

ANNOTATION
of the dissertation for the degree of Doctor of Philosophy (PhD)
majoring in 6D073000 “Production of building materials, products and
structures”

Anuarova Ayaulym Dalelbekkyzy

“Technology for the production of cements based on calcium and silicate containing chemical waste”

The relevance of the work. The message of the Head of State Kassym-Jomart Tokayev to the people of Kazakhstan was held on September 1, 2022 “A just state. One nation. A prosperous Society” was the first direction in his speech entitled “New Economic Policy”, as our President said: “The systemic problems of our economy are well known. These are commodity dependence, low labor productivity, insufficient level of innovation, uneven distribution of income. Of course, all these are complex problems, but there are concrete ways to solve them. These are macroeconomic stability, economic diversification, digitalization, development of small and medium-sized businesses, human capital, ensuring the rule of law. However, there is still no tangible progress on these issues. Obviously, new approaches are needed”.

The socio-economic development of the Republic of Kazakhstan, as in other civilized countries, should be based on scientific and technological progress. Economic development depends crucially on raw materials and fuel and energy resources, which are closely related to environmental protection problems.

Therefore, now, when determining the ways of technology development, along with improving product quality, much attention is paid to saving fuel, energy, and improving the use of raw materials in all industries, including cement production. To effectively solve this problem, it is necessary to increase the content of alite in cement, accelerating the reaction rate of its formation, but not increasing the firing temperature of the clinker, for which purpose calcium silicates were studied in this work instead of the traditional clay component of the Portland cement raw mixture. Granular electro thermal phosphorus (ETP) slags have been studied as such substances. In this form, the material has not been previously investigated. It was known that the addition of up to 10% of ETP slags to the limestone-clay mixture has a mineralizing effect on the clinker formation process. The work also investigated carbide lime-fluff instead of limestone. A certain positive effect of replacing limestone in the clay charge with lime-fluff was, in principle, known before this work.

The study is related to the raw materials in demand on the world market. In the production of yellow phosphorus by electrothermal method, the utilization of slag turns into a nodal problem.

Thus, the use of highly reactive calcium silicates in the form of waste from enterprises in the production of cement allows not only to solve the problems of rational environmental management, but also to increase the competitiveness of the

target product and contribute to the inflow of investments into the country's economy.

The dissertation work was carried out in accordance with the development objectives “State program of housing and communal development «Nurly Zher» for 2020-2025” Approved by Decree of the Government of the Republic of Kazakhstan dated December 31, 2019 No. 1054; “On energy conservation and energy efficiency improvement”, Law of the Republic of Kazakhstan as of January 13, 2012 No. 541-IV; “On approval of the Concept of development of the fuel and energy complex of the Republic of Kazakhstan until 2030”, Resolution of the Government of the Republic of Kazakhstan as of June 28, 2014 No. 724.

The aim of the work is to develop a physicochemically sound resource-saving technology for producing various cement clinkers by replacing natural silica-containing materials with granular ETP slags.

The objectives of the study include:

- analyze the thermodynamic possibility of the formation of clinker phases from a new type of raw materials and their decomposition products when interacting with lime-containing components, depending on temperature;
- to investigate the reactivity of new raw materials mixtures, to establish the chemistry of the interaction of components, to determine the kinetics of the formation of two- and tricalcium silicates depending on temperature;
- to study the influence of the composition and firing conditions on the variability of the properties of cements;
- to study raw materials mixtures for the production of stabilized white clinker;

As a result of the research, to develop energy-saving and more economical technological solutions for the production of cements.

Methods of achieving the set tasks.

The study of inventions and utility models, patents, copyright certificates, a review of the literature of domestic and foreign sources, conducting chemical, optical, X-ray and thermal analysis methods, conducting tests in accredited laboratories.

Scientific results (scientific statements) submitted for protection:

- to evaluate and find out the possibility and conditions for obtaining sustainable raw sludge from a charge consisting of limestone and slag of phosphorous production;
- to study new raw materials mixtures for the production of stabilized belite clinker;
- to determine the technological parameters of the manufacture of belite refractory.

