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Chemistry and engineering of the production process: State of the art

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ABSTRACT

The present paper discusses the evolution of the chemistry and engineering of the production process of cement since the last (12th) International Congress on the Chemistry of Cement held at Montreal in 2007 Beaudoin (2007).

In the last decade, the developed areas have addressed mainly the concrete design and its utilisation Young (2008). They are not treated here.

In addition to the concrete applications, significant trends of innovation in cement science concerning the chemistry and engineering of the production process are observed.

These trends are the consequence of the commitment of the cement industry towards the environmental constraints, the compliance with economic needs and the evolution of the market.

Based on analytical studies, it seems that the cement industry will have a sustainable future if, first of all, the rate of innovation becomes higher than the rate of the occurrence of constraints and if the cement industry is able to anticipate these constraints.

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1. Introduction

The goal of the present paper is to discuss the evolution of the chemistry and engineering of the production process of Portland cement as it can be detected from the literature published in this area since the 12th International Congress on Chemistry of Cement [1,2].

The chemistry of Portland cement clinker has been largely reviewed (past, present and future) during a conference held at Aberdeen (Scotland) that was dedicated to Frederik P. Glasser [3]. The plenary papers are published in the review *Advances in Cement Research* and their conclusions have been taken into consideration.

Most of the technological developments in clinker production aim at increasing the production of the most reactive and low cost clinker. This can be achieved a) by improving the kiln efficiency, in modifying the system (burner design) for the maximum use of alternative fuel (shredded tyres, waste oil, solvent, and biomass) and in reducing emission (heavy metal, NO_x, CO_2…), b) by increasing the homogeneity of the raw meal c) by saving energy during the grinding process and d) by developing automation and kiln monitoring to reduce the variability of the clinkering process.

Alternative fuel and raw material are proving to be of significant advantage in terms of both economic and environmental involvement. Their use impacts the burnability of the raw meal, the chemistry of clinkering (additional minor elements), the burning profile and burner design, the refractory lining, the chemistry of emission, the properties of the doped clinker and its grindability, the reactivity and the performances of the final product.

In the first part of this work, the preparation of the raw meal (burnability, mix proportioning, grinding and its control) is discussed. The second part is devoted to the clinker (clinkering reactions and emission) with a description of the recent technological development of the calciner, cooler, grinder, and online control. The last part states the chemistry and processing of new clinker types aiming at reducing the energy consumption and CO_2 emission.

2. Raw material

2.1. Chemistry of raw material

2.1.1. Burnability

The quality of the raw material resources and the raw meal must be evaluated before undertaking a strategy for the burning and cooling process. From the experiments, carried out on industrial raw meal using microscopic point counting integration on polished sections and a Rietveld XRD technique, a kinetic description of the alite formation is proposed [4].

During the course of an isothermal burning process, the formation of alite is followed by the evolution versus time (t) of a percentage of the conversion (α) expressed by means of a ratio of the alite formed to the maximum content of alite. It is described by the following equation:

$$\left[\left(1-(1-\alpha)^{1/3}\right)\right]^2-Q=Kt$$

The coefficient K, determined experimentally, is related to the calcium diffusion in a hot melt, to the amount of clinker melt, to the porosity and to the difference in concentration of CaO between the surfaces of the CaO cluster and the front of the alite layers being formed.

The parameter Q, present in the case of industrial raw meal, is related to belite formed from large particles of quartz. Silica forms large belite clusters with compact surface shells and an acid hot melt that reacts to alite very slowly. The rate of alite formation is not a function of an initial surface of the representative cluster of free CaO, but is instead a function of the total surface of free CaO in a polydispersed system at the end of the belite formation[4]. The method differentiates the effect of the raw materials used and the parameter of the raw meal preparation.

Four parameters are defined:

1) the reactivity of the raw meal (Rm). The reactivity of raw meal is defined by a relative velocity of clinker formation from the given raw meal, including all the effects of the raw material source and the method of preparation. Its variation is proportional to the change in the length of the rotary kiln-sintering zone. It is determined by the time in which 1% of free lime CaO is reached regardless of the conversion process.
2) the reactivity of the raw meal source (Rms) . The reactivity of the raw meal source is the same but at equal parameters as the preparation of the raw meal (equal chemical and granulometry).
3) the burnability of the raw meal (Bm). The raw meal burnability is defined by the relative performance of the rotary kiln at the burning of the clinker out of the given raw meal. It includes all the effects of the material source and the meal preparation method.
4) the burnability raw meal source (Bms) .The raw material source burnability is defined by the relative performance of the rotary kiln at an equal chemical and granulometry composition of the raw meal.

To summarise: with the same raw meal source, different raw meal preparation and the same thermal profile, Rm is obtained . If the thermal profile is modified, Bm is obtained. With different raw meal source, the same raw meal preparation and the same thermal profile, Rms is obtained. If the thermal profile is modified, Bms is obtained.

The determination of the four parameters gives complete information on the nature of lime, the formation and distribution of SiO_2 and the granulometry of the raw meal. It could be applied to forecast the changes of temperature of the sintering zone and predict the efficiency of the grinding of raw meal.

