

FACTORS INFLUENCING THE QUALITY OF CEMENT

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In our age cement is the most important binder in construction. Its two main types are: *portland cement* (a silicate binder) and *alumina cement* (aluminate cement). The hydraulic hardening is provided in portland cement by calcium silicates, in alumina cement by calcium aluminates.

Portland cement is produced by mixing strictly determined quantities and proportions of calciferous materials (limestone) with raw materials containing metal oxides (SiO_2 , Al_2O_3 , Fe_2O_3) necessary to develop clinker minerals, grinding to a fineness required by reactions of clinker formation; burning at 1400 to 1500 °C; and fine-grinding the half-product clinker. This complicated sentence itself shows how many conditions have to be satisfied to produce a high-quality portland cement, and what are the manufacturing possibilities to improve the quality. All these are joined by requirements or specifications by users.

Raw material of *alumina cements* is also limestone with a CaO content and raw materials with an Al_2O_3 component, first of all bauxite and, of course, not excluding other raw materials containing Al_2O_3 (e.g. nepheline, alunite). Production technology is in principle identical with that of portland cement. Mechanisms of the setting and hardening processes, however, much differ between the two main cement groups.

1. Silicate binders

Here chiefly the effects of clinker production, composition and cement grinding, as well as the effect of different admixtures to control the setting and to change purposefully the hardening properties will be discussed.

1.1 *Effect of the composition*

Portland cement hardening and strength much depend on the composition of the processed clinker. Strength properties are known to much depend on the *tricalcium silicate* (C_3S) content. In general terms this means that the higher the CaO content in the clinker, the better the hardening conditions.

This axiom has absolutely to be kept in mind in designing the raw material composition.

There are many publications on the size and form of alite, the tricalcium silicate grain, on differential hydraulic qualities of tricalcium silicate modifications stabilized by different admixtures, on transformation of the tricalcium silicate lattice, on introduction and role of atoms in the lattice, on cooling and its rate.

These problems are extremely important. This subject is among the most debated ones in the literature on cement chemistry. Here it might be enough to state that between the *alite* in portland clinker, produced by no special method with no special admixture, and the "artificial" alite there is no important difference from the viewpoint of general practical use.

The *tricalcium aluminate* (C_3A) content has a decisive effect on the clinker quality and on the hardening process of the cement made of it, although it does not harden hydraulically in pure state. As concerns the role of C_3A , tests made with the mixture of pure compounds and with technical cements used in practice showed the early strength of cement to increase with increasing C_3A content.

This effect is more definite with lower ($w/c < 0.4$) than with higher w/c ratios. Also development of the ultimate strength of the cement due to tricalcium aluminate is rather curious. Ultimate strength of the cement is much increased by air storage, and much reduced by water immersion.

The C_3A content greatly affects the corrosion resistance of cements. Its mode of action is, however, outside the scope of this study.

Thus, adjustment of the Al_2O_3 content $\left(\frac{Al_2O_3}{Fe_2O_3} \text{ module} = A_M \right)$ offers an interesting and important tool to produce cements with different properties.

The role of *iron oxides* (FeO , Fe_2O_3) is discussed extensively in the special literature. It is decisive in the development of the melt phase of the clinker and in reducing the temperature of clinker-forming reactions. The $CaO-Al_2O_3-Fe_2O_3$ system includes many compounds affecting composition and development of portland clinker. From the viewpoint of clinker chemistry only the crystal compound series likely to develop between the incongruous dicalcium ferrite (C_2F) and different calcium aluminates, primarily C_2A_7 , is of interest. Among these crystal compounds the brownmillerite (C_4AF) holds a notable place.

In the development of the cement quality, *ferric compounds* are only of significance by facilitating calcination and reducing the burning temperature. This feature of ferric compounds gets an increasing actuality by improving the *energy balance* of clinker combustion.

The *sulfate* and *alkali* contents of the clinker much affect the quality of clinker hence of cement, the setting time and the course of hardening.

