# Improvement Of The Energy Efficiency Of Portland Cement Production During The Use Of The Natural Gas Liquid Processing Residue

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**Abstract**. The possibility is shown 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 found that the use of gas condensation processing residues ensure 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. Problem positioning

The issue of the improvement of energy efficiency of the resource-intensive technological process is very topical and sets a challenge in front of the scholars as to searching the ways of energy consumption reduction, in particular, during the Portland cements production. This is connected not only with the limited natural resources and ecological problems, but also has the economic background which is constituted by searching the possibility of improving the energy efficiency of the industrial production.

Cements production is the energy-intense process, the production initial value is substantially dependent upon the rational use of natural energy resources under the conditions of growth of their deficiency and cost. Searching the ways of improving the energy efficiency of the Portland cements production is closely connected with solving the economic and ecological production problems. In particular, one of the problems of the oil and gas production is the issue of storage and utilization of the ecologically-hazardous production residues which, nevertheless, can be used for the improvement of energy efficiency of different production processes. One of the major gas processing residues is the gas residue of which 1 to 3 $m^3$ are formed on 11 ths. $m^3$ of the gas produced. Generally, as of 2017, Ukrainian gas-production companies possess over 7 mln. t. unprocessed gas residues. This index testifies to the substantial problem connected with searching the places and new technologies of

storage and utilization. Rational methods of solving the gas residues processing problem have not been elaborated so far. Thus, large land plots are rendered suitable for the gas production residues,which testifies to the essential environmental problem, since gas residues continue accumulating which calls for the allotment of the new places for storage. Besides, noteworthy that the places rendered for the gas residues storage cannot be further rationally used.

Thus, topical is the problem of searching the ways of improvement the cements production energy efficiency through searching the new energy-efficient methods of their production by introduction of different additions, in particular, the gas liquid recovery residues.

**2. Analysis of recent publications**

A number of authors [1] study the properties of the cement clinker when adding the casein and natrium tersulphate to the mixture, which provides for the increased indexes of the cement stone strength. The work [2] suggests using the phosphate combinations as additions during the production of construction materials, including the cements, which has a positive impact upon the physical and chemical properties of the materials. The scholarly periodical publications determine the perspectives of using the residues of different industrial branches for the production of construction materials, which leads not only to the improvement of the clinker properties but also will solve the environmental problems of residues processing [3]. The issues were considered of adding different ingredients for the purpose of improving physical and chemical properties of the Portland cements and their impact upon the hydration processes [4]. Besides, the possibility of using the coal supply residues as the organo-mineral component for the insurance of intensification of the high-temperature process was considered, mainly, the perspective directions of residues application for the improvement of energy efficiency of the Portland cement clinker production. [5]. The issue of improving the physical and chemical properties of cement was considered in the work [6] from the point of view of improving the efficiency of their use. A number of investigations are dedicated to the impact of the special bases on the Portland cement clinker properties [7]. The issues were considered of the cements rationalization for different construction works [8].

**3. Purpose and tasks**

The purpose of study is the elaboration of the technology of improving the energy efficiency of the high-temperature processes of the Portland cement clinker production through the application of the gas production industry residues.

To achieve the set objective:

1) thermodynamically, justify the possibility of synthesis of major clinker minerals at the lower temperatures under the conditions of using the residues of the gas liquid processing as an organo-mineral addition;

2) justify the introduction of the optimal amount of the gas liquid processing residues to the composition of the initial mixture of the Portland cement clinker;

3) study the mineral formation process at different temperature modes during the Portland cements production.

**4. Main material**

Requirements to the reduction of losses during the clinker burning require searching the new alternative fuel types, as well as employing the approaches which could allow introducing a part of fuel into the most energy-intense rotating furnace zone – the dicarbonation zone. This allows reducing general fuel consumption for the clinker-formation process by 8.6 %. Besides, for the purpose of introducing the clinker burning process into the clinkering zone about 65% excess heat shall be supplied. In its turn, it leads to the excess temperatures and causes the formation of seams on the surface of inwall, aggravates the conditions of using the refractory setting and coating [6, 7].

One of the ways of solving this problem is the introduction of a part of fuel (coal or heavy oil fractions) into the raw slurry during the wet production process. This will allow reducing the gaseous fuel consumption and at the same time – use the industrial wastes – coal beneficiation species, oil sludges, acid sludge, etc. Technical possibility of using such sludge was experimentally proved [8].

In Ukraine natural gas and gas liquid are one of the resources widely applied in different industrial

spheres. Liquid wastes are formed during the processing (gas residues) which are analogous to the oil sludge by their properties, chemical and phase composition.

