop, precalciners taking care of 85–95% of the endothermic carbonate decomposition reaction in matters of seconds, with 60% direct heat input, two-support rotary kilns of length-to-diameter ratio of 10–14 having material residence time (MRT) of approximately 21 minutes only fairly efficient grate coolers with clinker cooling time of 30–45 min and recuperation of heat from the exhaust gases for recycling into the process. The problem that lingers on with cooler design is the problem of achieving faster cooling and the resultant effects of uncontrolled periclase grain size, breakdown of alite, arresting the higher temperature forms of silicates, etc. in the clinker.

The behavior of the volatiles in the pyroprocessing is more complex due to the systemic effects than the simpler chemical reactions. Hence, recourse is being taken to modeling approach in predicting the volatiles behavior and in solving the associated operational problems.

The entire process control due to interactive complexity of chemistry and engineering, is still dependent on fuzzy logic, or rule based fuzzy or model-based approach. The soft sensors to support such control systems are still in the exploration stage. The online XRD facility appears to be emerging as a strong link with process control systems.

The emission chemistry and the required engineering solutions are progressing hand in hand, except the organic emissions like dioxins, furans, PCBs and PAHs, the specific precursors of which need to be identified more precisely for raw materials control.

Finally, one should take note of the stunted global scientific effort in finding newer pyroprocessing technologies that are not dependent on conventional rotary kiln process. The fluidized bed system, microwave heating, sol–gel process, electron beam bombardment technique, etc. were initiated decades back but have not been worked upon for developing any viable technologies. The biggest challenge for the future perhaps lies here in shaping up a more energy-efficient, environment-friendly and sustainable pyroprocessing technology, as the present process has plateaued to a fully mature state. A recent development of producing nanocement additives by using high-energy mills seems to hold some promise, subject to its economic viability.