It must be mentioned, however, beforehand that there is no perfect agreement between researchers on the role of sulfates and alkalis. Rather than to get involved in the discussion, here only some statements probalibilized by great many tests are summed up.

For an otherwise identical clinker composition, the SO_3 content — up to 1.0 or 1.5% — does not substantially increase the early strength of cements. Its effect on the 28-day strength is hardly noticeable.

Caution is due to the SO_3 content from the aspect of constant cement volume. Nearly all cement standards, all over the world, limit the SO_3 quantity in the cement.

Of the role of alkalis only so much should be mentioned that with increasing K_2O content the strength increases in the first days (up to 7 days) and then decreases.

An interesting item is the interaction of alkali and SO_3 contents. Increasing the sulfate content for a given alkali content also the early strength increases, and the ultimate strength (at 28 days) but slightly changes or decreases. The same applies to the common increase of alkalis and sulfate content. The initial strength (3 days) increases and the ultimate strength (28 days) decreases.

The role of alkalis and SO_3 is, however, much more important, so to say determinant for the clinker calcination technology in burning. Higher alkali and SO_3 raw materials are easier to melt. In case of local overheating and technological unevennesses, accretion occurs, either in hotter stages of dry exchanger cyclones or in rotary kilns.

Therefore their presence must be watched and it is advisable to control their quantity as a function of technology and equipment.

Trace elements present in the raw materials are generally irrelevant to the cement quality, so they need not be reckoned with.

Phosphate gypsum is, however, increasingly used in the cement industry, partly as a raw material component and partly as a setting control replacing gypsum.

Phosphate content of the phosphorous gypsum raw material reduces the clinker capacity to bind calcium by forming a mixed crystal in the form of tricalcium phosphate ($3\text{CaOP}_2\text{O}_5$) with dicalcium phosphate, a stable compound even in the presence of free CaO . Thereupon, the tricalcium silicate content or — according to the above, — the early cement strength decreases.

The role of a small amount of P_2O_5 is quite different. In a quantity of 0.1 to 0.3% it can combine with the tricalcium silicate part and increase thereby its strength, primarily the early strength.

This problem opens a new domain, that of admixtures used in small quantities, *mineralizers* by collective name. Also these questions having to do with crystal chemistry are outside our scope — though their importance and significance, too, are worth mentioning.

Among the secondary components, the role of *magnesia* (MgO) has to be examined. Magnesia has been interesting for volume stability since long. Its negative effect on the compressive strength of cement in ranges of higher calcium saturation is less known. In smaller quantities (about 0.5 to 1.0%) it can combine with the $3\text{CaO}=\text{SiO}_2$ lattice. Because of the mineralogical conditions of combination this means a certain strength increase. In higher quantities, however, it significantly reduces the strength of the cement, especially in long-term tests, partly attributable to swelling accompanying the periclase (MgO) hydration.

In any clinker, part of the calcium remains unbound. Under usual conditions the free CaO content, up to 2.5%, somewhat improves the compressive strength, in particular the early strength. A higher free calcium content, however, impairs the strength — chiefly in a later phase of hardening (calcium expansion).

1.2 *Effect of burning*

From heat management aspects, the clinker of standard composition is burnt in an *oxidizing atmosphere*, but economy reasons impose an oxygen excess as low as possible. The oxygen content of the furnace gases is 1 to 2%, but may be as low as some tenths percent. With so low an oxygen content carbon monoxide may be generated in the sintering zone, to oxidize into carbon dioxide only in the preheating zones.

The oxidizing atmosphere is necessary also from the viewpoint of quality. Namely, burning in a *reducing atmosphere* reduces the trivalent iron to bivalent, of which a relatively high quantity (1 to 2%) can combine with the tricalcium-silicate crystal lattice. As a consequence, stability of C_3S much decreases, so that even an abrupt cooling to below 1180 °C causes it to disintegrate into C_2S and free CaO, accompanied by cement strength loss and also the constancy of volume is impaired.