2.1.2. Mix proportioning

A method has been developed to calculate the lime saturation factor (LSF) when the difference between the calculated (Bogue) and the measured (by analytical methods) mineralogical composition becomes too important. It is the case when the amount of minor elements is high.

The lime saturation factor (LSF), associated with the silica ratio (SR) and alumina modulus (AM), is well known as a useful tool to design the raw meal of Portland cement clinker.

a) The lime saturation factor controls the ratio C_3S/C_2S.$LSF=100x(\%CaO)/[(2.8x\ (\%SiO_2)+1.65x(\%Al_2O_3)+0.35x(\%Fe_2O_3)]$ if $Al_2O_3/Fe_2O_3>0.65$
b) The silica ratio, $SR=SiO_2/(Al_2O_3+Fe_2O_3)$, controls the burnability.
c) The alumina modulus, $AM=Al_2O_3/Fe_2O_3$, fixes the ratio C_3A/C_4AF and impacts the burnability and the durability of the final cement.

The reactivity of the cement and clinker is mainly based on the quantity of C_3S and alite, not on the chemical composition or LSF (it is possible to obtain a different percentage of C_3S with the same LSF and, vice versa, to maintain the same C_3S with a different LSF). The LSF gives little information on the quality of the clinker (% of C_3S or alite) and the presence of minor elements, introduced by the use of alternative fuel or raw material, which highlights the necessity of a relation between LSF and the mineralogy of the clinker to fill the gap between the process and product.

The following relations have been established [5]:

$$LSF = 100x[(A + BxC_3S) / (C + DxC_3S)]$$

where the coefficients A, B, C and D are represented by the following:

$$A = 7.602xSRx(AM + 1) + 6.718xAM + 1.429$$

$$B = (AM + 1) \times (SR + 1) \times 0.01$$

$$C = [2.8x(AM + 1)xSR + 1.65xAM + 0.35] \times 4.071$$

$$D = -[2.8x(AM + 1)xSR + 1.65xAM + 0.35] \times 0.01$$

This formula shows that the LSF is not a linear function of the percentage of C_3S or alite. The application of this formula using the LSF versus mineralogy (alite) instead of chemistry appears to be more efficient in considering the presence of minor elements and their effect on the phase content [6].

2.2. Raw material processing

2.2.1. Grinding

The average CO_2 emission associated with the grinding process is approximately 0.1 t of CO_2 per tonne of cement and is mostly associated with the electricity production, which is low compared to the contribution of decarbonation and heating. Thus, the driving force for the innovation of the grinding process is not the CO_2 emission constraints but the energy savings.

The grinding process impacts the cement manufacture in at least two ways. First, an increase of the fineness and homogeneity of the raw mix accelerates the clinkering reactions, leads to less variability of the clinker due to the enhanced stability of the kiln and better energy efficiency in producing a clinker of better consistency. The second effect concerns the fineness of the cement and is developed in chapter 323.

The cement industry utilises four types of mills: a ball mill, a vertical roller mill, a roller press (high-pressure grinding roll HPGR) and a horizontal roller press mill. Different mill feeds, such as raw material, coal, clinker and slag, have different grindabilities, feed particle size ranges and moisture content as well as different throughput rates, fineness data and other quality parameters. Each mill type associated with the grinding process is more suitable for some applications and requirements over others.

Raw material grinding has the objective of producing a homogeneous raw meal with a fineness requirement (less than 10 to 15% residue on the 90-μm sieve) from a raw material containing moisture (3 to 8%) with a feed particle size of 100–200 mm. Usually, silos after the grinding mill are used for a final homogenisation of the raw meal.

A vertical mill is installed in 80% of all new grinding plants, which has lower power consumption and allows simultaneous grinding, drying and separation. A ball mill is still used for 12% of all raw material applications, such as grinding of dry or abrasive materials.

The efficiency of the utilisation of HPGR is due to the improvement of the separator. The technology of HPGR was limited to the applications characterised by low moisture, low abrasiveness and medium capacity. In contrast to cement grinding, in which the properties of the clinker and additives are consistent, the raw material preparation must deal with an almost unique raw material for each application. This necessitates the adjustment of the grinding system to the properties of the raw material in each case.

Two raw material grinding systems located in the same plant have been compared. One consists of a vertical roller mill with four rollers, an inbuilt dynamic classifier and a throughput of 120 tph (tonnes per hours) at a maximum residue of 2.5% at 212 μm when the feed size is restricted to 50 mm. The second system is a roller press with a static separator coupled to a ball mill with a dynamic separator and a 300-tph throughput. In both cases, the preheater gases are used for drying purposes [7].

The fineness was compared by analysing the residue quartz grains on the 45-μm sieve and the residues of calcite particles on the 125-μm sieve. The two grinding installation had considerable differences in their system design but appeared to produce raw mix with particle size and burnability characteristic that varied within a very narrow range [7].