The experiment was conducted for the purpose of confirming the theory about insurance of the temperature modes and acceleration of the mineral formation process during the Portland cements production through adding the mineral addition – the gas residue. For the formation of samples of the given phase composition the consecutive decomposition, formation and burning of the raw mixtures were conducted.

Mechanical processing of the raw elements was conducted in the porcelain mill using the wet method. The grinding fineness was controlled through the screen analysis.

The raw mixtures were formed into briquettes at the hydraulic press П-125 at the specific pressing of 60-80 MPa. The briquettes burning was conducted in the silit and kryptol furnaces. The temperatures in the burning zone were measured using the optical pyrometer "Smotrych-5П-01" and breaking stress – using the thermal element. The completeness of the combinations synthesis was controlled using the chemical analysis with the absence of the free calcium oxide.

The value of the cement specific area was measured using the porosity method according to DSTU EN 196-3: 2007.

Mineral part of residues, phase composition of the raw mixtures burning products and cement hydration were studied using the physical and chemical analysis method. Thermogravimetric studies were conducted on the derivatograph Q-1500D F of Paulik system – J. Paulik – L. Erdey with the samples heating up to 1000 °C in the air medium. Phase analysis was conducted on the diffractometer ДРОН-3М (copper anode, nickel filter, anode pressure – 35 kW, anode current – 20 mA). The combinations identification according to the X-ray patterns was conducted according to the default data card index ASTM. Petrographic analysis was conducted using 3D scanning laser microscope Confotec 150.

Physical and mechanical tests of the cement were performed according to the small samples methodology by M. I. Strelkov, and optimal cement compositions were tested according to DSTU N 196-(1, 3): 2007 "Cement testing methods".

The reactions of major clinker minerals formation were considered: $Ca_2SiO_4$, $Ca_3SiO_5$, $Ca_3Al_2O_6$, $Ca_4Al_2Fe_2O_{10}$ out of the initial raw materials: limestone, clay and pyrite cinders with and without the cement carbon. The results of thermodynamic calculations of the minerals formation reactions are shown in figure 1-4 [11].

It was determined that if the carbon is present in the mixture, major clinker minerals formation reactions become more possible from thermodynamic point of view.

