International Journal of Applied Engineering Research ISSN 0973-4562 Volume 10, Number 21 (2015) pp 42688-42691
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Influence of Cooling on the Quality of Clinker with Different Content

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Abstract

It has been estimated the influence of conditions of cooling clinker of different composition on phase composition, microstructure and quality of cement. It has been synthesized with different aluminous modulus varying from 0, 67 to 2, 85, subjected to different conditions of cooling. It has been studied the phase composition of the derived clinkers and also their microstructure and hydration activity. In the clinker with $C_3A \leq 8\%$ with elevation of temperature of quenching the intermediate phase is presented with enriched iron solid solution $C_2A_xF_{(1-x)}$ and high C_3A, and for high aluminate composition – just the reverse, the quantity of aluminate phase is reduced. Quench from maximum temperature of the clinker with C_3A = 15% provides reduction of sizes of crystals of allite and reduces hydration activity of the clinker to the 28 days of hardening. Maximum activity of the clinkerto 28 days is achieved by moderate composition C_3A ~ 8% and quenching from 1150ºC.

Keywords: clinker, cooling mode, microstructure, activity, content of C_3A.

INTRODUCTION

Burning conditions and refrigeration of the clinker influence the structure of clinker, the form and size of crystals, mineralogical makeup, grindability and, therefore, the amount of derived cement [1-8]. Changing the process of cooling, one may directly affect the properties of clinker, obtaining optimum results. Considering that basic materials are crystallized from melt that is formed with clinker burning, it should be paid attention to transformation of clinker phases in the process of cooling with different properties and composition of high-temperature liquid phase. Since clinker melt is higher than 1300ºC and consists more than 80% of transient formation $C_2A_xF_{(1-x)}$andC_3A, than it is necessary to consider the properties of clinker with different ratio C_3A/ C_4AF, that is, variable aluminous modulus ***p***.

Synthesis of Clinkers of Different Composition

For this purpose it has been calculated the raw mixes from chalk, clay, bauxite and chemical agent Fe_2O_3withKH = 0, 92andaluminous modulus ***p*** = 0, 64 (mix#1), ***p*** = 1, 33 (mix#2) and***p*** = 2, 85 (mix#3), to have 0; 8 and 15% of C_3A in the clinker.

From raw component in certain ratio it has been prepared raw mixes in accordance with needed conditions (table 1). It should be noted that the resulting mixtures in accordance with calculation vary in content of aluminium oxide and iron. With increasing ***p***to 2, 85the content of oxide calcium and losses by calcination in raw mix insignificantly rise. The increase of losses by calcination is connected with the presence of bauxite in terms of 2, 15 and 4, 26% respectively, along with clay, in raw mixes.

Table 1. Chemical composition of raw mixes, masses, %

#mixes and content of C_3Ain the clinker	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	R_2O	ППП
#1(C_3A = 0%)	14, 44	2, 67	4, 17	43, 06	0, 44	0, 15	0, 28	34, 80
#2, (C_3A = 8%)	14, 10	3, 65	2, 75	43, 32	0, 43	0, 16	0, 26	35, 31
#3, (C_3A = 15%)	13, 70	4, 61	1, 62	43, 48	0, 41	0, 17	0, 24	35, 75

On the curves of differential-scanning calorimetry (DSC) of raw mixes (figure 1) the following physicochemical changes are observed. Endoeffects at the temperature of 243ºCand 249°Con the curves ofDSC of mixes#2 (C_3A = 8%) and#3 (C_3A = 15%) correspond to partialdehydration of gibbsites $Al_2O_3 \cdot 3H_2O$with formation of boehmite $Al_2O_3 \cdot H_2O$.