The grinding and drying capabilities for moist raw materials were limited at only 4%. The disagglomeration of the roller press product by a high-speed rotor and the separation of fines and a disagglomeration process by a high-efficiency separator can extend this limit.

Excessive wear was the main problem faced by most of this grinding circuit and has occurred after start up. The sharply edged grain, up to 10 mm in size, came into direct contact with the rotating parts and caused high wear to the separator and disagglomeration.

There is a strong correlation between the concentration of quartz in the separator and the wear rate (in a closed circuit).

2.2.2. Advanced techniques for process control

In every cement plant, fast and direct feedback on the elemental composition of raw materials and the clinker is essential for an efficient process and the best cement quality.

This process starts in the quarry where the analysis of the drill cutting liberated from the blast hole during the drilling process is analysed in real time. This procedure not only eliminates the need to gather material samples manually and send them away for laboratory analysis but also delivers valuable information about the varying composition in three dimensions.

Two types of analysers are used to obtain the chemical composition of the passing material on a belt: one uses a radioactive isotopic source of neutrons (Californium 252, Cf 252) and the other utilises an electric source of neutrons. In the latter, neutrons are produced by a high voltage in a vacuum ceramic sealed tube containing deuterium and tritium. Unlike Cf 252, for which neutron emission is permanent and drops considerably, neutrons electrically generated are emitted on demand and the neutron output is stable. The pulse fast thermal neutron activation (PFTNA) involved illuminating the raw materials with neutrons and then measuring the energy of gamma rays induced by the interaction of the neutrons and nucleus atoms. Unlike photon-based technologies, such as X-ray or infra-red, which measure the surface only, neutron analysis is more representative as it measures deeply the whole material on the belt [8].

3. Clinker

3.1. Clinker chemistry

3.1.1. Clinkering formation

As a first approximation, Portland cement clinker can be described as a four-component system consisting of the four major oxides: CaO, SiO_2, Al_2O_3 and Fe_2O_3 (Fe^{2+} being neglected). When the clinker cools to a subsolidus temperature, an assemblage is formed consisting of C_3S, C_2S, C_3A and C_4AF.

Chemical zoning of calcium aluminoferrite and the crystallisation of $C_{12}A_7$ are sometimes observed in Portland cement clinker. The conditions of these phenomena were studied during the crystallisation of a melt having a composition close to the invariant point ($C_3S/C_2S/C_3A/C_4AF$) in the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ pseudo quaternary system [9,10]. During the cooling, a melt differentiation was induced and could explain the presence of the zonal structure of calcium alumino-ferrite and the absence of $C_{12}A_7$ in Portland cement clinker. When a melt with 52.9% CaO and $Al_2O_3/Fe_2O_3 = 0.70$ was cooled from 1673 K, the C_3S and C_2S solid solutions and calcium aluminoferrite began to crystallise according to the $CaO–SiO_2–Al_2O_3–Fe_2O_3$ pseudo-quaternary phase diagram. The composition of calcium aluminoferrite at equilibrium with the melt is $Ca_2Al_{0.43}\,Fe_{0.57}\,O_5$. During cooling, the quantity of alumina contained in the ferrite increases up to 0.57, giving a zonal structural formation of the calcium aluminoferrite. This zonal structure is preserved at an ambient temperature because equilibrium with the ferrite crystal is not attained. At approximately 1613 K, solid solutions of C_3S, C_2S and C_3A start to precipitate. The phase composition at an ambient temperature would be a solid solution of C_3S, C_2S, C_3A and calcium aluminoferrite if the ratio of

Al_2O_3/Fe_2O_3 of the calcium aluminoferrite is between 0.7 and 1.5; whereas, if the ratio of Al_2O_3/Fe_2O_3 exceeds 1.7, then $C_{12}A_7$ will precipitate. The threshold of 1.7 corresponds to the ratio $Al_2O_3/Fe_2O_3 = 2$ of the interstitial melt of the cement clinker. Consequently, the crystallisation of $C_{12}A_7$ is unlikely because the chemical composition of the melt, finally differentiated, would lie within the $C_3Sss/C_2Sss/C_3A$/ferrite phase assemblage.

The presence of MgO (2%), Al_2O_3 (1%), and Fe_2O_3 (1.1%) modifies the lattice parameter of the solid solution of C_3S (tri- or monoclinic). Their measurement characterises unequivocally the concentration of the combination of MgO, Al_2O_3, and Fe_2O_3 and could be used to predict the reactivity of alite (for laboratory clinkers) [11]. The presence of MgO in high concentration gives rise to the crystallisation of the M3 polymorphic form of C_3S with a large increase in the number of small faceted crystals [12]. The incorporation of iron leads to an expansion of the lattice of C_3A [11].

3.1.2. Minor elements

The growing use of alternative fuel and raw meal introduces minor elements into the kiln. For example, phosphorus is present in meat and bone meal, and chlorides are present in refuse-derived fuels. These minor elements affect the burning process (clinkering, cooling, and emission) both thermodynamically by modifying the phase assemblages in the system $CaO–SiO_2–Al_2O_3–Fe_2O_3$ and kinetically by modifying the chemical and physical properties of the interstitial melt.