A reducing atmosphere may develop even in the presence of sufficient oxygen if the raw clinker flour contains sulfide absorbing oxygen, resulting in the same phenomenon described above.

In an oxidizing atmosphere, however, the iron component oxidizes to trivalent, to combine with the calcium-aluminate-ferrite compounds.

In strong reducing burning not even the bivalent iron is constant. Metal iron forms which cannot influence the stability of C_3S anymore (it does not penetrate its crystal lattice). The strength properties of the cement are slightly impaired but the power consumption of clinker burning considerably increases.

Besides, in reducing burning a decrease in aluminate ferrite formation has to be reckoned with. Under such circumstances bivalent iron forms com-

pounds other than does trivalent iron, with an increase of aluminate content, influencing, in turn, the setting.

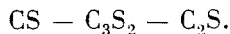
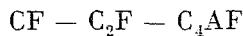
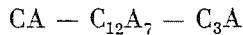
From the aspect of clinker chemistry, burning is especially interesting because of the simultaneity of *dehydration*, *dissociation* and *decarbonation* processes of the crude mixture's components and those of new phase formations. Investigation of these phenomena is rather interesting for the construction and development of the kiln.

The sequence of clinker formation has been established by several researchers as follows:

a) For mixtures containing $\text{CaCO}_3 + \text{MgCO}_3$, montmorillonite, illite (possibly quartz), the reaction sequence is practically the same for wet, semi-wet or dry-process equipment.

b) Dissociation and decarbonation of crude mixture components begins at 550° to 600° C, at the same time they start to react with the released calcium. Thus at 1000° C, with the end of decarbonation, only about 15% free CaO is in the system.

c) The first phases to develop are CF, CA and CS, which as an effect of the temperature change into



d) At about 1300° C the solid phase reactions end and a melt phase forms, with complete melting of C_3A and C_4AF and slight melting of C_2S and CaO, incorporation of components such as FeO, MgO, P_2O_5 . In presence of the melt C_3S is formed and with crystallization of the remaining melt the final clinker phase composition consists of the following compounds and clinker minerals: C_3A , C_4AF , C_2S , C_3S , MgO, free calcium, CaSO_4 and glass.

Secondary reactions in presence of minor components, induced by catalysts, are of paramount importance for the clinker quality.

Disregarding the otherwise debated presence of intermediate phases such as CS, C_3S_2 , C_2AS , etc., several researchers have observed different transient compounds and complexes when heating either standard raw material mixtures or even a mixture of calcite and clay minerals (kaolinite, montmorillonite, illite). These are formed in the temperature range of 1000 to 1300° C with different catalyst or with materials present in the raw material mix in small quantities (P_2O_5 , Cr_2O_3 , SO_3 , Na_2O , K_2O , Sr_2O_3 , MgO, CaF_2 , CaCl_2), an infinity of complex compounds. Not even their individual effect is always known, let alone their multifold, complex effect.

Undeniably, however, these materials of catalyst character suit to influence the properties as wanted.

Also this detailed enumeration shows the complexity of the clinker formation process, with thermodynamics and kinetics depending on many factors, any change of which supposes a fundamental knowledge of the system.

1.3 *Effect of cooling*

Cement clinker burning yields a melt, containing, beside CaO, practically all the alumina and iron oxide present in the original crude flour. At a calcination temperature of 1420 to 1450 °C the percentage by weight of the melt is 20 to 25%. It can be deduced from the proper melt balances that the CaO content in the melt is not enough for the complete crystallization of the tricalcium aluminate and the aluminate ferrite. In slow cooling the missing CaO is abstracted from C_3S , solid even at sintering temperature, thus becoming C_2S . Practically, cooling is generally rapid enough to cancel the reaction — unfavourable for the quality (thus, for the strength) of cement. Thus, in practice, the method of cooling can only influence the development of clinker compounds itself, decisive, in turn, for the setting and hardening conditions of the cement.