Scientific novelty of the dissertation:

- thermo-dynamic analysis of high-temperature decomposition of minerals of complex composition in a new type of raw material. Depending on the temperature, the thermodynamic possibility of the formation of clinker phases from minerals, as well as from their decomposition products, during their interaction with lime-containing components is determined;

- high- temperature clinker processes are described. The dependences of the kinetics of the reactions of the formation of two- and tricalcium silicates on the temperature for firing various SC (Saturation coefficient) mixtures are given;

- structural and mechanical properties of slurries have been studied depending on their composition, humidity and dispersion. An assessment of stability is given, ways to increase (if necessary) the stability of slurries are indicated. The dispersive ability, dissolution and hydration of ETP slags, thickening and setting of slurries during prolonged storage have been studied;

- the peculiarity of calcination limestone-slag sludge in industrial rotary kilns has been established;

- the mechanical-and-physical properties of new cement differences, as well as the construction and technical properties of cements from ETP slags were investigated. The variation of properties is traced depending on the content of impurities, composition and structure of clinker;

- the peculiarity of the phase composition, hydration and hardening of cements from ETP slags has been established. Experimental methods involving thermodynamic analysis have established the cause of the retarding effect of phosphorus pentoxide admixture on the initial stage of cement hydration;

- economical technologies of cements from granular ETP slags have been developed, a technology for obtaining stabilized belite clinker from ETP slags suitable for the production of refractory materials has been proposed.

Practical significance of the dissertation:

Technologies for the production of cements from a new type of raw materials (slag ETP, chemical waste) have been developed, which is more economical than the technology of conventional Portland cement from clay-limestone mixtures. Technologies of stabilized belite clinker, which is an autoclave or low-grade ($C_3S \sim 30\%$) binder, have been created. In addition, this clinker is suitable for the manufacture of refractory materials.

A technological map for the production of high-grade cement based on granular ETP slags has been developed and approved. This technology has been adopted for implementation at the Karaganda Cement Plant of “Asia central cement” JSC (KCP). The expected economic effect from the introduction of the technology will amount to 240 million KZT per year.

Experience in implementing the results of work in production.

The technology has passed pilot tests at the KCP, as a result of which the principal possibility of producing Portland cement using this technology has been established with a significant economic effect by reducing fuel consumption for clinker firing, increasing the grade of cement and increasing the productivity of cement kilns.

Validity and reliability of scientific statements, conclusions and recommendations. Laboratory studies were carried out in the following accredited laboratories: laboratories of Chemical and Metallurgical Institute named after Zh. Abishev RSE “National Center of complex processing of mineral raw materials of the Republic of Kazakhstan” of MIT of RK, Karaganda; on the basis of “KazCentrExpertiza” LLP testing laboratory equipped with modern equipment

“Laboratory of non-destructive testing, measurements and tests of technical devices and materials”, Karaganda; laboratories of the Institute of Building Materials Vilnius State Technical University named after Gediminas, Vilnius, Lithuania. The results of laboratory studies are justified in accordance with the conclusions and recommendations, confirmed by pilot tests.

Summary of the work.

The first chapter of the dissertation analyzes the possibility of obtaining Portland cement from unconventional raw materials by completely replacing the clay component of ETP with slag.

The second chapter describes the methods of achieving the objectives. Experimental data were obtained by chemical, optical, X-ray and thermal analysis methods.

The third chapter analyzes the thermodynamic possibility of the formation of clinker phases from a new type of raw materials and their decomposition products in interaction with lime-containing components depending on temperature;

In the fourth chapter, the possibility and conditions for obtaining a stable raw sludge from a charge consisting of limestone and slag of phosphorous production are evaluated and clarified. At the same time, stability means the ability of the sludge to retain the solid phases of the charge in a suspended state.

The fifth chapter is devoted to the study of a new raw material mixture for the production of stabilized belite clinker, the technological parameters of the manufacture of belite refractory are also determined.

Many scientific and technical tasks solved by this work were related to the technological processes of the KCP.

The author's personal contribution to science consists in:

The main provisions of the dissertation work have been published in 8 printed works, a patent of the Republic of Kazakhstan for a utility model has been obtained, 2 copyrights have been obtained. The results were obtained by the author independently.

Approbation of the work.

The main results of the dissertation were reported at scientific and technical conferences of the faculty of Karaganda Technical University; at the annual International scientific-practical conference “Science integration, education and production - basis of the implementation of the Plan of the nation” (Saginov’s Readings No. 7), Karaganda city - 2015; International scientific-practical conference “Science, technical regulation and engineering in construction: condition, prospects”, Karaganda city – 2016; at the annual International Scientific Conference “Integration of science, education and production as a basis for implementing the Nation Plan” (Saginov Readings No. 11), Karaganda city – 2019.

The main provisions of the dissertation work have been published in 8 printed works, 2 patents of the Republic of Kazakhstan for a utility model and 2 copyrights have been obtained. Articles by Scopus Shaikezhhan A., Anuarova A.D. Believe-containing clinkers from phosphoric slags for refractory materials. Magazine of Civil Engineering. 2022. No. 02. Pp. 11010. doi:

10.34910/MCE.110.10; Shaikezhan A., Anuarova A.D., Antonovic V. Cement slurry from electro-phosphoric slag. Magazine of Civil Engineering. 2020. No. 06. Pp. 9806–9806. doi: 10.34910/MCE.98.6.

