Cement clinker structure during plasma-chemical synthesis and its influence on cement properties

N Sazonova[1], N Skripnikova[2], A Lucenko[2] and L Novikova[1]
[1]Angarsk State Technical Academy, Department of Industrial and Civil Engineering, Angarsk, 665835, Russia
[2] Tomsk State University of Architecture and Building, Department of Applied Mechanics and Materials Science, Tomsk, 634003, Russia

E-mail: n.a.sazonova@mail.ru

Abstract. The aim of this study was to determine the degree of influence of cement clinker cooling modes, synthesized in a low-temperature plasma, its structure and physico-mechanical properties. The raw mixture consisting of marble, sand, ash from thermal power plants and pyrite cinders were used, which are characterized by saturation factor (1,045); silicate (2,35) and alumina (1,22) modules. It was found that the use of different cooling rates of fused cement clinker entails changes associated with the mineralogical composition (increase of alite of 8.7-19,2 %), morphology (variation of the mineral alite aspect ratio of 6,7–17,5), density of the structure (change in distance between the minerals from 1 to 7,5 microns), grindability, specific surface area (2600–3650 cm^2/g) and, in consequence, the activity of cement (56,9–73,2 MPa). Disorientation of alite mineral blocks against each other, a significant amount of microcracks, affect the increase in cement specific surface area of 14,3–21,6 %, which leads to activity growth of the system. Along with this, with the rapid cooling of the samples, alite $54CaO \cdot 16SiO_2 \cdot Al_2O_3 \cdot MgO$ is formed, with single units of the structure, more deformed relatively to C_3S, which has a positive effect on the hydraulic cement activity.

1. Introduction

Crystals of clinker minerals, formed during the non-equilibrium crystallization of a multicomponent melt in a low-temperature plasma, undergo considerable changes [1]. Significant impact on the morphology modification of clinker minerals is made by technological modes, where the main one is cement clinker cooling mode [2–4], whose correction allows not only to influence the shape, size of new growths, but also their structure and most importantly properties of the binders obtained on them. The present work is a separate part of a series of experiments in the study of cement clinker, synthesized in a highly concentrated heat fluxes. The aim of this study was to research the structural changes of clinker minerals when the raw material mixture is exposed to highly concentrated heat fluxes, with cooling modes being adjusted, and to study their impact on the activity of the synthesized binder.

2. Materials and research methods

The following raw materials were used: marble, sand, ash from thermal power plants, pyrite cinders, with the help of which the raw mixture was made. Modular characteristics of the charge are represented by the saturation factor (SF) equal to 1.045; silicate modulus (n) – 2,35; alumina mod-

ule (p) – 1,22 [5]. The chemical composition of the mixture by weight, %: SiO_2 – 12,98; Al_2O_3 – 3,03; Fe_2O_3 – 2,49; CaO – 43,86; MgO – 3.2; LOI – 0,25.

The study of materials and cement clinker synthesized in a low-temperature plasma (LTP) was performed by using chemical analysis method in accordance with the requirements of GOST 5382-91 "Cements and materials in cement production. Methods of chemical analysis". Sampling was carried out with the method of cone quartering. The material was prepared by drying to constant weight and grinding to full pass through a sieve № 0063. X-ray analysis was carried out using the equipment Shimadzu XRD-7000 X-ray Diffractometer. The diffraction peaks were studied in the range of 2θ, equal to 3–80°, with a tube with radiation Cukα, 40 kV and 30 mA. Sampling step was 0,05; speed – 1 deg/min. Microstructure analysis was performed on petrographic microscope POLAM-R312 with the magnification of 450× and a scanning electron microscope Phenom Pro in the range 20–10000×, resolution up to 17 nm. We studied polished thin sections of the fused clinker etched for 2–3 sec. with a 1 % solution of nitric acid, and its chippings.

Heat treatment of the raw mixture was made using plasma-chemical reactor [6], where the temperature reached 3000 °C. Fractional composition of the raw mixture was less than 140 microns. Technological modes of thermal treatment of the samples: the exposure time of highly concentrated heat fluxes was determined by complete melting of the mixture and was 140 sec; with current intensity of 140–160 A; voltage 180–200 V. Under otherwise equal conditions cement clinker was cooled in different ways: under the air pressure (sample №1), in the open air (sample №2), in a closed kiln (sample №3). Subsequently the synthesized fused cement clinker was milled using a planetary ball mill PQ-N2.