The way of clinker cooling has a more marked effect on the development of compounds crystallizing from the melt. These are primarily C_3A and C_4AF . Therefore the clinker cooling rate from the sintering temperature to 1250—1300 °C, where the melt hardens completely, is of decisive importance.

The *kiln construction* is such that in general the clinker does not fall into the cooler at the sintering temperature but is more or less chilled in the cooling zone of the kiln. Thus, not alone the construction of the cooler or its efficiency is responsible for the development of the clinker minerals, but also the mode of fire control.

The effect of clinker cooling on the cement properties has much been discussed in the literature. Here too, opinions are often opposed. As a conclusion it may be stated that a very rapid cooling of the clinker reduces the strength and with slow cooling the setting time is shorter. Even that is not quite unambiguous. In an experiment the clinker burnt at 1450 °C was abruptly cooled in water for short times varying from 0.5 to 10 sec. The submersion into water for less than 1 sec increased the compressive strength compared to air cooling, and longer submersions reduced it. These favourable results are practically meaningless because this cooling method cannot be realized under plant circumstances. X-ray tests showed water submersion to reduce the crystallization of C_3S and to increase its reactivity. On the other hand, the hydration tendency of glassy C_3S is lower. Such a short submersion creates an optimum between both processes.

For shorter setting times due to slow clinker cooling, first of all the development of C_3A is responsible. Different observations point out that C_3A is

the more reactive — thus the faster reacting with water — the better it has developed i.e. the slower it has crystallized from the melt, and finally, the slower it cooled. The more this fact affects the setting conditions of cement, the higher the C_3A content. Based on this it might be favourable to abruptly cool the clinker even after being cooled to 1200 °C. Such a clinker is easy to grind.

Behaviour of clinkers produced in different kiln atmospheres may be different, depending on the *cooling rate*.

C_3A contents in clinker burnt in different kiln atmospheres and cooled in different ways have been determined. The C_3A content was found to abruptly increase if the cooling of the clinker started below 1250 °C. This change was, however, essentially greater in a reducing than in an oxidizing atmosphere because of the decisive effect of C_3A on the cement setting rate. Clinker burnt at 1450 °C in a CO atmosphere and immediately air cooled behaves similarly to that burnt in an oxidizing one and cooled at 1250 °C. If rapid cooling of clinker burnt in a reducing atmosphere starts at a lower temperature, the setting rate is essentially accelerated. Clinker cooled at 1150 °C sets immediately after mixing with water. The rapid setting may be attributed to the rapid formation of calcium-aluminate hydrate. Mixed with water, too much of C_3A is dissolved of the clinker and because of the slow reactions with the present calcium sulfate solution to form ettringite, there is a rapid (or more rapid) setting going on.

1.4 Role of the grinding

In general, the faster the cement setting, the finer the hydraulically active components are ground, or — according to established plant control methods — the greater their specific surface. Namely, the quantity of hydration products — under identical conditions — depends practically on the surface area reacting with the mixing water.

Development of hydration is a prolonged process in the course of which — after a time — the reaction rate decreases, since the hydration products coat the still unhydrated cement grains, hindering the water to reach the unhydrated core. Subsequently these unhydrated cement particles are not — or barely — taking part in the hardening process and do not contribute to the strength.

Hereupon it seemed logical to suppose that a cement of a given quality yields — under identical hardening conditions — always the same ultimate strength, only that the sooner, the finer it is ground.

In reality this is not so. The coarser cement, although slower setting, reaches a higher ultimate strength than the finer ground cement. Namely, in a slower hydration the calcium silicate hydrate whiskers (tobermorite) are

longer interlacing, and their assumed higher whisker strength results in a hardened cement structure of higher ultimate strength.

Many researchers investigated the effect of grain size on setting. Evaluation of the share of different clinker grain sizes in strength is summed up below.

The fraction 0 to 3 μm achieves a very high 1-day strength, that does not increase essentially thereafter.