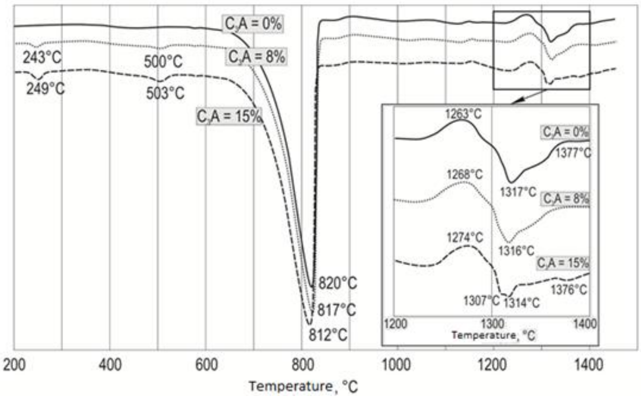

Fig. 1. The curves ofDSC of raw mixes

Endothermic effects at the temperature of 500ºCand 503°Ccorrespond to dehydration of kaolin $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, that is contained in bauxite, and to dehydration of boehmite. Difference in temperatures of these endoeffects is explained by different composition in mixes of bauxite.

Further temperature rising leads to decarbonization of calcite$CaCO_3$at 812…820ºC. Endothermic effect on all the curves of DSC of the studied mixes with maximum at temperatures of1263…1274°C, corresponds to exothermal reaction of belitC_2S. The following endothermic effect characterizes appearance of clinker melt. In mix#1 the melt is formed at 1317ºC, in mix#2 – at 1316ºC. Melting ends in mix #1 at the temperature of 1377…1400ºC. Existence of double effect on the curve of mix #3 at the temperatures of 1307°Cand

1314°Cand then little effect at 1376ºCis connected with the feature of melt creation.

High content of aluminium oxide from 2, 67 to 4, 61% andaluminousmodulusfrom 0, 64 to 1, 33 and 2, 85 in the mixes leads to growth of viscosity of melt from 0, 14 to 0, 19 and 0, 31 Pa·c[9] and to somewhat different intensity of allite formation. In spite of augmentation of the sum of minerals of fusing agents in mix #3 (22, 5%) in comparison withmix#1 (19, 5%), amount of the melt is gradually increasing, and allite is also gradually forming up to the temperature of 1450ºC.

The change of the position of clinkering zone and, consequently, the temperature of the clinker from kiln depends on running regime of refrigerator and can change mainly from 1100 to 1300ºC[10, 11]. The raw mixes were burnt in laboratory kiln at the temperature of 1450ºCwith delayed 40 minutes. Refrigerating conditions of the clinker with different content C_3Awere changed via temperature changing at the beginning of quenching which models the position of clinkering zone of the rotary kiln and the temperature of the clinker at the kiln output up to 1150°C(optimal position of clinkering zone) and 1250ºC (approximate) was effected in the kiln at the speed ~20ºCper minute, and then – distinctlyin the open air. One series of clinkers was quenched straight from the sintering temperature of 1450ºC. Each content of clinker was cooled according to three modes.

The characteristic of clinkers is demonstrated in table 2.

Table 2. Characteristics of synthesized clinkers

Clinker	Calculation phase composition, mass. %					KH	Modulus	
	C_3S	C_2S	***C_3A***	C_4AF	C_3A+ C_4AF		n	***p***
#1	64, 0	15, 3	***0, 01***	19, 5	19, 51	0, 92	2, 1	***0, 64***
#2	63, 0	15, 0	***7, 8***	13, 0	20, 8	0, 92	2, 2	***1, 33***
#3	61, 6	14, 7	***14, 8***	7, 7	22, 5	0, 92	2, 2	***2, 85***

As it is seen, the content ofalliteC$_3$S and belitC$_2$S in the clinkers changes to little degree, only clinker#3, in connection withincrease of minerals of fluxing agents, the sum of minerals of sillicates reduced.

The Study of Qualities of Synthesized Clinkers

The characteristics of synthesized clinkers were studied using X-ray and petrographic analyses and determining hydration activity according to magnitude of the compressive strength of samples from cured cement stone in 3 and 28 days.

X-ray analysis shows slight differences in both composition and content of silicate phases C_3S andC_2S in synthesized clinkers (fig. 2). As one would expect, the obtained clinkers Are significantly different in content of tricalcium aluminate $C_3A$and variable composition of solid solution of calcium alumoferrite$C_2A_xF_{(1-x)}$, where x = 0…0, 7.