The minor elements are defined as those present uniquely in solid solution in the major phases instead of forming separated phases.

Two main techniques are used to study their effects: the analysis of minor elements in industrial clinkers with the limits imposed by the analytical measurements or the synthesis of laboratory clinkers with a controlled introduction of the minor elements. The way in which the incorporation of minor elements in the silicate phases modifies the contents of alite and belite is related to the charge and size of cations and their site occupancy in alite and belite. It is possible to evaluate this effect in the case of a limited number of minor elements but there are no well-established methods for evaluating the effect of the simultaneous presence of many minor elements [12].

Phosphorus: studies of industrial clinker show that phosphorus (up to 0.7%) is distributed into belite grains without any structural modification and the corresponding cement developed the highest strength at 20 °C (up to 0.7% of P_2O_5) [13].

In laboratory experiments, it is known that a small amount of P_2O_5 is added to suppress the “dusting effect” due to the transformation of β-C_2S to γ-C_2S and allows the microscopic examination [10].

Phosphorus replaces silicon in both alite and belite and, therefore, increases the content of belite with phosphorus contents in the clinker of up to 1%. The distribution of P^{5+} in the silicate phases is closer to 1 [3].

The increased belite contents that are often reported can easily be compensated by increasing the calcium content of the clinker.

Burnability is improved when HPO_4^{3-}, HPO_4^{3-} with F^-, or with F^- and SO_3^{2-} were added into the raw meal. The strengths were increased with the addition of $HPO_4{}^{3-}$ and F^- [14].

Halogen: the addition of chloride-containing components increases the burnability of the raw meal and allows higher alite contents at the same clinkering temperature. Halogens have a great capacity for reducing the viscosity of the liquid phase. CaO is highly soluble in liquid phases rich in halogen [12]. Chlorides show a strong preference for alite and the increase in chloride concentration led to the occurrence of the compound called alinite, which provides a solution for the utilisation of chloride-rich refuse-derived fuels to produce a low-energy clinker for non-reinforced concrete.

Sulphur: S^{6+} has a strong preference for belite. By increasing SO_3 in the clinker, the alite became richer in Al and Fe, particularly in Al, with an increase in the Al/Fe ratio.

The C_3A content decreased and C_4AF increased with increasing SO_3 content. An increase in the SO_3 content causes a reduction of the primary phase volume of C_3S (decrease of C_3S/C_2S ratio); 2.5% of SO_3 seems to be the threshold of formation of C_3S.

SO_3 and P_2O_5 decrease both the viscosity and surface tension of the liquid and the polymorphic form of C_3S, M1, is predominant as the constituent phase.

MgO and SO have opposite effects on the size and the phase constitution of alite. MgO favours the occurrence of the M3 polymorph, whereas SO_3 favours M1 [12].

The addition of SO_3 or $SO_3 + HPO_4^{3-}$ simultaneously reduces the burnability, whereas it improves with the addition of $SO_3 + HPO_4^{3-}$ and F^-.

Alkali metals: the increase in Na_2O content modifies the polymorphism of C_3A (Orthorhombic) with a limit of 4%. Na is partially incorporated in C_2S, stabilising the form α and α' at room temperature. When Na_2O is added, C_2S decreases and C_3S increases with a possible occurrence of free lime [15].

Alkali metal oxides, Na_2O/K_2O, increase the viscosity and decrease the surface tension of the liquid phase. The nucleation and growth decrease in rate and large alite crystals are grown with distinct facets.

A small content of chromium is found in cement. It arises primarily from the raw material and the wear of steel devices. When it is present as chromate CrO_4^{2-}, it provokes skin allergies. Reducing agents such as ferrous iron sulphate are added to prevent this shortcoming [16].

The maximum of Cu, Ni, Sn, and Zn that could be incorporated in a laboratory clinker has been determined experimentally. This threshold limit is found to be 0.35% of Cu, 0.5% of Ni, 1% of Sn and 0.7% for Zn [17].

The analysis of minor elements in the cement can be used to identify the origin of the cement and to explain the reasons of the deterioration of a structure. In addition, Mg, Sr and Mn can be used as “fingerprints” [18].

3.1.3. Emission

The mechanism of volatile cycles in cement manufacturing (mainly sulphur, chlorine and alkalis) has been studied experimentally and theoretically [19]. A comprehensive review is published as a keynote in the present congress by A. K. Chatterjee.

The alternative fuels have different properties from traditional fuels, such as coal, lignite, petcoke, fuel oil or natural gas. Chlorine, sulphur and alkalis evaporate in the kiln, interreact in the gas phase, are transported into the preheater and condense at lower temperature. If these substances pass back into the kiln, they can evaporate and an internal recirculating system is formed. Theoretically, these recirculations build up until the quantity discharged (clinker and gas) equals the quantity introduced. The increasing level of recirculating components leads to an increase in the process malfunction and requires a bypass system at the kiln inlet or the riser duct. The removal of the gas flow coming from the kiln results in energy loss composed of the sensible heat and the chemical reaction enthalpy in the gas and the dust. In many cases, the internal circulation stabilised at a level where by pass is not needed.