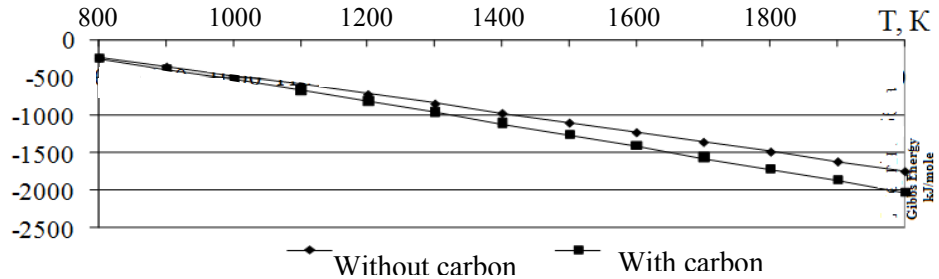


**Figure 1.** Dependence of the Gibbs energy upon the temperature during the formation of $Ca_2SiO_4$

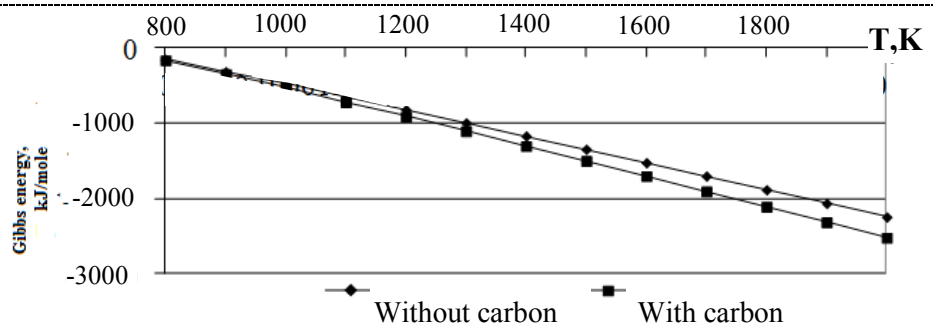


**Figure 2.** Dependence of the Gibbs energy upon the temperature during the formation of $Ca_3SiO_5$

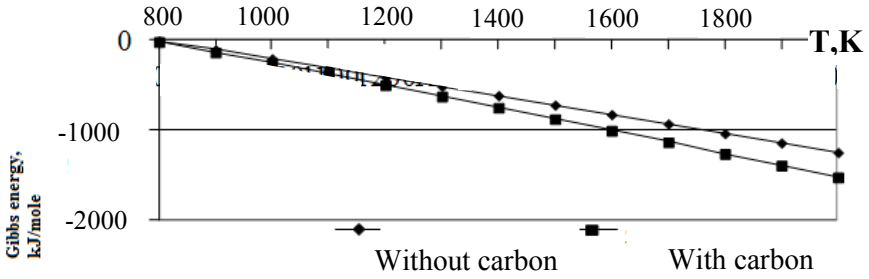


**Figure 3.** Dependence of the Gibbs energy upon the temperature during the formation of $Ca_3Al_2O_6$

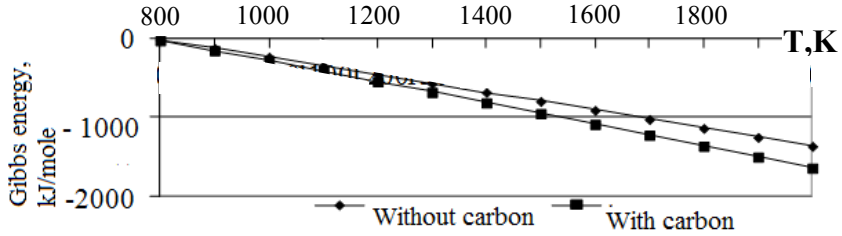


**Figure 4.** Dependence of the Gibbs energy upon the temperature during the formation of $Ca_4Al_2Fe_2O_{10}$

It was found that during heating the gas processing residues between the mineral and organic components of residues the interaction reactions begin which imposes an intensifying effect on the chemical reaction of calcium carbonate decomposition. This creates the conditions for the reaction of the dicalcium silicate and tricalcium silicate formation at lower temperatures.

The chemical structure was studied of the product of distillation of the gas residues liquid part which showed the following: at the boiling temperature the oil component releases the lower cycloalkanes, and at the end of boiling it releases higher cycloalkanes. Study of the phase composition of the mineral part of gas processing residues showed that it is mostly represented by salt rock NaCl, red ochre $Fe_2O_3$, and other silicate-containing compositions.

The formation of alite is substantially accelerated in the halogen-containing fusion of the gas residue mineral constituent. The chlorine ions in the fusion, increasing the fusion acidity, accelerate the rate of $Ca_2SiO_4$ dissipation by more than twice. The $Ca_2SiO_4$ dissipation is especially accelerated in the alkali-containing fusion with the appearance of highly mobile ions $Na^+$. Thus, the gas processing residues can be used as one of the components of the raw mixture of the Portland cement clinker (burning correcting ingredient) [12].

At the given saturation factor KH = 0.9 and silicate module n = 2.3 the three-component raw mixture was calculated for the obtainment of Portland cement clinker with different amount of the correcting ingredients of the gas residue.

The processes was studied of the raw mixtures recovery with different amount of gas residue addition, and it was found that the raw mixture of the Portland cement without additions at the heating up to 1000 °C acts analogically to the raw mixture with 10 % wt. addition.

The thermogram of the raw mixture with 5 % wt. addition demonstrates the increase of thermal effect within the temperature range 400-700 °C. This is connected with the intense separation of the organic phase of the residues and intensification of the processes of the raw materials transformation. The effect intensification is observed at the burning temperature 960–980°C, which is accompanied by the decomposition of $CaCO_3$ in the raw mixture structure.

The activation energies of CaCO3 decomposition were determined in the presence of the gas liquid processing residue. As a result of conducted calculations it was found that the introduction of 5 % wt. addition of the gas liquid processing residue into the Portland cement raw mixture reduces the activation energy of $CaCO_3$ decomposition by 19,046 kJ/mole

Introduction of the increased amount of addition (10 mass %) is inefficient, since the activation energy increases.

**Conclusion**

As a result of the study conducted a number of tasks were solved and the following conclusions can be drawn:

1) The possibility of synthesis of the major clinker minerals Ca3SiO5, Ca2SiO4, Ca3Al2O6, Ca4Al2Fe2O10 was justified from thermodynamic point of view at the reduced temperatures (800 K) with the use of the gas liquid processing residues as a mineral addition;

2) It was found that during the heating of the gas processing residues between the mineral and organic components of residues the interaction reactions begin, the product of which facilitates the intensification of the reaction of calcium carbonate decomposition which creates the conditions for the dicalcium silicate and tricalcium silicate formation at lower temperatures, as compared to the ordinary clinker burning technology. The rational amount of the organo-mineral addition was determined which intensifies the transformation of the raw materials – 5 % wt.;

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