3. Physical and chemical analysis of cement clinker

As a result of the chemical analysis of the synthesized cement clinkers, it was found that the difference between the estimated and actual mineral content, which was caused by the occurrence of non-equilibrium solidification process, is significant. The amount of alite grows by 8,7–19,2 % against the estimated content (Figure 1), while C_2S, C_3A, C_4AF decreases respectively by 4,5–16,3 %; 2,0–3,2 %; up to 1,7 %. The maximum number of alite is produced in the sample №1 and makes 79,1 %.

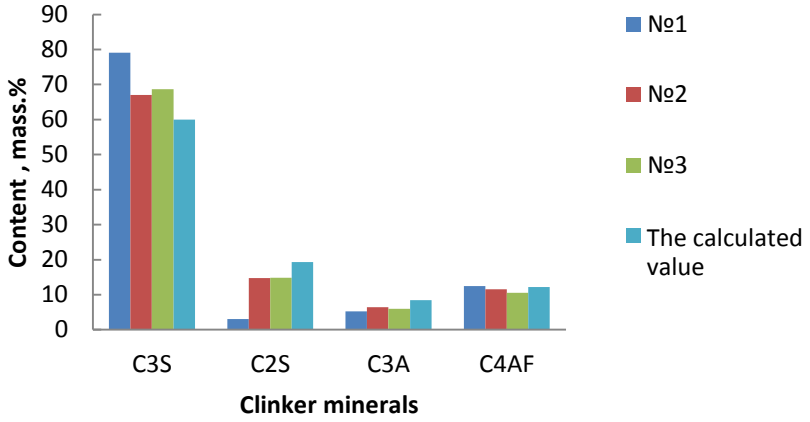

Figure 1. Estimated and actual content of the clinker minerals in samples No.1–3.

The microstructure of fused cement clinker, observed using an electron microscope and a petrography (Figures 2–4), varies considerably depending on technological regimes. The sample №1, quenched with cold air pressure after 140 sec exposure of highly concentrated heat fluxes contains mainly alite crystals and to a lesser extent belite. Alite has an irregular geometric shape of a platelet,

which is characteristic of clinkers containing large amounts of mineral fluxes, as well as obtained by the process of fusion. In the thin sections alite newgrowths are evenly spaced in blocks that are disoriented relatively to one another at an angle of 30°. The sample has a very dense structure: the distance between the minerals is mainly of 1–2 microns.One can see inclusions in crystals of alite, whose number indicates the intensity of the melting process of the raw material mixture, when the fast-growing seed crystals "bypass" and include small particles of foreign matter. One can observe round or oval-shaped belite crystals that are enveloped by alite crystals. Their content is very slight. Alit has a size of (1–13)×(8–150) μm, belite is 1–7 μm (figure 2, a). Length/beam ratio of alite minerals (l/d) is 17,5 which indicates their high hydraulic activity [7]. Single cracks are present traversing both crystals and interphase, whose presence may be related to tensile stress which arise when the mixture is heated and compression strain with a significant thermal gradient during cooling of the melt. This effect may also indicate the transition from β-C_2S into γ-C_2S, because the latest modification has a lower density and increases in volume by 12 % while cooling [4]. However, X-ray analysis (figure 2, b) of the sample No.1doesn't show diffraction peaks characteristic of this modification, which confirms the presence of significant stress, reducing the strength of fused cement clinker and increasing their grindability.

