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INCREASING OF HEAT EXCHANGE EFFICIENCY IN CLINKER REFRIGERATOR

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Abstract. One of the promising ways that significantly expands the technological possibilities of cement clinker production is the application of the method of chemical heat regeneration (HRT) and the use of gas synthesis (a mixture of H₂ and CO) as the main process fuel. The influence of the use of chemical fuel regeneration in heat recovery systems (clinker coolers) on the activity of clinkers with a low content of the aluminum-ferrite phase is considered in the article.

The cement industry in Russia is a very energy-intensive industry, consuming more than 12 million tons of conventional top-oil annually. Taking into account the consumption of energy resources for the extraction of raw materials and its processing, it ranks third after the fuel and energy and metallurgical industries. In the production of cement by wet method, the share of costs for process fuel in its cost price exceeds 40%, and the unproductive fuel consumption is about 75% [1].

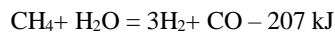
When improving the technology of cement production, designing new or upgrading existing furnaces, special attention should be paid to the processes of heat recovery and efficient use of secondary energy resources [2]. In this regard, the clinker cooler should be considered not only as an aggregate, the purpose of which is to cool the clinker, but primarily as a recuperator, providing an increase in the air capacity (its exergic potential) going to fuel combustion. With the development of a dry method of cement production and a reduction in the fuel and air consumption for its combustion, a limitation is established on the amount of heat that can be recovered by the refrigerator. Due to the limitation of heat recovery, there is a limit to which the clinker can be cooled. Existing types of clinker coolers, for cooling the clinker below 100 ° C at the request of the technological regulations, are forced to use more air than necessary to completely burn the fuel in the furnace. To maintain the clinker temperature in the range from 100 ° C to 50 ° C, 3 to 4 kg of air / kg of clinker is necessary. When returning all the air to the furnace as a secondary one, the efficiency of the refrigerator will approach 100%. However, the combustion process requires only 2 kg of air and the maximum theoretical efficiency will not exceed 86%. The implementation of practical recommendations for the rational distribution of cooling air in the sublattice space of the grate refrigerator type "Volga" at a number of cement plants ensured an increase in the thermal efficiency of the grate cooler from 0,7 to 0,93 and, as a result, a significant reduction in fuel consumption [3]. Since an increase in the efficiency of the refrigerator even by 1% leads to a decrease in the specific heat consumption of the entire furnace by 17-21 kJ / kg cl., Effective measures for the modernization of refrigerators still justify themselves.

The application of the method of chemical heat regeneration (HRT) in recuperative systems and the use of gas synthesis (a mixture of H₂ and CO) as the main process fuel is one of the most promising ways that significantly increases the technological possibilities of cement clinker production and requires the solution of a number of scientific and applied tasks. In particular, the creation of thermochemical reactors (TCR) and the organization of the combustion of modified fuels.

Previous studies [1,4] have shown the possibility of a water-steam conversion of natural gas in the clinker layer at a temperature above 700 ° C. The heat of reaction has a significant effect on the amount of heat absorbed in the thermochemical reactor [5]. As a result of heating, evaporation and overheating of water and methane mixtures, with a stoichiometric ratio of components (0,47 kg CH₄ and 0,53 kg H₂O), the methane vapor conversion reaction changes the enthalpy of the initial components in the preparation



stage (the so-called physical cold storage). In the temperature range from $T = 273$ K to $T = 1000$ K, it is $\Delta H_{\text{phys}} = 3.2$ MJ / kg of the mixture.



