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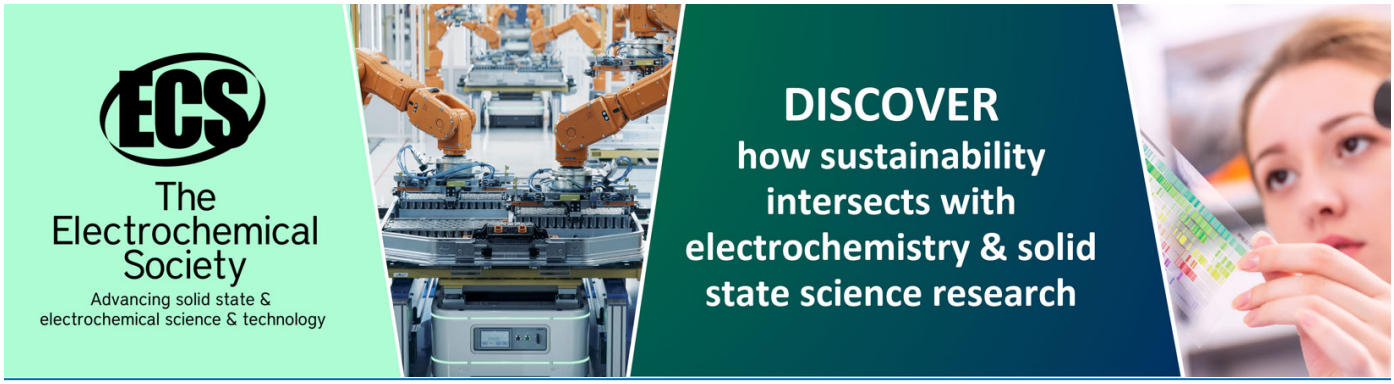

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Analysis of the Efficiency of Elaborating the Technology of Producing the Portland Cement Clinker Through the Application of the Gas Production Industry Wastes

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Abstract. The authors show the possibility of improvement the energy efficiency of the high-temperature process of the Portland cement production through adding the organic-mineral addition – the gas residues. It was determined that the use of gas condensation processing residues provides for the intensification of the phase formation during clinker burning with the reduction of maximum temperature by 150°C, which facilitates solving the issues of the resource preservation through the reduction of energy consumption when producing the Portland cement and gas residues recovery.

1. Introduction

1.1 Problem statement

Modern production develops under the conditions of limited natural resources. The resource exhaustiveness forces the business structures look for the ways of improving the production processes efficiency through the insurance of their energy efficiency and creation of the innovative technologies. It would be reasonable to determine the topical issue of the energy efficiency provision of modern production and searching the ways of its solution through the implementation of energy-efficient technologies, including the use of different production residues. Gas residues are the fuels perspective for the economic development considering their amount when producing the gas, minimization of the ecological danger during their efficient recovery and potential for the energy efficient application in other spheres of economy.

In fact the use of gas residues as the fuel components for the work of boiler houses or as a self-consistent fuel type is quite widespread. However, such technology is not eco-friendly and does not provide for the maximum residues recovery in order to solve the problem of their recovery. Besides, the gas residues are used as a fuel-containing and combustible additive in the high-temperature energy-demanding processes. Accordingly, adding the gas residues during the high-temperature

process of clinker production may improve the energy efficiency of the process and will solve a number of economic, ecological and technological issues. Thus, topical is the issue of searching the ways of improving the cement production energy efficiency through searching for the new energy-efficient methods of their production.

1.2 Analysis of recent publications

One of the most topical issues of modern studies in the sphere of producing the construction materials of modern science is the issue of the production processes rationalization. Production of the cementing construction materials as one of the energy-intensive processes needs the investigation of approaches to the progress of thermodynamic processes [1]. Studying the possibilities of applying the mineral substances able to influence the acceleration of the synthesis processes in the Portland cement mixture became one of the ways of the composite construction materials production processes energy efficiency improvement, which is researched in the works by H.M. Shabanova [2]. V.I. Vinnychenko also studied the possibilities of using the carbon supply residues through their application as the intensifying admixture, in particular, for the cements production [3]. Ye.F. Vegman proved the efficiency of using the intensifying additions when producing the Portland cement clinker through the results of the analysis of X-ray patterns and petrogram [4]. In the work by H. Beyer [5] the perspectives are considered of using the additions and their efficiency in the process of clinker burning. However, the issue of efficiency of using the intensifying additions for improvement of the cement clinker burning remains topical.

1.3 Purpose and tasks

The task of the research is the analysis of the efficiency of the development of Portland cement clinker production technology through the application of the gas-production industry residues. To fulfill the task: 1) study the processes of Portland cement and organo-mineral addition hydration processes; 2) study physical and mechanical properties of the obtained substance.