In clinker processes, three principal issues for the particle formation and trace element behaviour during the combustion of solid fuels are defined: the release into the gas phase (kiln and preheater), the chemical transformation as a function of the local environment and the subsequent aerosol dynamics.

Heavy metal emission from combustion sources originates from the release of metals into the vapour phases. The emission limit values for the cement plant under the “co-incineration” source category are classified into three groups of metals: $Sb + As + Pb + Cr + Co + Cu + Mn + Ni + V = 0.5$, $Cd + Ti = 0.05$ mg/m^3 and $Hg = 0.05$ mg/m^3 at 273 K 101.3 kPa, 10% oxygen) [20].

The particle limit values are based on a condensed-phase metric (particulate mass or number) without regard to the chemical composition.

During experiments carried out in a cement plant, the operation and monitoring parameters and emission values were continuously recorded [21]. It is shown that cement kiln dust (CKD) and the emission have a different profile of the relative abundances of heavy metals.

The Tl and Pb condensed species are likely to occur in the preheater, whereas other metals such as V or Cr are expected to condense in the kiln. Tl forms a volatile halide that forms a closed loop. Less volatile and insoluble species of lead condense in the clinker.

Decreasing the total particle emission does not necessarily decrease the fine particle emission and an efficient control of heavy metal emission must be based on fractional efficiency criteria. There are no direct emission limit values for fine particles.

A source signature is determined by the feed and fuel nature and flows by operating practises, by particle control device performances and, finally, by the effect of secondary particles (NO_x, SO_x and alkalis). It is difficult to establish the actual contribution of fine particle emitters.

3.2. Engineering of the process

3.2.1. Calciner

As a result of the technological improvements of clinker burning, the specific energy consumption has continuously decreased from the wet process of the long kiln (5000/6000 Mj/t of clinker), semidry process (3300/4500 Mj/t), dry process with a preheater (3100/4200 Mj/t) and the short kiln with a multistage preheater and cooling system (3000 Mj/t). The theoretical enthalpy requirement is around 1800 Mj/t.

A model of the cement burning process has been developed with the aim of providing a realistic simulation of plan operation. From this model with a rotary kiln as reference state with 5 stages of cyclone preheater, a calciner with a tertiary air duct and a grate cooler producing a clinker with a LSF of 97%, silica ratio of 2.5, an alumina modulus of 1.8 (64.3% alite, 14% belite, and 0.7% free lime) and with a throughput of 3000 t/d, it is demonstrated that the energy requirement of 3000 kJ/kg cannot be achieved as an annual average but punctually as a short term performance [22].

The main factors affecting the energy requirement are the local moisture level of the raw material, its composition and burnability, the properties of the fuels used and their proportion, the production capacity of the plant and the target quality. The raw material moisture determines the suitable number of stages for the cyclone preheater: 3 stages for a moisture higher than 12% and 4, 5, or 6 stages for a moisture of 8%, 6% or lower than 6%, respectively [22].

The higher preheater exhaust gas temperature by decreasing the number of stages indicates an initial increase in the energy losses for the preheater-kiln-cooler system; as a consequence, the clinker specific energy requirement also increases. A plant with a lower clinker throughput will have a higher specific energy requirement.

Simultaneously with the modification of the process, the nature and quality fuel were changed. Oil has, to a large extent, been replaced by coal, which in turn has been replaced by petcoke and natural gas, and now alternative fuels are used at an important percentage.

When converting from coal to petcoke, the effect of lower reactivity can be offset by raising the operating temperature of the calciner. However, the possible temperature increase in the calciner is limited. The combustion behaviour of solid alternative fuels and solid fossil fuels also differ [23].The pyrolysis rate normally has a large influence on alternative fuel burnout, whereas this influence is insignificant for fossil fuel. The diffusion of oxygen limits the combustion rates of alternative fuels to a much larger extent than fossil fuels. Temperature does not have a strong effect on the burnout of alternative fuels. In addition to the effects of different physical characteristics such a particle size, the calciner and burner design must also address these fundamental differences.

The use of alternative fuels leads to a modification of the thermal profile of the kiln and often to an instable kiln operation. As an example, for a long wet or dry process, whole tyres are inserted preferentially into the mid kiln area or injected into the front end of the kiln. For a short dry process, the kiln is equipped with a preheater or a preheater and precalciner, and shredded tyres are inserted into the riser duct above the tertiary duct inlet, which helps maximise the thermal substitution rate.

This imposes difficult challenges for designing calciners because the reliable ignition and burn from lumpy, secondary fuel often demands design features that are contrary to the requirements of achieving a high and consistent degree of meal calcination. In spite of these difficulties, alternative fuels are used in cement production all over the world.

Enrichment of the combustion gas/air with oxygen allows the alternative fuel to burn more consistently and at a higher flame temperature. By adding oxygen, the current fuel substitution rates can increase by 30 to 80%, can maintain or increase production and can lower operating cost.