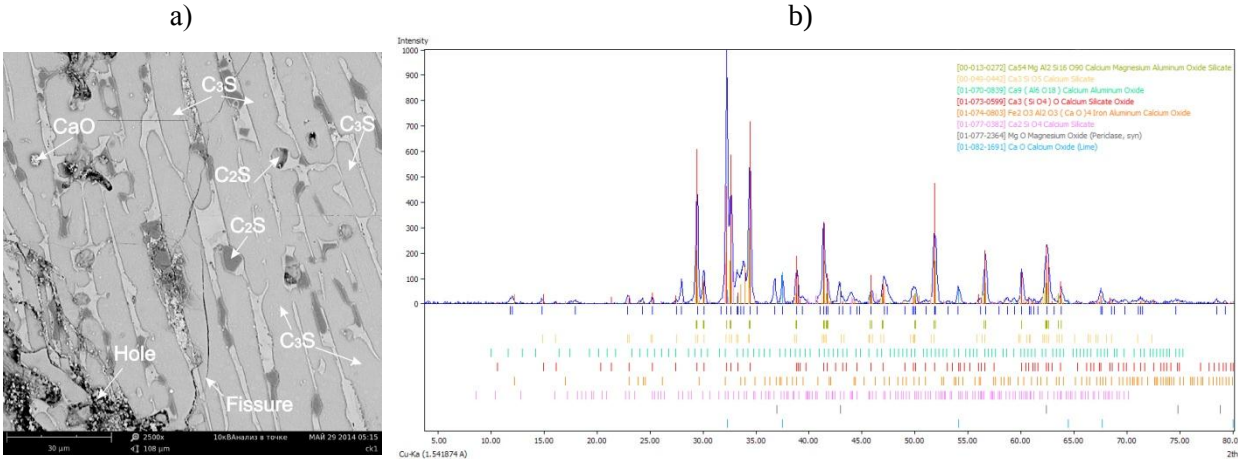

Figure 2. Fused cement clinker (sample No.1): a) structure, increase in 2500×; b) diffraction pattern.

As a result of X-ray phase analysis of cement clinker №1 it was found that the sample contains the diffraction maxima C_3S, β-C_2S, C_3A, C_4AF (Figure 2, b). The property that defines the cement clinker synthesized in a low-temperature plasma is the presence of alite having formula $54CaO{\cdot}16SiO_2{\cdot}Al_2O_3{\cdot}MgO$, whose formation occurs during the replacement of two Si^{4+} ions with the two ions Al^{3+} and Mg^{2+} introduction into the interstitials of the lattice site. Individual elements of the structure of the compound are more deformed relatively to C_3S, which increases their hydraulic activity [8].

The morphology of sample No.2 (Figure 3), cooled at room temperature, is distinguished by less dense monadoblastic structure having fewer enveloped belite crystals. The structure is more ordered against sample №1 and has a greater number of disoriented alite blocks with the angle between them varying from 30 to 90°. The distance between the minerals varies from 1 to 3 microns. Alite and belite size is 1,5–2 times smaller than in the sample No.1 and is respectively (2–10)×(10–100) μm, 1–3 microns. However, there is a reduction ratio l/d, which is equal to 14. C_3S crystals have an irregular geometric oval and plate shape; C_2S are dense oval. On the thin section, some crystals of alite are perforated, which may indicate slow cooling. The sample is transpierced with a web of microcracks, whose

number greatly exceeds the sample No.1 and should lower the micro-hardness of the samples more, which indicates an increase in the internal stresses during cooling of the melt. The X-ray pattern shows clinker minerals similar to sample №1. There is a slight decrease in the diffraction peaks belonging to $C_{54}S_{16}AMg$ showing that the synthesis of the represented compound is influenced not only by the highly concentrated heat fluxes, but also by the cooling mode.

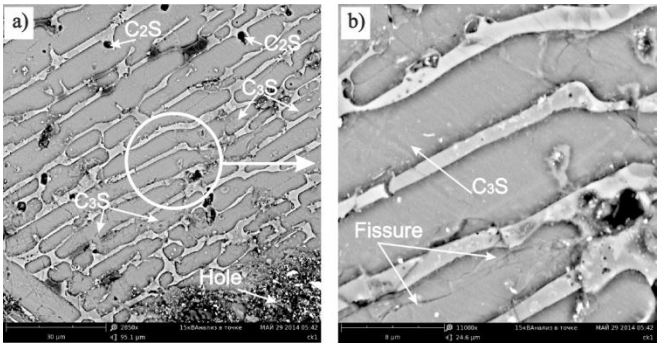

Figure 3. Structure of fused cement clinker (sample No.2), increase in: a) 2850×; b) 11,000×.