The chemical cold resource, equal to the heat of reaction, is $\Delta H_{\text{him}} \approx 6.1$ MJ / kg of the mixture. The total cold resource of conversion of gaseous fuel will be $\Delta H_{\Sigma} = \Delta H_{\text{phys}} + \Delta H_{\text{him}} = 9,3$ MJ / kg mixture. For comparison, the change in the enthalpy of liquid hydrogen heated to the autoignition temperature ($T = 850$ K) is $\Delta H_{\text{phys}} = 12$ MJ / kg. As can be seen, the hydrocarbon plus water composition that undergoes a physico-chemical conversion to TCP approaches the liquid cooling option by the available cold resource, and exceeds it by the relative cooling resource $\Delta H / H_u$ (H_u -heat of combustion). Thus, the physical and chemical utilization of heat and subsequent combustion of converted synthetic fuel lead to an increase in the efficiency of energy devices and fuel economy [7]. In addition, the burning of synthesis gas significantly reduces the amount of emissions into the atmosphere of carbon dioxide. Therefore, the considered TCP process can be considered an example of a new energy-efficient technology that reduces harmful impact on ecology.

However, the use of the TCP method in the heat recovery system in the clinker refrigerator, in addition to the technical task, suggests the study of the effect of a highly reducing medium on the phase composition of the clinker and the quality of the resulting cement.

The object of the study was clinkers of CJSC Belgorod Tsement and an experimental clinker synthesized from chemical reagents Al_2O_3 , Fe_2O_3 , $\text{SiO}_2 \cdot n\text{H}_2\text{O}$, CaCO_3 of the brand CHDA. The skilled clinker was distinguished by an increased content of iron oxide and had $\text{KH} = 0,93$; $p = 0,7$ and $n = 1,7$. The chemical composition of clinkers is given in Table 1. An increased proportion of calcium aluminoferrites should respond more clearly to changes in cooling conditions. The peculiarity of the experiment is that the clinkers undergo sharp cooling, in which the processes of crystallization of the liquid phase have passed, which should greatly slow down the possible diffusion of ions. The annealing temperature did not exceed 1100°C . For comparison, the other part of the samples was annealed at the same temperature in the air.

Table 1. Chemical composition of raw mix

Components	Composition, %					Total, %
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	
Experienced clinker	13,92	3,37	4,82	43,49	0,00	100,00
Clinker of CJSC Belgorodsky	19,34	4,09	3,46	63,21	0,97	91,07

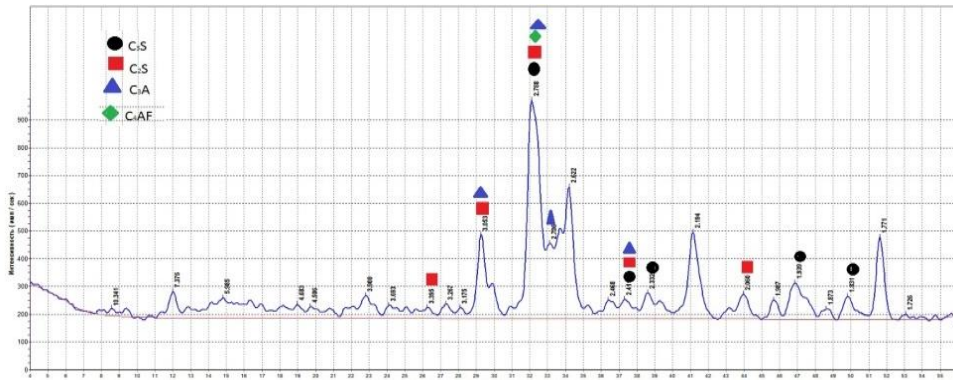
Synthesis of gas was obtained in the layer of test clinkers on a model installation. Butane and steam were blown through the layer for 10 minutes in a ratio of 1: 4. The composition of the gases from the reactor was estimated from the indications of the VARIO plus industrial gas analyzer. In the composition of gases, CO and N₂ were fixed. Hydrogen was not determined. The presence of carbon monoxide indicates the reaction of steam-water conversion of hydrocarbons.

The phase composition of the cooling products was determined on a DRON-3 diffractometer. Diffractograms are shown in Fig. 1 and 2.

The air-cooled pilot clinker is represented in [5] by the main silicate phases: C_3S (3,047; 2,78; 1,769 Å), C_2S (2,89; 2,75; 2,61; 2,18 Å), A-F the AF phase is predominantly C_4AF (7,24; 2,65; 1,94 Å) и C_3A (2,71; 1,91 Å). The presence of reflections (4,89; 2,69 Å) indicates the possible presence of the C_{12}A_7 phase.