Increasing the use of alternative fuels has also resulted in increased demands on refractories. It has been proven in practise that the products containing between 5 and 15% of SiC present excellent sticking and abrasion resistance at high temperatures and are much less sensitive to oxidation [24].

In parts of the kiln system, such as the combustion chamber, the hot part of the calciner, riser duct, kiln hood and the hot part of the cooler, materials with lower Si content may perform better and low SiC and $SiC + ZrO_2$ are implemented.

3.2.2. Cooler

Cooling the clinker is necessary to prevent damage to the clinker handling equipment, such as the conveyor, to minimise the clinker temperature as it enters the clinker mill (transformation of gypsum into hemi hydrate), to reduce energy consumption by extracting heat from the clinker and to enhance silicate reactivity, preventing alite transformation into C_2S and blocking the β form of C_2S.

The main trends of innovation in clinker cooling, aim at improving clinker transport and increasing thermal efficiency.

A model has been developed to calculate the temperature profiles of the clinker, air and wall along the cooler which the air and the clinker are inaccessible by experimental measurement. The model is based on a representation of gas–solid continuous cross-flow heat exchange by a series of stages fully mixed countercurrent contacting. The particle diameter, grate frequency, cooling air pressure and temperature and cooling air flow rate are the main parameters introduced in the model.

The entropy balance is necessary to evaluate the production of entropy generated by the irreversibilities of heat exchange between the air and the clinker.

From the model, the heat losses are estimated at 50% for the level of heat exchange between the air and the clinker and at 5% for the exhaust air. It is shown that the entropy production of the cooler decreases by increasing the cooling air temperature. It is confirmed that the heat recovery of the exhaust air contributes to the preheating of the cooling air and decreasing the external heat losses [25].

3.2.3. Clinker grinding

Grindability of the products, excessive wear of the equipment and energy efficiency are among the main problems that arise in the grinding process.

Chemistry and mineralogy impact the grindability. MgO has no influence, whereas Fe_2O_3 and Al_2O_3 increase the grinding time [11].

High belite cements are harder to grind, but the grindability of slags (GBFS) is up to 30% worse than that of cement clinkers, while the fineness requirements are higher (4200/5600 m^2/g) with a moisture content reaching 20%. The relative order of grinding tends to be in the following order:

$$\text{Gypsum} > C_3S < C_3A\,/\,C_4AF > C_2S >> \text{Slag}.$$

Grinding technology has undergone fundamental changes since the utilisation of the conventional ball mill. As for raw material, four types of grinding systems are used: ball mill, vertical roller mill, high-pressure roller press and horizontal roller press mill. The ball mills are still used in clinker grinding even though its application has decreased in new plant projects.

A vertical roller mill uses approximately 40% less power compared to traditional ball mill. Vertical mills with an integral separator are used for finish grinding with a mill capacity of 350 tph. The grinding conditions (grinding speed, pressure, water injection and grindings aids) must be optimised for each mill feed material.

An HPGR/roller press is used in various systems with ball mills for primary grinding and semi-finish grinding or as a single-stage grinding process for finish grinding.

Horizontal roller press mills are suitable for use as a single-stage grinding process. Energy savings are 50% compared to ball mills and 20% compared to vertical mills, but the throughput rates are limited at 120 tph.

The result of treatments with HPGR and conventional ball meal has been compared. The particle size distribution (<90 μm) for the ball mill-grinding mode (laboratory) and HPGR mode (industrial) is similar, down to 20 μm. With HPGR, higher BET results are obtained, but the water demand for the HPGR products was higher than the ball meal products [26].

When a continuous particle size distribution of sample is concerned, ball milling gives higher strengths, except for particle sizes of less than 20 μm. The compressive strengths of ball mill products were slightly higher than for the HPGR products. The particle size distribution (<30%μm) had the most important impact on the service properties.

These results agree with developments during recent years that have shown only small differences in the cement quality produced by different cement mills.

It may be presumed that a single-stage grinding process with a vertical roller mill or roller presses will continue to expand at the cost of the ball mill.

Chemical compounds are used to improve the particle comminution during the grinding of materials (grinding aids). The most commonly used grinding aids include propylene glycol, triethanolamine, triethanolamine acetate and tri-isopropylamine. The mechanism of action of grinding aids is not known precisely and their efficiency possibly varies with the type of grinder. The toxicity associated with the use of such chemicals must be taken into account [27].

3.2.4. Advanced techniques for process control

Throughout cement plants, different methods of measurement corresponding to different parameters are undertaken. Some parameters concern the process, including measurements of temperatures, pressures, filling levels of silos, flow rates, motor powers and gas analysis parameters. Some other methods concern the product, chemical and mineralogical analysis of the raw material, of the final products, characteristic analysis of the fuel and particle size analysis of the cement. Some measurements are carried out in a laboratory, while others are obtained online with sequential or continuous sampling. Some of these applications do not require sample preparation, while, for others, sample preparation is essential. Online measurement methods are increasingly necessary and are the main trend of advanced processes and product control.