Increasing time for cooling samples leads to aggregation of alite crystals (sample No.3), having dimensions of (10–30)×(40–160) μm, the ratio l/d is 6,7 and irregular geometric shapes: plate and perforated multi-faceted (Figure 4, a). The number of additional inclusions on the surface of alite increases. The structure is less dense relatively to the previous samples: the distance between the minerals varies from 2 to 7,5 microns. Cracks in the minerals are nearly absent. In the interstitial material we can clearly see crystallized minerals tricalcium aluminate and tetracalcium alumoferrite. X-ray diffraction analysis of samples No.3 (Figure 4, b) revealed that there was a synthesis of the main clinker compounds. However, the diffraction peaks $C_{54}S_{16}AMg$ are difficult to identify because in most cases they are overlapped by lines C_3S, whose number is dominating.

a) b)

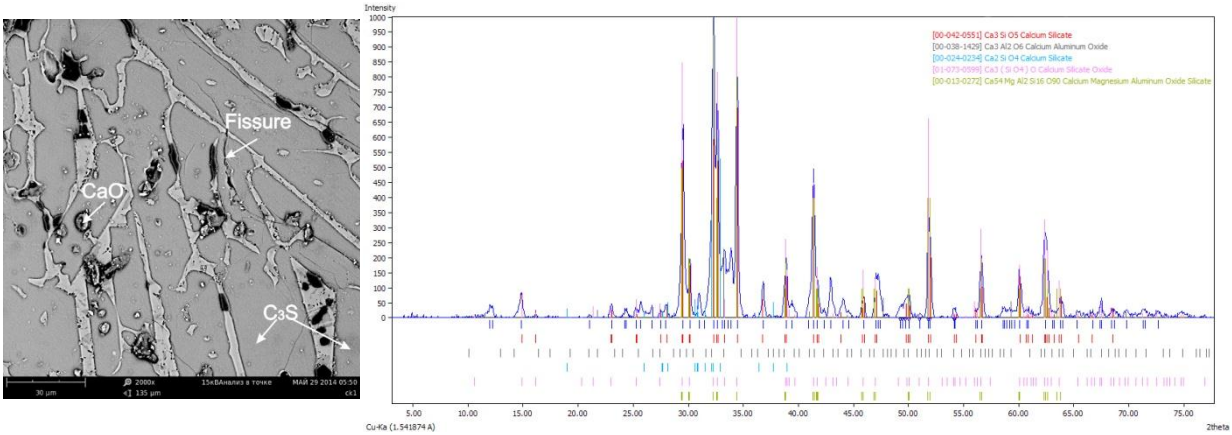

Figure 4. Fused cement clinker (sample No.3): a) structure, increase in 2000×; b) diffraction pattern.

4. Building and technical properties of cement

Dispersing capacity of cement is one of the key properties that influence the rate of hydration, kinetics of supersaturation of the liquid phase and heat release in the formation of hydrated compounds [9]. At this stage we were interested to follow the changes of the specific surface of the samples during the milling, depending on the method of cooling. With this objective in view, the fused clinker was

previously crushed in the laboratory jaw crusher to a fraction of 4–10 mm. Equal test portions of clinkers synthesized under different conditions, were subjected to grinding in a laboratory planetary ball mill, under identical process conditions. Milling fineness of the cement was evaluated by the residue on the sieve number 008, and the specific surface area, which made 4,5–5,1 % (3000–3150 cm^2/g); 3,2–3,6 % (3600–3650 cm^2/g); 8,4–9,2 % (2600–2750 cm^2/g) for the samples number 1, 2, 3 respectively. Thus, the specific surface area of cement clinkers No.2 exceeds sample No.1 on 14,3–21,6 %; and sample No.3 on 32,7–38,5%. The results indicate a significant reduction in the time of cement clinker grinding, whose structure is dominated by cracks that run both through the minerals as through the interstitial material. Grindability is affected not only by the presence of pores, micro and macro-cracks, but also by the type of the packing of clinker minerals and their size. Structure solidification and increase of the crystal size increases the time of cement clinker milling. Therefore, the natural cooling of the melt in the air provides optimal conditions for the formation of significant internal stresses, which decrease the mechanical strength of the cement clinker and make the structure uniform and porous.