The grain fractions 3 to 9 μm and 9 to 25 μm set slower but achieve the same 28-day strength as the 0 to 3 μm fraction, or even much exceed it.

Strength tests on different grain fraction mixtures showed the early strength of portland cement to be the higher, the more the 0 to 3 μm fraction but for a high 28-day strength much of fractions 3 to 9 and 9 to 25 μm are needed.

However, the tests went further. The setting of portland cement with identical specific surface was seen to depend on the grading i.e. on the slope of the grading curve. It was also revealed that a cement of the same specific surface but a steeper sloping grading curve, hence a narrower grading, containing both less fines and less coarse grains, attained a higher strength than the cement of reference, displaying a flatter grading curve, value n in the RRS net. The narrower the grading, the higher the n value. For an identical specific surface but a higher n value, i.e. for a narrower grading, 2, 7 and 28-day strengths are essentially higher.

This is how this factor intervenes in the appreciation of cement strength, or in evaluating the cement. This means also that the faster a cement of a given specific surface hydrates, the narrower its grading.

Thus the grinding fineness has an outstanding effect on the cement strength, especially on its early strength. Numerical values are but reluctantly mentioned here, but if the Blaine specific surface of the standard portland cement is 3000 to 3500 cm^2/g ; then for a high early strength cement, specific surfaces of 5000 to 6000 (cm^2/g) have to be taken into account. Here, however, agglomeration has to be considered as an important limiting factor.

1.5 High early strength portland cements

A decisive factor of producing high early strength portland cements is selection and design of a *chemically and mineralogically optimum composition*.

The precondition of high early strength is the presence of the mineral component alite (C_3S) in proper quantity. Besides, the hydration rate of tricalcium aluminate (C_3A), surpassing that of the other mineral components of the clinker, contributes also essentially to a higher early strength, without, however, substantially influencing the development of the final strength.

One index of the contribution of mineral components to the acceleration of the setting process is the *hydration heat* value. This is especially true for

C_3A . The hydration heat is directly related to the setting and hardening process. A low hydration heat release is concomitant to a slower hydration process. But an excessive hydration heat value excessively accelerates setting and hardening, may even generate high internal stresses and reduce the mechanical strength.

Examining elements of high early strength from this aspect shows their production to require an as high C_3S content as possible and an optimum of C_3A content.

Numerically expressed, the following approximative relationship can be set up:

High early strength cements require:

$$(C_3S + C_3A) = 65\%; \quad C_3S = 55\% \quad \text{and} \quad C_3A = 6-15\%.$$

The potential ability of tricalcium silicate and tricalcium aluminate to yield a high early strength cement can more or less be influenced by the presence of other mineral phases in the clinker, the C_2S , the ferrite phase, the glass phase, their relative proportion and morphology.

Formation of clinkers adequate for mineral built-up and crystal-chemistry characteristics of the components depends not only on the chemical composition, but on the nature of the used raw material and, decisively, on technological factors, such as the grinding fineness, correct control of the chemical composition of the crude flour, the use of mineralizers, burning, cooling and cement grinding.

A special aspect of this problem is the effect of the size and form of alite grains. Detailed investigation of this question would lead too far. It should be mentioned, however, that development of the liquid phase is important for eliciting reactions, resulting in clinker minerals, especially alite. For the same reason the burning temperature and range, and the cooling rate are of paramount importance.

These extremely complex effects had been involved in developing a high early strength clinker named "Regulated Set Cement", burnt at 1275 to 1400 °C of a crude mix, rich in alumina, admixed with 1 to 2% fluoride. The chemical composition is adjusted to replace the usual quantities of tricalcium silicate and dicalcium silicate and a limited quantity up to 30% of aluminate ferrite in the clinker, by higher quantities of $11 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3 \cdot \text{CaF}_2$ up to 40 to 60%. The C_3S content must not be less than 30% or more than 50%. (If CaF_2 or AlF_3 is added to the starting material before burning, $11 \text{ CaO} \cdot 7 \text{ Al}_2\text{O}_3$ is formed instead of $3 \text{ CaO} \text{ Al}_2\text{O}_3$.)