For a closer look at these differences, Figure 3 demonstrates the fragments of radiographs that characterize these phases. So, for clinker#1, quenched from 1150 and 1250ºC, actual composition is close the expected, that is, there are no diffraction maximums $C_3A$and it is considered considerable reflections$C_2A_xF_{(1-x)}$ (d = 2, 66Å). In clinker, quenchedfrom1450ºC, it is manifested further the maximum at d = 2, 70Å, which, undoubtedly, belongs to C_3A. This is due to the fact thatat 1450ºCthe aluminate and alumoferrite phases are in the molten state and, supposedly, the quenching from this temperature will crystallize more refractory minerals, to which are enriched with iron oxide solid solution C_6AF_2, crystallizing at 1415ºC, whereastotal crystallization of calculated compositionC_4AF occurs at a lower temperature of 1395ºC[12]. Thus, released aluminum oxideat crystallization C_6AF_2formsC_3A.

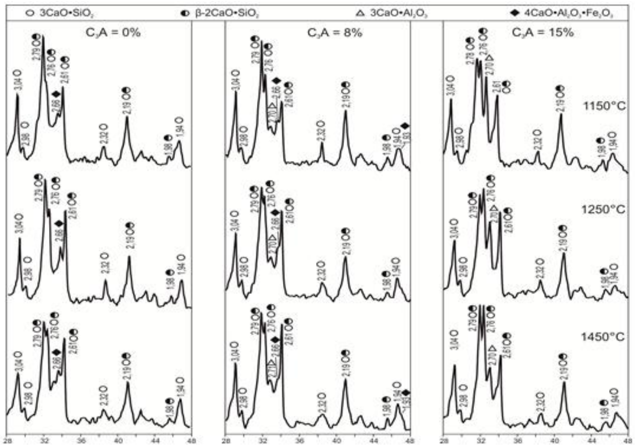

Fig. 2. The change of phase composition of the clinker

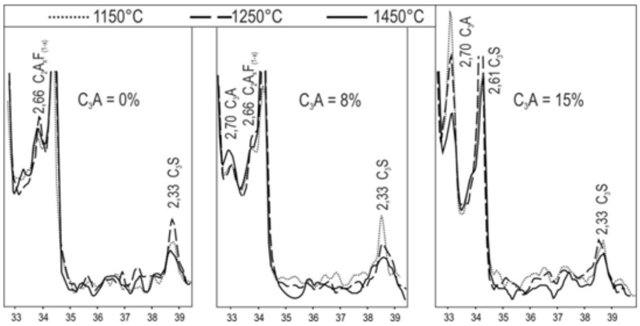

Fig. 3. Influence of composition and mode of cooling clinker on crystallization C_3A

The actual composition of clinker #2 with calculated valueC_3A = 8% is close to the composition of ordinary clinker, here presentC_3A (d = 2, 70 Å) и$C_2A_xF_{(1-x)}$ (d = 2, 66Å). But with the increase in the initial temperature of quenching from 1150 to 1450°C it is observed some tendency to increase the content $C_3A$and decrease – C_3S, which is due, probably, to the above given features of the process of crystallization of the individualized phases, leading to a redistribution of CaOfromC_3S toC_3A.

Unlike clinkers#1 and#2 under cooling clinker#3, with the increased content C_3A, it is observed the opposite dependence, and, namely, with the increase of initiating temperature of the sudden cooling from1150 to a maximum 1450ºC, C_3A (d = 2, 70 Å) is not increased as in previous cases, and significantly decreased (fig. 3).

This anomaly is explained by the fact that with the increase of aluminous modulus from 0, 64to 2, 85 the viscosity of the clinker melt is 2, 2 times as much. Therefore, The increasing viscosity of high aluminate melt impedes crystallization C_3S and C_3A. Therefore, in the X-ray picture the reflection C_3S (d = 2, 61Å) is somewhat less andespeciallyC_3A, which is likely to remain in the glass, and that is why at quenching the clinker by high temperatures the proportion of the crystallized C_3A is reduced.

It is known that the clinker cooling mode exerts significant influence on its microstructure. Petrographic study of polished sections of clinkers has shown significant differences in their microstructure (fig. 4).