Some data are used for feeding a database in case of a modification of the process (change of fuel or raw material) and represent a quality assurance evaluation. Some others monitor a regulation loop to control the process.

As a consequence of using alternative fuel, the level of various elements is increasing. This includes toxic elements, such as lead, cadmium, mercury, thallium, chromium, cobalt, nickel, vanadium, zinc, tin and antimony. Analysis and control of these elements become necessary.

X-ray fluorescence (XRF) is the most universal technique to obtain a quantitative chemical analysis with a variety of samples. There are two methods: wavelength dispersive XRF (WDXRF), which is used in central laboratories for accurate measurements and energy dispersive XRF (EDXRF) for a screening of medium to heavy elements. Typical materials used in the cement production can be analysed using standards and matrices with specific software.

The lack of standards for the alternative fuels has led to the development of standardless XRF. This method provides quantitative analysis on any unknown sample without the need for matrix specific calibration or standards. XRF is fast, requires only simple sample preparation (grinding and pressing) and provides high precision results.

The mineralogical analysis is necessary to analyse the calcium bearing minerals such as free lime, the alite and belite content, to identify the alkali salts and to control gypsum dehydration through the cement mill temperature to provide a consistent setting time [28].

XRD replaces traditional wet chemistry or other methods. The comparison between microscopy and truly quantitative XRD data shows that it is possible to exploit the integrated XRD system.

X-ray powder diffraction using the Rietveld methodology has been developed during the last decades for the quantitative analysis of clinker and cement (anhydrous or hydrated system).

Nevertheless, to apply this method, the crystal structure of all the components must be known, which is not the case for the main compound C_3S because of its presence as a solid solution containing minor elements, such as Mg and Al. The association of the X-ray diffraction, Rietveld refinement and neutron diffraction data allows a new structural description for low magnesium-bearing alite. The T3 type polymorphic form fits the pattern of alite from the laboratory and industrial clinkers (with MgO less than 1%). Three room temperature crystal structures are available for alite: T1 for stoichiometric C_3S, T3 for low magnesium-content alite and M3 for high Mg-content alites [29].

Despite these shortcomings, the role of XRD has been increasingly solicited to perform the mineralogical analysis of the clinker.

3.2.5. Global heat management

In addition to the major sources of energy savings (i.e., burning, cooling and grinding) some other methods exist that have been neglected (i.e., the regulation of electrical operations, the use of an integrated model of global heat exchanges and the recovery of low temperature heat).

The preheater and kiln are equipped with large power full fans (for extraction), while coolers are equipped with smaller and less powerful fans (for blowing). The regulation of an engine rotating at a constant speed consumes more energy than a fan driven by a speed variator (20% less energy). When a fan operates below its nominal load, it is less efficient. A control reduces the amount of power consumed and can lower the operating cost.

Stabilisation of the process by the optimisation of the burning conditions, leading to a global performance of a cement plant, is increasingly assisted by models that involve an integrated strategy of automation.

A large quantity of low temperature waste heat (below 350 °C), approximately 30% of the total heat consumption of the system, is still not recovered. Several different low temperature waste heat power generation technologies for cement production have been developed including the Steam Rankin cycle with three main patterns: single and dual pressure or flash steam generation system [30].

4. Chemistry and processing of new clinker types

Two trends can be defined in the new clinker type's areas: clinkers able to replace Portland cement clinker in the concrete and clinker or "binders" used for special applications. The first one is produced in large quantities and at low cost, while the second one is required when the properties of the first one do not satisfy the applications (refractory, high early strength development, service in hard conditions, biocompatibility with human tissues, etc.). Of course, the cost is higher and linked to the difficulty of achieving the required properties. The later examples are not mentioned here because they have been widely reported in the literature and are already industrially produced [31,32]. Rare cross-linking exists when Portland cement is used for dentistry (mineral trioxide aggregates) [33]. We focused our analysis to clinkers compared to Portland cement clinker and aimed at producing conventional concrete.

The qualification of the tem "new" for this type of clinker is not, stricto sensu, appropriate and all the novelty consists in the strong renewal interest in the low energy and/or the low CO_2 emitter cement.

The alternative clinkers are based on belite, belite combined with calcium sulphoaluminate (also called Klein's phase or Yeelimite) [34].

High belite cements are an alternative to reduce CO_2 emissions in the cement production process. They need less calcium than Portland cement (0.5 t of CO_2 per tonne instead of 0.54) and require a lower burning temperature (100 °C less) but are harder to grind. Belite clinkers are the most interesting in view of forming the same hydrate phases as conventional Portland cement.

The slow reactivity and mechanical strength at the early age of belite cements are overcome by adding alkaline oxide or fluoride to stabilise reactive polymorphs of C_2S (α for example) or by the simultaneous production of C_2S and Yeelimite.

The simultaneous presence of alkali oxides and SO_3 promotes a large quantity of α'_h, but the presence of SO_3 inhibits the crystallisation of α C_2S. Fast cooling is also necessary [35,36,37,38].