The clinker is ground to cement by adding more than usual of gypsum. At an extremely high early strength, the setting rate slows down very much with time to lag behind the conventional high early strength cements at 28 days of age.

The early strength of high-lime portland cements can be increased by mineralizers. Adding a small quantity of Cr_2O_3 , MnO and F to the crude mix, an adequate fine grinding and increasing the SO_3 content, a cement can be produced with a 1-day compressive strength twice the early strength of the standard high early strength cements. The cement tested also in concrete specimens contained 0.5% of CrO_3 , 0.4% of MnO and 0.2% of F .

Appreciation of the economic importance of high early strength cements requires knowledge of strength data from some hours to 1 day of age, in order to determine the expenditure to achieve the same concrete strength with cements of standard composition, e.g. by increasing the cement dosage, by a lower w/c ratio, or by heat curing.

1.6 Interference in the hydraulic setting process

In the first phase of hydration, during the reaction of C_3S with water, a solution saturated or supersaturated with calcium hydroxide is soon formed, of which $\text{Ca}(\text{OH})_2$ is precipitated. Practically at the same time the sulfate compounds (gypsum) are dissolved, reacting with the calcium aluminates, aluminate ferrites with simultaneous formation of ettringite, $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3 \text{CaSO}_4 \cdot 31-32 \text{H}_2\text{O}$. Ettringite whiskers hamper the otherwise very quick reactions of the aluminates. (This is fundamentally the function of the gypsum.) Practically there is no hardening in this stage.

In the next stage of hydration (after about 1 hour) calcium silicate hydrates begin to develop. The long calcium silicate hydrate whiskers grow undisturbed in the water-filled cavities and intertwined with the ettringite whiskers they represent already some strength.

In the third stage of hydration the pores of the "hardened cement" are increasingly filled with short-whisker calcium silicate hydrate compounds. Formation of ettringite stops after having exhausted the sulfates, and even it reacts with the still unhydrated aluminates and aluminate ferrites forming mixed crystals of $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12 \text{H}_2\text{O}$, or $4 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13 \text{H}_2\text{O}$. Thus the ettringite impeding the reaction is decomposed and the further reaction is again accelerated between calcium aluminates and calcium silicate hydrates, while further $4 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13 \text{H}_2\text{O}$ and its mixed crystals of iron oxide content develop.

The described reaction mechanism implies the presence of calcium sulfate in a definite though minimum quantity. Namely the sulfate quantity has to be used up in about 24 hours, otherwise a reaction between the sulfate and the aluminates would impair hardening.

Beside control of the setting time, calcium sulfate has a substantial effect on the hardening process. With increasing calcium sulfate content both

the initial and the 28-day strengths increase. After a strength peak, further increase of the sulfate content reduces the strength.

The optimum of the calcium sulfate content, resulting in the highest cement strength, is in general the higher, the higher the C_3A content of the cement, the finer it is ground, and the higher the ambient temperature.

Phosphate gypsum, used in some countries for setting time control, contains water-soluble phosphates and complex flour compounds — delaying the start and end of the setting even applied in very small quantities.

1.7 Hardening control

If some particular property is expected from the concrete, small quantities of special materials solved in the mixing plant may essentially change the hydraulic setting and hardening processes.

Phosphates, silicofluoride, borates, sulfonates, gluconates are effective *retarders*.

For *setting acceleration* alkali carbonates, silicates, aluminates, nitrites, nitrates are used.

The most active *catalyst* is calcium chloride ($CaCl_2$) the use of which is, however, prohibited in reinforced concrete structures in most countries because of its corrosive effect, the amino-salts of amine acid have a similar effect.

Testing the so-called alinite cement may be instructive on the effect of Cl^- ions, still awaiting a comprehensive study.