Clinker#1 (C_3A ~ 0%) hasa clear crystallization. Alit in clinker#1, quenchedfrom 1150 and 1250ºC, is mainly represented by fused crystals with an average size of 20…30 micron. There are crystals with a size of 40…60 micron. Upon cooling clinker#1 sharplyfrom 1450ºCan average size of crystals reduces to 5…15 micron. There are the crystals of alit with belit inclusions, which is indicative of rapid cooling of the clinker and, thus, caused rapid crystallization of alit from the melt. Due to the lack ofC_3Ait underestimated the amount of melt which leads to a large number of fused crystals of alit. Under any refrigeration conditions belit is formed to be rounded crystals, distributed unevenly. The average size of belit crystals is 15 – 30 microns.

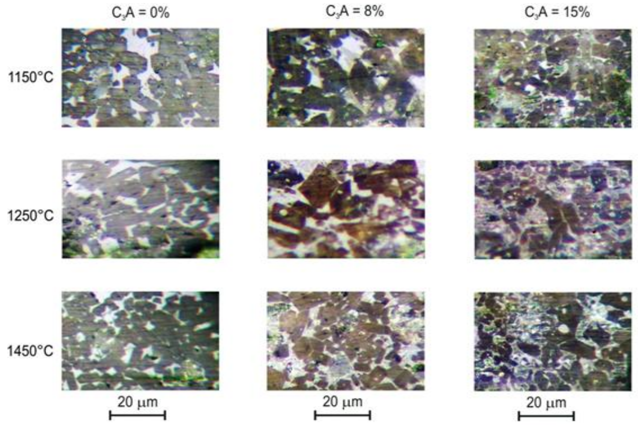

Fig. 4. The microstructure of synthesized clinkers

Clinker#2 (C_3A = 8%) has a clear microstructure with even distribution of clinker minerals. Alit clinker #2 has clear crystals with smooth faces being not destroyed. The average size of the alit crystals with increasing initial temperature of quenching the clinker decreases and accounts for20…30 microns for the temperature of 1150ºC, 10…20microns – 1250ºC, 5…15 microns– 1450ºC. With quenching from the maximum temperature it is found the fused alit crystals and C_2S crystals. Belit, the average size of which is 20…35 microns, has a clear face and is mainly distributed evenly between the alit crystals. Sometimesthere is a cluster grouping of this phase. The intermediate phase is represented by light (C_4AF) anddark (C_3A) substance and is contained in a sufficient amount.

Clinker#3 (C_3A = 15%) has a vague microstructure and fine crystallization regardless of refrigeration conditions. The increased content of aluminate phase and high viscosity prevent the growth of the alit crystals, providing thereby formation of a large number of small crystals.

The average size of the alit crystals in clinker #3, quenched from 1150ºC, accounts for 5…10 microns, while there is a large number of the fused crystals C_3S. With increasing temperature, from which quenching occurs, up to 1250ºC, the amount of the fused crystals C_3S decreases, but the average size remains the same – 5…10 microns. Sometimes there occurs the alit of elongate shape up to 25 mcm. Clinker quenching from 1450ºC provides reduction of the number of the fused and elongated crystals but the average size of the crystals C_3S remains 5…10 mcm. For the belit phase of clinker #3 the fine crystallization with unclearly marked facets is also characterized. There occur the clusters of belit around the pores. The average size of the crystals C_2S is 10 – 15 microns. Intermediate substance is represented mainly by aluminate phase.

To determine the strength of cement the clinker with added gypsum was milled to a specific surface of 300±10 m^2/kg. Depending on tricalcium aluminate content the amount of the incorporated gypsum into the clinker was 3, 5% for#1, 5% for#2, 7, 5% for #3. The strength of cement at the age of 3 and 28days, determined in small samples, is shown in figure 5.

For the clinkers synthesized with C_3A = 0 and 8%, it is characteristic the cement strength increase at the age of three days at the maximum temperature of 1450°C, from which the quenching was effected. It depends on the fact that the cooling mode promotes the formation of fine crystal structure of the clinker providing, first of all, the strength of cement at the initial stage of sample hardening by virtue of intensive hydration.