Sulphoaluminate clinkers based on calcium ferrite (5 to 25%), Yeelimite, (15 to 35%) C_2S, (40 to 75%) and minor phases (perovskite, gehlenite, periclase and free lime) are produced by sintering at a maximum temperature of 1350 °C [39]. The polymorph α' of C_2S is stabilised by boron. Sulphoaluminate-type clinkers are already manufactured in some countries.

The hydration of the Yeelimite compound can be accelerated and controlled by the addition of calcium sulphate (gypsum or anhydrite). Ettringite and gibbsite form as hydration products. When calcium sulphate is consumed, the Afm phase is formed. The addition of calcium hydroxide leads to a rapid setting of the binder due to the formation of C_4AHx. The compressive strengths of a mortar of calcium sulphoaluminate cement are comparable to those of Portland cement at 28 days [40].

Fluidised-bed combustion ashes can be used as raw materials in the production of belite-rich calcium sulphoaluminate cement. Laboratory experiments show a good combination at 1250 °C and 60 min [41].

Steelmaking slags are also used as raw materials to produce sulphoaluminate belite cement on the laboratory scale [42]. Their limit of utilisation due to the iron content is thwarted by mixing slags from different processes (Argon Oxygen Decarburisation, Basic Oxygen Furnace, Ladle, and Electric Arc Furnace).

Higher reactivity is possible with the combination of alite and Yeelimite, but their simultaneous presence is not thermodynamically possible because the Yeelimite is unstable above approximately 1200 °C (before the alite is normally stabilised). It could be possible to stabilise the alite at lower temperatures by incorporating in its structure other components, such as fluoride or Mg, Cu, Zn, or Ba.

Belite barium calcium sulphoaluminate is based on the mineral assemblage containing C_3S, C_2S, C_3A, C_4AF and $C_{2.75}B_{1.25}A_3\$$, (\$ for SO_3). Its hydration with the addition of gypsum shows a good strength development with more CSH gel and a dense structure. A substitution of Fe^{3+} to Al^{3+} is possible with an optimum of 0.5 to 1.7% BaO and SrO, respectively, to replace lime in the synthesis of aluminate. However despite the interesting prospects for refractory applications, the issues of water solubility, scarcity of raw materials, difficulty of synthesis and the low working time of concrete render the future of these binders to be limited [43,44].

Aluminium-rich belite sulphoaluminate cements are another solution to obtain more reactive cements. The mineralogy composition is C_2S (50/60%), Yeelimite (20 to 30%), CA (10%) and $C_{12}A_7$ (10%). The burning condition (between 1250° and 1350° held for 15 or 30 min) is defined by high-temperature microscopy and thermal analysis. The hydration behaviour shows that β C_2S reacts at an early stage (34 h) for the cement containing β C_2S (50%), Yeelimite (30%) and CA plus $C_{12}A_7$ (10%) compared to conventional belite-rich Portland cements. At the early stage, the belite appears to react with amorphous AH_3 to produce C_2ASH_8 (Stratlingite). The hydration mechanism of the aluminate phase seems to be dependent on the initial amount of gypsum added [45].

5. Conclusions

During the last 20 years, two main innovations in the engineering of production processes of Portland cement have occurred. They were driven by the energy conservation constraints. These developments include that of the precalciner with a multistaged preheater and the grinding process by pressure instead of shocks.

During that time, the evolution of our civilisation has led to an increased number of constraints for the cement industry. After the energy conservation arises the emission (dust, CO_2, NO_x…) problems, the quarry rehabilitation, the scarcity of the mineral source and the chromium content of the cement, among other issues.

It is unlikely that the number of constraints would decrease in the future and thus several questions must be asked.

1) With the present technologies, is the cement industry going to achieve the constraint imposed by our society?
2) What are the limits of the present technologies independent of these constraints?
3) Are the level of improvements scientific or technologic? In other words, are more understandings of the clinkering reaction necessary?
4) What are the new constraints to be erected by our society?

The analysis of industrial data and calculations with a processing engineering model can answer the first two questions and show that with an up to date process of production, (precalciner with a six-stage preheater), a specified fuel energy of 3000 Mj/t can be achieved only in a short term performance and not as an average. This level is still far from the theoretical value of 1800 Mj/t [22].

Others studies of the variations of the process parameters and their comparison with the variation of the CO_2 emissions for the same period show that the emissions are controlled by the production evolution. The highest investment in Portland cement with conventional technology cannot reach a global world reduction of 50% CO_2 by 2050 [46]. The answer to the last two questions would be speculative.

What is next for the cement industry?

While waiting for a breakthrough, continuous improvements have been and continue to be achieved by the cement industry in the direction aiming at energy savings and emissions of CO_2, dust and others:

a) by paying attention to details that increase the operating and production costs (wear due to handling, optimisation of the consumption of the fan, etc.);
b) development of new online analyses, control and modelling of the process and product;
c) increasing the renewal of the old cement plant;
d) integrating the clinker as a part of the concrete and
e) combining the improvement of concrete and construction technology.

These developments are probably not sufficient for complete solutions but can contribute to possible solutions.

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