References

[1] H.F.W. Taylor, Cement Chemistry, Academic Press, New York, 1990.
[2] A.K. Chatterjee, Raw materials selection, in: J.I. Bhatty, F.M. Miller, S.H. Kosmatka (Eds.), Innovations in Portland Cement Manufacturing, PCA, Skokie, Illinois, USA, 2004, pp. 37–64.
[3] A.K. Chatterjee, Materials preparation and raw milling, ibid, pp. 84–136.
[4] Con G. Manias, Kiln burning system, ibid, pp. 239–268.
[5] Clans Bech and Alex Mishulovich, Preheaters and precalciners, ibid, pp. 269–286.
[6] Gerald L. Young and F.M. Miller, Kiln System Operations in cement manufacturing, ibid, 287–330.
[7] F.P. Glasser, Advances in cement clinkering, ibid, pp. 331–368.
[8] A.K. Chatterjee, Chemico-mineralogical characteristics of raw materials, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, Oxford, 1983, pp. 39–68.
[9] Philip A. Alsop, The Cement Plant Operating Handbook, ICR, Tradeship Publications Ltd, Surrey, UK, 2007.
[10] S.P. Pandey, P.K. Mohanty, A.K. Tiwari, M.C. Agrawal, A.K. Chatterjee, Intra-plant evaluation of raw mixes from two modern grinding systems, Cement International 4 (3) (2006) 65–69.
[11] Mathias Mersmann, Pyroprocessing technology — continuous improvement, IEEE — IAS/PCA Conference, Charleston, USA, May 2007.
[12] J.A.H. Oates, Lime and Limestone — Chemistry and Technology, Production and Uses, Wiley — VCH, Weinheim, 1998.
[13] FL Smidth A/s, Brochure for kilns and firing, Rotax-2 development, http://www.flsmidth.com, December 2005.
[14] D. Stephen, J. Plank, Influence of foreign oxides on lattice parameters and reactivity of pure clinker phases of OPC, Proceedings of the 12th ICCC, Montreal, Canada, July 2007.
[15] Zongfu Guan, Yimin Chen, Show Wan Qin, Sui L. Guo, Effect of phosphor on the formation of alite-rich Portland clinker, Proceedings of the 12th ICCC, Montreal, Canada, July 2007.
[16] E. Gotto, M. Marchi, U. Costa, Influence of alkali and sulphates on the mineralogical composition of clinker, Proceedings of the 12th ICCC, Montreal, Canada, July 2007.
[17] S. Plang-ngem, M. Rattanussam, The effect of sulfur to alkali ratio on clinker properties, Proceedings of the 12th ICCC, Montreal, Canada, July 2007.
[18] Khadiya Morsli, Angeles G. de la Torre, Mohammed Zahir, Miguel A.G. Aranda, Mineralogical phase analysis of alkali and sulfate bearing belite rich laboratory clinkers, Cem. Concr. Rcs. 37 (2007) 630–646.
[19] CemProTec Gmbh, Revolving Disc Cooler, http://www.cemprotec.comDecember 21 2010.
[20] A.K. Chatterjee, S. Krishnan, B.S. Rangnekar, Clinker Coolers — Types, Efficiency and Effect on Clinker Quality, All India Seminar on Cement Manufacture, NCB, New Delhi, 1981.
[21] A.K. Chatterjee, Modernization of cement plants for productivity and energy conservation, in: S.N. Ghosh (Ed.), Cement and Concrete Science & Technology, Vol. 1, Part I, ABI Books Pvt. Ltd., New Delhi, 1991.
[22] A.K. Chatterjee, Role of volatiles in cement manufacture, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, Oxford, 1983, pp. 203–244.
[23] Aalborg Portland Cement Company, The Cement Environmental Yearbook, , 1997.
[24] Luca Danuvola, Wolgang Freimann, Chlorine bypass, World Cement, January 2006, pp. 107–111.
[25] VDZ Research Institute for the Cement Industry, Modelling the circulating sulfur, chlorine, alkali systems in the clinker burning process, part 1: comparison of measurement and calculation, part 2: theory and discussion, Cement International, Nos. 3 and 4, Vol. 7, 2009, pp. 75–87 and 65–75.
[26] Javed L. Bhatty, Minor elements in cement manufacturing, in: J.I. Bhatty, F.M. Miller, S.H. Kosmalka (Eds.), Innovations in Portland Cement Manufacturing, PCA, Skokie, Illinois, USA, 2004, pp. 403–452.
[27] Lars Skaarup Jensen, Fulfilling emission guarantees, World Cement, December 2005, pp. 87–94.
[28] Mike Sumner, Charlotte Porteneuve, Leslie Jardine, Michael Maklin, Advances in chromium reduction, World Cement, March 2006, pp. 33–36.
[29] Shunsake Hahehara, Osamu Yamaguchi, John Saunders, Considering chromium, World Cement, March 2006, pp. 23–32.
[30] David Haspel, Expert thinking, International Cement Review, April 2007, pp. 81–87.
[31] Peter Storer, Con Manias, On-stream XRD analysis, World Cement, February 2003, pp. 49–54.
[32] David Rapson, Peter Storer, Improving control and quality, World Cement, March 2006, pp. 67–71.
[33] Anjan K. Chatterjee, Re-examining the potential of calcium sulphoaluminate cements from the perspective of versatility, durability and GHG emission, Indian Concrete J. vol. 84 (11) (2010) 7–20.
[34] Hiroshi Uchikawa, Present problem in cement manufacturing, J. Research Onoda Cement Company 45 (128) (1994) 7–44.
[35] Isao Hashimoto, Yoshito Aranishi, Tatsuya Watanabe, New fluidized bed pyroprocessing from KHI, Asian Cement and Construction Materials, April/May 1999, pp. 29–38.
[36] T. Tamashige, et al., A new method of incorporating fly ash from municipal incineration plants into cement production, Ecocement Progress, Chichibu-Onoda Cement Corporation, Tokyo, Japan, 1996.
[37] A.B. Ryzhik, M.V. Kougiya, A.V. Alexandrov, Thermal treatment of cement raw materials through intensive heat exchange, Proc. 9th ICCC, Vol. II, New Delhi, 1992, pp. 210–214.
[38] C.H. Page, C.H. Thombare, R.D. Kamat, A.K. Chatterjee, Development of sol–gel technology for cement manufacture, in: S. Mindess (Ed.), Advances in Cementiti9ons Materials, Am. Cer. Soc, Ohio, USA, 1991, pp. 643–660.
[39] Yi Fang, Della M. Roy, Rustum Roy, Microwave clinkering of ordinary and coloured Portland cements, Cem. Con. Res. 26 (1) (1996) 41–47.
[40] C.K. Park, J.P. Lee, D.M. Roy, Clinkerization of Portland cement raw meal in the microwave processing system, Proceedings of the 12th ICCC, Montreal, Canada, July 2007.
[41] S.K. Handoo, K. Goswami, Application of electron beam process technology for production of cement, Proc. Indo — USSR Seminar on Industrial Applications of Electron Accelerators, Vol. II, BARC, Bombay, November 3 1988, pp. 118–126.
[42] Armando Garcia Luna, Nanotechnology for sustainable development of the cement industry, Indian Cement Review, April 2010, pp. 11–19.