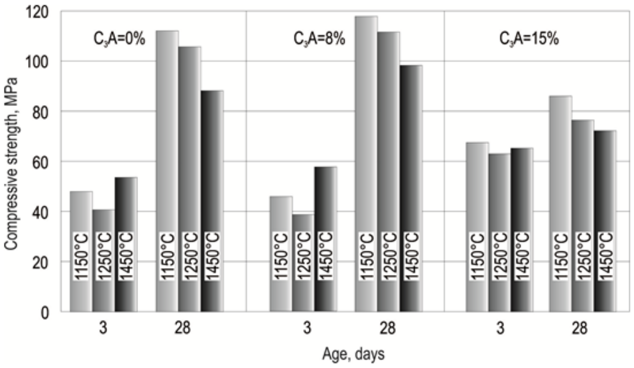

Fig. 5. The change of clinker activity depending on the conditions of cooling

The strength of cements #1 and#2 from the clinkers cooled from 1150ºCis several times higher the strength of cement from the clinker quenched from 1250ºC, and accounts for48…46MPaas compared with 40…38MPa. Quenching from the temperature of 1250ºCleads the appearance to some jagged crystals of alit and belit.

Cements#1 и#2 to 28 days, regardless of the temperature of initial quenching have shown significant hardening. So, the strength of cements #1 and#2 from the quenched clinkers from the temperature of 1150ºC is112and118MParespectively. Increasing the temperature of the initial quench of the clinker up to 1250ºCleads to some cement strength degradation up to 106and112MPa.

The cements, made from the clinker containing 15% of C_3A, irrespective of the temperature of quench, possess higher strength to 3 days, 68…63MPa, as opposed toclinkers#1 and#2. It is conditioned by the increased content of C_3Ain the clinker, which promotes increase in hydration activity of such cement and the strength on the first days of hardening, respectively.

The strength of samples from the cement with the increased content of $C_3A$is practically not changed with the change of cooling mode of the clinker. It is connected with the fact that the microstructure of the clinker with high content of C_3A, due to the viscosity of the liquid phase is presented by the crystals of small sizes. Therefore the temperature of initial quench has insignificant influence on the cement strength in the initial period of hardening. But to 28 days of hardening the cement strength has increased insignificantly, just up to86…74MPa.

For all compositions of the clinker at increasing the initial temperature of the quench up to 1450°C the strength of cements at the age of 28 days is significantly reduced, but from the clinker of optimum chemical-mineralogical content with C_3A = 8%, the cement has the strength of98MPa, that is, it is possible the output of the cement brand 500. By quenching from the temperature of 1450ºCthere is an unfinished formation of microstructure of clinker phases with emerging more number of small crystals to be 5 microns of the size, which determine for the most part the strength of the cement stone in the initial period of hardening. The number of the crystals of the size of10…30 microns, which determine the brand strength at 28 days, reduces.

SUMMARY

1. The mode of cooling considerably influences the phase composition, microstructure and hydration activity of the cement clinker. By calculated content in the clinker $C_3A \leq 8\%$ its quenching from 1450ºC leads to crystallization of alumoferrite phase enriched by iron with formation of additional amount C_3A. For the composition with the content of C_3A = 15% with increasing the temperature of quenching from 1150 to 1450°C the content of C_3A decreases, the part of which by cooling чis set in the form of glass.
2. The change of cooling mode has effect on crystallization of the clinker minerals. At increasing of initial temperature of the quench from 1150 to 1450°C for the clinkers with C_3A 0 and 8%, it is observed the refining of alit crystals from 20…30 to 5…15 microns. The size of belit crystals irrespective of the cooling mode is 15…30 microns. The clinker with C_3A = 15% has unclear microstructure and fine crystallization regardless of refrigeration conditions.
3. The strength of all cements at the age of28 days reduces at increasing temperature of the initial. It is connected with formation of fine-crystalline structure which causes the reduced strength of the cement stone obtained on the basis of such clinker. The optimum mode is quenching the clinker from the temperature of1150ºC, which provide its high activity.

CONCLUSION

Thus, the study of clinkers of laboratory synthesis of different composition has shown that the mode of cooling changes the processes of mineral formation and phase composition of the clinker, its microstructure and brand strength of cement. An optimal mode is quenching the clinker from the temperature of 1150ºC which providesits high activity.

ACKNOWLEDGEMENTS

The study wassupported by RFFI in the framework of research project № НК-14-41-08031 r_ofi_m.

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