1.4 Main material

The energy efficiency topicality sets and objective in front of the production as to the reduction of energy losses during the Portland cement clinker burning as the energy-intensive process of the cements production. The dicarbonation zone is considered the most energy-consuming zone in the rotating furnace. The technology is developed of applying the Portland-cement clinker during the production as an intensifying addition of gas condensation processing residues, which allows reducing the fuel consumption by 8.6 % in the clinker formation process. [6, 7].

One of the ways of solving this problem is the introduction of a part of fuel (coal or heavy cuts of oil) into the raw slurry during the wet production. This will allow reducing the gas fuel consumption and using the industrial wastes – coal beneficiation species, oil sludge, acid sludge etc. Technical possibility of using such sludge is experimentally proved. [8]. The experiment was conducted for the purpose of proving the theory of the temperature modes reduction insurance and acceleration of the mineral-formation process when producing the Portland cements through adding the mineral admixtures – gas residues. For the formation of samples of the given phase composition the consecutive disintegration, formation, and burning of the raw mixtures was conducted. Physical and chemical studies were conducted of the Portland cement clinkers of the developed compositions (fig. 1) and determined that Ca_3SiO_5 is an inhibiting phase. Phases Ca_2SiO_4, $Ca_3Al_2O_6$, $Ca_4Al_2Fe_2O_{10}$ are also present.

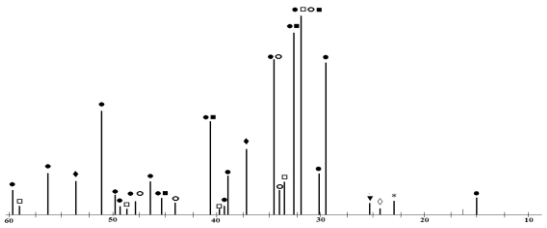
For clinker with 5 % wt. of the addition of the solid residues of the gas condensation processing the essential increase of the peak points is noticed, characteristic of the major clinker minerals, which testifies to the phase-formation processes intensification.

Physical and mechanical tests of the cements obtained were conducted according to DSTU EN 196- (1, 3):2007.

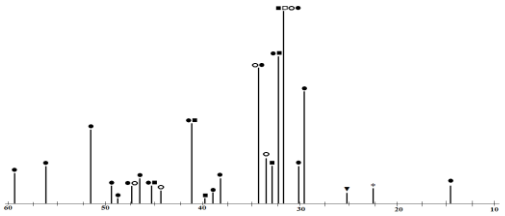
Based on the results of the research conducted it was determined that the developed cements belong to the hydraulic cementing materials.

Short time (beginning – 4-6 min., ending – 7-10 min.) caused the necessity of adding the 3 % wt. gypsum rock during the grinding. The obtained Portland cements have the water-to-cement ratio 0.27-

0.34, setting time: beginning from 54 to 60 min., ending from 90 to 150 min. Based on the results of determining the compression resistance of standard samples the grade of the Portland cements received is “400”.



◆ – CaO, ● –Ca_3SiO_5, ■ – β-Ca_2SiO_4, * – γ-Ca_2SiO_4,❍ – $Ca_4Al_2Fe_2O_{10}$, □ – $Ca_3Al_2O_6$, ◇ – $Ca_2Fe_2O_5$, ▼ – $CaSiO_3$ a



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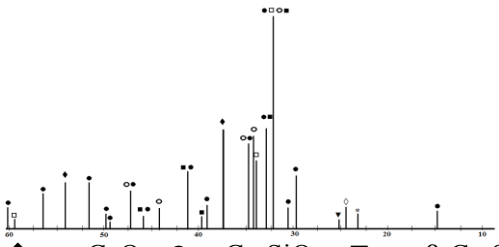
□ – $Ca_3Al_2O_6$, ◇ – $Ca_2Fe_2O_5$, ▼ – $CaSiO_3$ b



◆ – CaO, ● –Ca_3SiO_5, ■ – β-Ca_2SiO_4, * – γ-Ca_2SiO_4,❍ – $Ca_4Al_2Fe_2O_{10}$, □ – $Ca_3Al_2O_6$, ◇ – $Ca_2Fe_2O_5$, ▼ – $CaSiO_3$

Figure 1. Stroke X-ray patterns of Portland cement clinker with different amount of additions: a – no addition; b – with 5 % wt. of addition: c – with 10 % wt. addition.

The phase-formation processes are studied in the Portland cement raw mixtures with the organo-mineral addition. The results of the experimental research of the solid-phase processes in the mixture for the obtainment of clinker with the organic and mineral admixture within the temperature interval 900–1200 °C prove that the reactions of interaction of the calcium oxide with the acidic oxides start already at 900 C. The reactions end at 1200 C.

The straight lines do not quit the starting point of the coordinates, but cut off the sections on the axis of ordinates. This testifies to the fact that during the initial period of the process the rate is limited by chemical interaction of the raw mixture components at the phase-boundary and only after the formation of continuous layer of the solid-phase reaction products the process rate is determined through the diffusion.