The time of cement setting, depending on the mineralogical composition, ambient temperature, additives of gypsum, milling fineness, etc., has been determined in accordance with GOST 310.3-76. The content of calcium aluminate has a special influence on this characteristic. However, the fused cements are less sensitive to the content of the aluminate phase, because of the nonequilibrium mineral crystallization and the presence of the glass phase, and can be easily adjusted with gypsum [7]. In this regard, the additive of gypsum in amount of 5% was added during the grinding of the fused cement clinker, which provided the normal setting time, which varied in the following ranges: start – 1 hour 30 minutes, the end – 5 h 50 min. Fundamental differences in the samples with identical specific surface area were not observed.

Despite the use of raw material mixture with a saturation ratio greater than 1 and the presence of increased amounts of MgO, the cements produced from a fused clinker withstand soundness test during solidification, steaming and autoclave treatment at a pressure of 2,1 MPa. Ensuring of the soundness during the solidification of the studied cements may be explained by the non-equilibrium process of crystallization of minerals in the conditions of the continuous process when magnesium oxide either does not crystallize in the form of periclase and remains in the glass phase, or is intruded additionally in the crystal lattice of the other components [1, 10]. Free calcium oxide is extremely rare in the structure of the samples and does not form clusters and has a size less than 5 microns, which has no negative influence on the soundness during solidification of the processed binder.

Water demand of the studied cements produced from samples No.1, 2, 3 is stable and essentially depends on their specific surface, whose increase raises the water demand. In this case, the normal density, characterizing the rheological properties of cement paste and used to determine the rational value of W/C, was determined in accordance with the requirements of GOST (Russian national state standard) and was 0,28–0,32.

Thus, the application of different rates of cooling of cement clinker entails a chain of changes associated with both mineralogical composition, morphology, grindability, specific surface area and, as a consequence, the cement activity. Homogeneity of the sample No.1, predominate formation of alite minerals $54CaO{\cdot}16SiO_2{\cdot}Al_2O_3{\cdot}MgO$ with a ratio l/d equal to 17,5 and density of the cement clinker matrix affect favorably on the strength characteristics of the cement. For example, at the age of 3 days they are 17,2–18,0 MPa, at the age of 7 days – 50,4–52,1 MPa; at 28 days – 71,5–73,2 MPa. Thus, the introduction of foreign ions (Al^{3+} and Mg^{2+}) into the crystal lattice of alite is accompanied by a disturbance of its structure and increases the activity of its interaction with water. It is of interest that the strength characteristics of the samples obtained by using the cement clinker No.2, increase

by 10–14 %. Microstructure of the sample is similarly represented by alite minerals, but with a smaller ratio l/d equal to 14, which should reduce the activity of the cement. However, due to the larger mineral blocks disorientation against each other, more microcracks increasing the specific surface of the cement by 14,3–21,6 %, the activity of the system increases. Therefore, these factors are essential. In this regard, the strength characteristics of the samples No.3 are significantly inferior to their predecessors and being 3 days old they are 10,3–11,8 MPa; 7 days – 39,9–40,5 MPa; 28 days – 56,9–59,3 MPa.

5. Conclusion

According to the obtained data, as a result of physical-chemical and physical-mechanical studies it may be noted that the cement clinker synthesized in a low-temperature plasma has increased the amount of alite minerals due to non-equilibrium solidification processes, raising defectiveness in the lattice of tricalcium silicate, which positively influence the cement quality. It has been established that one of the parameters for assessing the activity of a binder, based on the fused cement clinker, may be not only the morphology of minerals; length-beam ratio of alite mineral (l/d); sealing of crystals in thin section, but also the presence and nature of microcracks arising in the structure, which have a significant influence on the microhardness of the samples, the time of their milling and specific surface area. Air-cooling of a fused clinker leads to fine-grained matrix model composed mainly of alite minerals, with less amount of belite. Despite the larger ratio l/d of alite and less dense structure of the sample No.1, cooled under the air pressure, the activity of cement No.2, whose clinker is cooled naturally, is higher. This is due to a web of microcracks in the structure helping to increase the specific surface of binder (3600–3650 cm^2/g) and strength (78,6–83,4 MPa).

Reducing the rate of cement clinker cooling leads to considerable enlargement and clearer form of alite crystals, which is accompanied by a marked decrease in the activity of the system – 56,9–59,3 MPa. Herewith, the mineral, as a chemical compound, continues to maintain its active state, but due to the fact that its crystals are approaching the maximal sealing and saturation of bonds not neutralized previously by charge of intruded ions, it affects adversely the activity of its interaction with water.

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