In the experimental "iron" clinkers cooled in the HRT reactor, a certain decrease in the characteristic diffraction maxima of C_3S (2,78; 2,61; 1,769 Å) and C_3A (2,71 Å), and at the same time an increase in the intensity of reflection 2,648 Å. Reducing the interplanar distance from 2,657 Å to 2,649 Å indicates an increase in the share of Al_2O_3 as part of A-F phase, which makes it possible to identify this phase as $\text{C}_6\text{A}_2\text{F}$. In the clinker composition, in both cases a small amount of phase is fixed C_{12}A_7 . At the same time, under reducing conditions when gas synthesis is processed, the intensity of reflections characteristic of Mayenite and C_3A decreases. A distinctive feature of clinkers cooled in a gas synthesis medium is the appearance of a phase of free CaO (2,41; 1,70 Å).

a)



b)

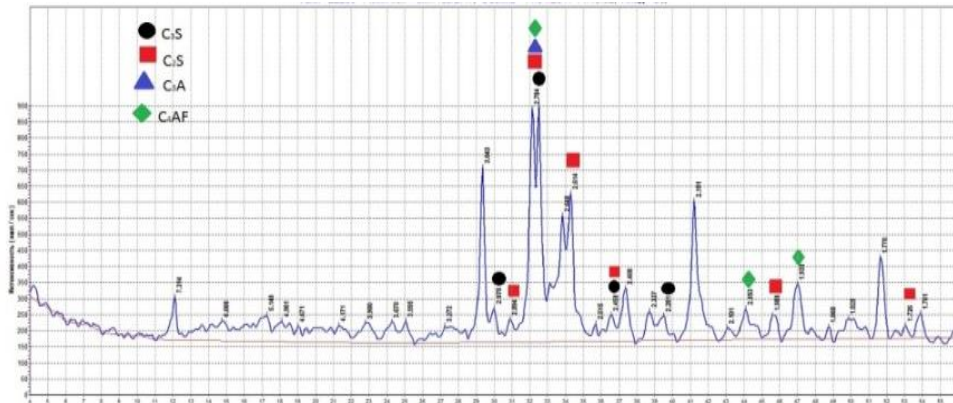
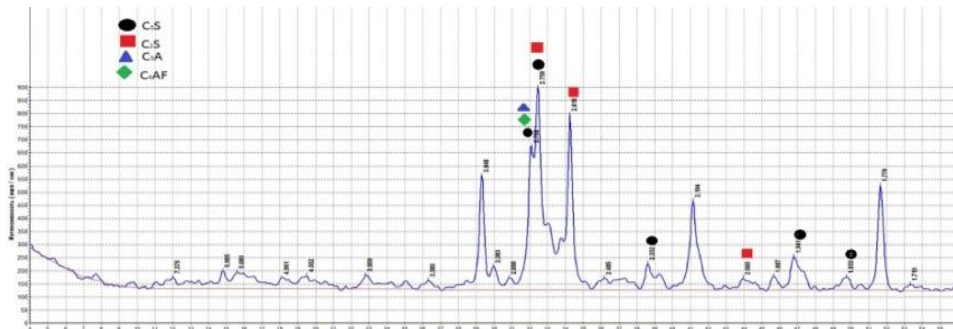


Figure 1. Diffractograms of an experienced clinker:
a) cooled in air; b) in the HRT reactor

a)



b)