The phase-formation processes in the Portland cement clinker with the organo-mineral admixture proceed due to the reactions in the solid phase, the rate of which is adequately described by the *Ginstling-Braunstein equation.* The constant of the rate of Portland cement clinker and organo-mineral addition phase-formation reaction looks as follows [15]:

$$K = 7{,}24 \cdot 10^{-2} \cdot e^{-\frac{18{,}21}{RT}}$$

It was found that the data obtained for the energy of the phase-formation reaction rate activation are adequately consistent with the data obtained for the activation energy of the reaction of calcium carbonate decomposition. As the phase formation reaction activation energy (18.21 kJ/mole) is a sequence higher than $CaCO_3$ decomposition reaction activation energy (209,382 kJ/mole), the formation of the main clinker minerals will start at the moment of calcium carbonate decomposition. The reaction will proceed without any additional energy consumption. It is compensated by the gas residue organic component burning energy.

It was determined that obtained sintered material does not contain the free calcium oxide, ferrite and calcium monosilicate. Phase composition is characterized by the presence of basic clinker minerals Ca_3SiO_5, β-Ca_2SiO_4, $Ca_3Al_2O_6$, $Ca_4Al_2Fe_2O_{10}$, which testifies to the mineral formation processes termination at 1300 °C, which is 150 °C lower than the temperature of the Portland cement clinker burning without the addition. Clinker is characterized by the presence of separate blocks – aggregates formed by the parallel-oriented layers of the scaled poly-crystals. Parallel stratification on separate sections is quite distinct which testifies to the calcium silicates. Fine-crystalline formations are represented by the calcium aluminate and clinker glass [13]. The hydration products of the optimal composition cement obtained are studied using the complex of modern methods of physical and chemical analysis (fig. 7, 8).

The effect of consolidation of the Portland cement with the organo-mineral addition is ensured by the change of the character of formation of the crystal-hydrate aggregations, quantitative and qualitative changes of the main phases crystallization conditions.

The complete hydration of Ca_3SiO_5 is observed with the simultaneous provision of $Ca_4Al_2Fe_2O_{10}$ hydration completeness. At the same time the reduction of the released Portlandite is observed with the increase of the synthesized ettringite of the pointed morphology. This element reinforces the crystal-hydrate hetero-phase aggregates in the structure of the cement stone. Polymorphic modifications of the calcium carbonates are increased.

The hydro-silicates and calcium hydro-aluminocarbonates are present which facilitates the presence of the colloidal components in the crystal-hydrate aggregates and damps the mechanical stresses in case the amount of the main phase crystals grows.

The data obtained are fully confirmed by the thermogravimetric and petrographic studies. Microstructure of the cement stone is dense without any substantial pores.

2. Discussing the results of studying the impact of organo-mineral addition on the Portland cement production energy efficiency

Thus, as a result of the studies conducted, it was found that the major products of the hydration of obtained Portland cement with the organo-mineral addition are the hydro-silicates, calcium hydro-carboaluminates, Portlandite, ettringite and secondary calcium carbonate in the colloidal, crystal and crypto-crystalline condition. Such combination of the hydrate formations ensures the strength of the consolidated cement stone. For the purpose of producing the industrial batch of the Portland cement with the organo-mineral addition the specifications “Portland cement with the organo-mineral addition” were elaborated.

The flowchart was elaborated of producing the Portland cement with the organo-mineral addition in the industrial conditions with the use of the equipment available without any additional capital investments. It was found that the developed Portland cement with the organo-mineral addition at the burning temperature reduction by 150 °C has higher physical and mechanical properties than the Portland cement obtained from the standard clinker. The technical and economic calculation was conducted as to the operating parameters of the rotating furnace of burning the clinker cement. It was found that average annual economy of the natural gas may amount to 1, 290 ths. m^3/annum. General economy of natural gas expenses per annum will constitute 10.7 mln. UAH/per annum. General

economic effect during the implementation of the elaborated technology of producing the Portland cement with the organo-mineral addition will amount to 10.5 mln. UAH/annum[14].

3. Conclusion

It was found that the major products of hydration of the obtained Portland cement with the organo-mineral addition are represented by the hydro-silicates, hydrated calcium carboaluminate, portlantide, ettringite and secondary calcium carbonate in the colloidal, crystal and crypto-crystal condition. Such combination of the hydrate formations provides for the strength of the consolidated cement stone; the developed cements belong to the hydraulic cementing materials. Quick setting time (beginning – 4-6 min., ending – 7-10 min.) condition the necessity of adding 3 % wt. gypsum stone during the disintegration. The obtained Portland cements' water to cement ratio: 0.27-0.34, setting time: beginning: 54 to 60 min., ending: 90 to 150 min., the Portland cement's grade is 400.

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