The results of the research were introduced into the educational process, namely: in lectures, for course work and diploma projects, in the disciplines “Chemistry of building materials”, “New types of cements”, “Use of industrial waste in the technology of concrete and ceramic materials”, “Progressive building materials and technologies”.

Structure and scope of the dissertation:

The dissertation consists of an introduction, five sections, general conclusions and appendices, contains 128 pages of typewritten text, 26 figures, 44 tables, a list of used sources from 126 titles.

The results of the work were obtained by the author independently.

The author expresses deep gratitude to the staff of the Department of “Building Materials and Technologies” of Karaganda Technical University, the laboratory of the Chemical and Metallurgical Institute named after Zh. Abishev RSE “National Center of complex processing of mineral raw materials of the Republic of Kazakhstan” of MIT of RK, the testing laboratory of “KazCentrExpertiza” LLP “Laboratory of non-destructive testing, measurements and tests of Technical devices and Materials”; the laboratory of the Institute of Building Materials Vilnius State Technical University named after Gediminas, Vilnius, Lithuania.

The main conclusions.

1. Granular ETP slags have been investigated as a new type of silica-containing cement raw material. The lime-containing component was limestone, carbide lime.

2. Chemical, kinetic and technological studies are preceded by a thermodynamic analysis of hypothetical high-temperature reactions involving solid-phase thermal decomposition of minerals and the formation of clinker phases. The analysis covers all the main minerals and substances that make up new types of raw materials.

3. The study of the influence of the concentration of the dispersed phase on the rheological and elastic-plastic-viscous properties of sludge from a charge consisting of limestone and slag of phosphorous production, first used for the production of high-alloy Portland cement, showed the ability of the sludge to retain the solid phases of the charge in suspension.

4. Slags of phosphorous plants can be used for the production of cement by the wet method of raw material preparation. As a cement raw material component, granular slag is preferable to cast.

5. It is recommended to control the fineness of the grinding of slag sludge by the amounts of residues on sieves 02 and 008. The remainder on the 008 sieve should be within 8-14%. The residue on the 02 sieve should not exceed the existing norms.

6. It is recommended to take 37% for the lower limit of sludge moisture.

7. The stability of slag sludge is achieved by existing methods of mixing sludge.

8. The mixing mode in vertical sludge basins should be worked out taking into account the characteristics of the slag sludge.

9. For the combustion of 1t Portland cement clinker from slag mixtures of ETP compared with limestone-clay mixture of KCP with a wet production method, the conditional fuel consumption is reduced by at least 15%, which is confirmed in the pilot case.

10. The statement of experiments to study the possibility of obtaining a stabilized belite refractory by replacing ETPs with slags of known natural silica-containing materials in a cement raw material mixture is justified. As the second ingredient of the charge, both limestone and lime-fluff were used.

- it is shown that granular ETP slag is mainly represented by pseudovollastonite glass. The crystalline phases of the slag are represented by wollastonite and quartz.

- thermal transformations in ETP slags, clinker formation processes in mixtures of ETP slags with lime-containing components have been studied. The chemistry and kinetics of the processes are described. The parameters of obtaining refractory materials are determined.

11. Belite clinkers with SC (saturation coefficient) = 0.60 – 0.85 were studied. Clinkers with SC = 0.70 and 0.75 with a firing temperature of 1350 - 1400°C are optimal for obtaining refractories.

12. To determine the technological parameters of the production of refractories based on white-containing clinkers, a mathematical model was compiled. The apparent density and apparent porosity are chosen as optimization parameters, and the factors are grain composition, pressing pressure, firing temperature and exposure.

13. To obtain refractories with the best physical and technical indicators, it is necessary to use a raw mixture with 25% of the fine fraction (less than 0.5 mm), 5% of the medium fraction (1 - 0.5 mm) and 70% of the large fraction (3 – 1 mm), apply a pressing pressure of 100 MPag, burn at a temperature of 1450 ° C.

14. Based on experimental data and a mathematical model, a refractory made of white-containing clinkers with the following calculated physical and technical parameters is proposed: with SC = 0.70 – P0 = 22.82%, p = 2.47 g/cm³; with SC = 0.75 – P0 = 23.05%, p = 2.49 g/cm³. White clinkers were tested to obtain refractory products that have confirmed the results of research

Based on the results of theoretical and experimental studies, a rational technological scheme for the production of alite and belite clinker from granular ETP slag has been developed. From a technological and environmental point of view, the main factors of increasing the efficiency of the proposed production compared to traditional technology have been identified.