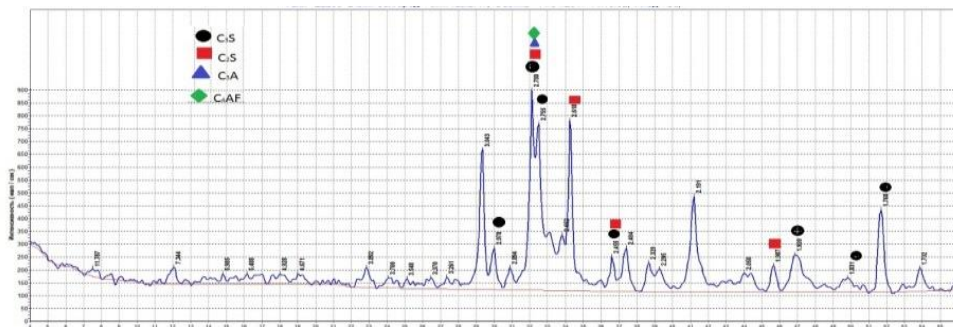
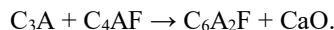


Figure 2. Diffractograms of clinkers of CJSC “Belgorodsky Cement” :
cooled in air; b) in a gas synthesis medium

Microscopic analysis of clinkers showed an increase in the bright intermediate substance, identified with the iron-containing phase, which indirectly confirms the data of the diffraction analysis.

Probably, the mechanism proceeding according to the reaction:



Cooling of the clinker of CJSC "Belgorodsky Cement" in the gas synthesis environment (Figure 2) showed a slight decrease in the characteristic peak C_3S (2,97; 2,76; 1,76 Å) и C_3A (2,70 Å). At the same time, an increase in the intensity of the diffraction reflections of characteristic for $\beta\text{-C}_2\text{S}$ (2,78; 2,19 Å) and an increase in the amount of the alumino-ferrite phase represented by C_4AF (7,24; 2,63 Å).

Cooling of this clinker in the gas synthesis medium was also shown by the appearance of unbound calcium oxide (2,41; 1,70 Å).

Microscopic analysis of apparent destruction of alite crystals did not show, but in the composition of the intermediate substance an increase in the fraction of the light phase was recorded, which can be identified as C_4AF . The obtained results suggest that the free CaO is released during phase decomposition C_3A .

Clinker Belgorodsky Cement CJSC, cooled under air conditions, is represented by the main phases: C_3S (3,03; 2,76; 1,76 Å), C_2S (2,89; 2,759; 2,61; 2,19 Å), C_4AF (7,24; 2,63; 2,04 Å) и C_3A (2,71; 1,91 Å).

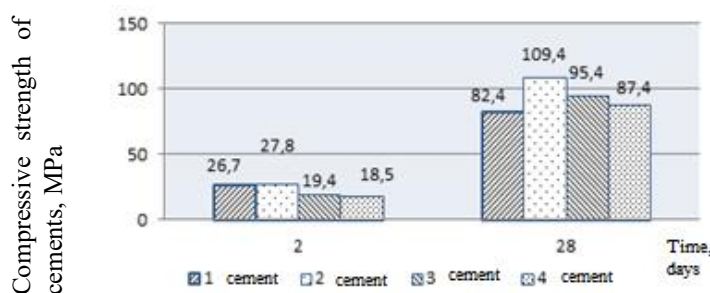


Figure 3. Compressive strength of cements:

- 1- cement of CJSC "Belgorod cement" and 2 - experimental cement cooled in air; 3 - Cement CJSC "Belgorod cement" and 4 - experimental cement, cooled in the synthesis gas

2-

Physical-mechanical tests (Figure 3) showed that the cement of CJSC "Belgorod cement" possesses the greatest activity in the early stages of hardening, and by 28 days the most durable was gained by the experimental cement cooled in air.

The results of the performed studies testify to the positive effect of the clinker cooling method in the reactor of chemical regeneration of fuel on the activity of clinkers with low content of the alumina-ferrite phase. For clinkers with a high content of iron oxides, cooling under reducing conditions leads to a significant change in the composition of calcium aluminoferrites, which is accompanied by the appearance of a new phase - $\text{C}_6\text{A}_2\text{F}$ release CaO and reduces the cement strength.

The use of chemical fuel regeneration in heat recovery systems makes it possible to use the heat of the cooled clinker more efficiently, and obtaining a significant amount of gas synthesis provides an increase in the exergic level of natural fuel, which increases the energy efficiency of production and reduces the cost of production.

Acknowledgments

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