The hardening can be accelerated and the strength increased by adding a small quantity of finely ground hardened cement. Particles of the hardened cement act in hydration as crystallization nuclei and accelerate the course of hydration. This effect can be even enhanced by adding to the finely ground cement — employed as crystal nucleator — a small quantity of a mixture of caustic lye of soda and sodium-methyl-siliconite. Thereby addition of 2% of this nucleator produces the same effect as a similar quantity of $CaCl_2$.

2. Alumina cement

Alumina cements based on calcium aluminates i.e. on their hydration are superior to portland cements by rapid hardening hence high early strength. It is known from the literature that high early strength is due first of all to monocalcium aluminate (CA). The other important clinker mineral of alumina cements is CA_2 .

Burning of a raw material mixture corresponding to the composition of the two calcium aluminates is accompanied, in addition to the basic minerals,

by the temperature and time dependent development of a high number of other, partly transient, partly lasting clinker minerals. These will not be discussed here. Neither will minor contradictions of the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ or the function of different components likely to be integrated in certain aluminate lattices, changing their crystallographic properties and reactivity and affecting hydration conditions without essentially altering the structure and properties of alumina cements.

Formation of CA, the most reactive clinker mineral, can be simply stated to consist in the continuous increase of the quantity of crystalline CA of adequate composition with increasing intensity of burning. In the meantime also C_{12}A_7 and Ca_2 are temporarily formed. C_{12}A_7 varies according to a maximum curve to finally disappear. CA_2 does not disappear completely.

In the clinker of CA_2 composition CA disappears after a relatively low temperature maximum. Temporarily also C_{12}A_7 develops. Quantity of crystalline CA_2 continuously increases with increasing intensity of burning.

Accordingly, clinkers of a composition corresponding to the CA, yielding high early strength cements, are obtained by intensive burning. For a CA_2 composition, burning has to be gentle, at a temperature corresponding to the maximum of CA development. Care is needed, however, not to leave any free CaO in the clinker, else strength is impaired. The optimum is at 0.2% of free CaO.

In the course of alumina cement hydration, according to the known constitutional diagram of the $\text{CaO}-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system, the formation of stable compounds (AH_3 , regular system C_3AH_6 , CH) is accompanied by that of several unstable hexagonal alumina hydrates (C_4AH_{13} , C_2AH_8 , CAH_{10}) with existence conditions differing as a function of concentration and temperature. Equilibrium conditions are rather uncertain even in the transient state. An understanding is impaired even by the lack of a comprehensive treatment of colloid-chemical processes during hydration. Though the stability and solubility of AH_3 and FH_3 gels, their behaviour in air, water or in the presence of atmospheric CO_2 are decisive for the strength, stability and durability of alumina cement concretes.

Alterations depend on the simultaneous effect of several factors, such as:

- w/c ratio;
- high porosity of alumina cements;
- presence of CO_2 ;
- warm and moist environment;
- presence of alkalis.

In concrete production, the w/c ratio should be minimized with a view on workability. A critical w/c ratio (about 0.35% or lower) has to be applied, likely to minimize the concrete porosity.

The concrete compactness requires a cement dosage of at least 300 to 350 kg/m³.

Alkalis, sulfur compounds should be kept away both from the setting cement and the hardened concrete.

A concrete temperature not exceeding 20 °C has to be provided for.

These are the measures assuring a relative stability of alumina cements in useful but restricted application domains.

Summary

The most important factors acting on the cement quality are the chemical composition of the raw materials and the clinker, the effect of ferrioxide, SO₃, alkalis and magnesia!

A similar importance is due to the way of burning, to the kiln atmosphere, to the sequence of clinker formation.

Cooling and cement properties are strictly related.

The grinding fineness markedly affects the early strength.

For portland cements of high early strength, hydraulic setting and hardening can be influenced by admixtures. Alumina cements rely on the formation of CA and CA₂. In connection with the hydration of alumina cements both the concrete porosity and the water/cement ratio have to be kept at a minimum.

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