



Dissertation

Master in Civil Engineering – Building Construction

***The complex binder based on Portland cement and
ash-and-slag wastes from thermal power stations***

Maryia Vysotskaya

Leiria, *October of 2018*



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Dissertation developed under the supervision of Doctor Paulo Alexandre Lopes Fernandes, professor at the Department of Civil Engineering of the Polytechnic Institute of Leiria and the co-supervision of Doctor Liudmila Parfionava, professor at the Department of Construction Industry of the Polotsk State University.

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RESUMO

No saldo de caldeiras e fornos de combustível do setor de energia da República da Bielorrússia a proporção de recursos próprios de energia (moagem de turfa e aparas de madeira) coloca prioridade em resolver as questões da utilização de resíduos de cinzas-e-escórias e reduzindo a área de locais de eliminação de cinzas-e-escória, que causam danos irreparáveis no ambiente.

Uma quantidade significativa de pesquisas tem sido dedicada à utilização de resíduos de cinzas e escórias. Existem mais de 300 tecnologias de reciclagem e uso. Os resíduos de cinzas e escórias são utilizados na produção de betão, argamassas, cerâmicas, materiais isolantes de calor e água, construção de estradas. A experiência mundial mostra o potencial de 70-80% de utilização de cinzas e escórias, como, por exemplo, em alguns países europeus. No entanto, o custo da reciclagem de resíduos de cinzas e escórias com a produção e neutralização simultânea de resíduos pode ser superior ao custo da produção.

Uma das direções do uso de resíduos de cinzas e escória é a produção de aglutinante que aumenta a resistência e o baixo custo primário. A substituição de uma parte de um cimento com mineral ativo. Os métodos existentes para a produção de ligantes complexos incluem os estágios de moagem conjunta ou separada de clínquer de cimento e aditivo mineral com a seguinte mistura. Custos de energia significativos para moagem.

A este respeito, o desenvolvimento do ligante complexo eficaz com o uso de resíduos de cinzas-e-escória da usina distrito de Estado bielorrusso em Orekhovsk usando tecnologia de poupança de recursos é o objetivo real de pesquisa.

Palavras-chave: mistura de cinzas e escórias, cimento Portland, aglutinante complexo, substituição de cimento, aditivo mineral.

ABSTRACT

Increase in the balance of boiler and furnace fuel of the energy sector of the Republic of Belarus the proportion of own energy resources (milling peat and wood chips) places priority on resolving the issues of utilization of ash-and-slag wastes and reducing the area of ash-and-slag disposal sites, which cause irreparable damage to the environment.

A considerable amount of research has been devoted to the utilization of ash-and-slag wastes. There are more than 300 technologies of their recycling and use. Ash and slag wastes are used in the production of concrete, mortars, ceramics, heat and water insulating materials, road construction. The world experience shows the potential of 70-80% utilization of ash and slag, as, for example, in some European countries. However, the cost of the recycling of ash-and-slag wastes with the production and simultaneous neutralization of wastes can be higher than the cost of the production.

One of the directions of the use of ash and slag wastes is the production on their basis of new types of complex binder that have increased strength and low prime cost. The replacement of a part of cement with active mineral additive allows to achieve significant saving of binder. The existing methods of the production of complex binders include the stages of joint or separate grinding of cement clinker and mineral additive with following mixing. Significant energy costs for grinding increase the cost of binder.

In this regard, the development of the effective complex binder with the use of ash-and-slag wastes of the Belarussian state district power station in Orekhovsk using resource-saving technology is the actual research objective.

Keywords: ash-and-slag mixture, Portland cement, complex binder, cement replacement, mineral additive.

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1. INTRODUCTION

1.1 General

At present, the use of biomass as fuel in thermal power plants is increasing in the Republic of Belarus. Energy development plans are aimed at creating a sustainable energy system oriented towards the use of renewable energy sources, largely to biofuel, namely peat and wood chips. The experience of Sweden, Austria, Denmark shows [54] a negative impact on the environment and people of ash and slag heaps generated in thermal power plants from the burning of wood, straw, by-products of the pulp industry, woodworking and logging residues.

It should be noted the high level of utilization of ash and slag wastes in European countries - about 50%, in France and Germany - 70%, in Finland - about 90% of their current output [55]. The greatest practical application of ash and slag wastes are found in concrete technology. Partial replacement of part of cement with ash solves the problem of saving clinker stock, obtaining strong and durable reinforced concrete structures and utilizing multi-tonnage ash and slag wastes [56].

To determine the feasibility of effective use of ash and slag peat and wood mixture of the Belarussian state district power station for replacement of a part of cement, a complex of studies was conducted to study the influence of the water-binding ratio, conditions and dates of hardening, and the proportion of ash in the complex binder on the properties of cement-ash stone, such as density and compressive strength.

1.2 Objectives

The aim of the master's thesis is the development of the effective complex binder based on Portland cement and ash-and-slag wastes of the Belarusian state district power station in urban settlement Orekhovsk.

The following tasks have been solved in the work to achieve the goal:

1. The analysis of the present trends in the processing and use of ash-and-slag wastes of thermal electric power stations;
2. The study of the influence of water-binder ratio, conditions and terms of hardening on the strength and density of cement-ash stone;
3. The study of the maturity (with corresponding curing curves) of the complex binder and the effective ratio of the components of the complex binder has been determined;
4. The analysis of the influence of complex binder and plasticizing additive Stakhement 2000M Zh30 on the strength and deformation properties of concrete.

1.3 Structure

Present research work consists of 5 chapters. Chapter 1 contains the introduction, objectives and structure of the work done.

Chapter 2 is a study of the world practice of using ash-and-slag wastes from thermal power stations.

Chapter 3 describes the main materials, techniques and equipment used in research work.

The main experimental work is set forth in Chapter 4. In this part, the characterization of the strength of cement-ash stone, mortar and concrete made with this complex binder, produced with the ash-and-slag wastes of the Belarusian district power station in urban settlement Orekhovsk is carried out. Further, the study of the curing curves for the complex binder made with ash-and-slag wastes were carried out and the physico-mechanical characterization of the combined use in concrete of the complex binder and the plasticizing additive Stakhement 2000M Zh30.

Chapter 5 outlines the conclusions on the work done and the results obtained.

2. MODERN TRENDS OF PROCESSING AND USE OF THE ASH-AND-SLAG WASTES OF THERMAL POWER STATIONS

2.1 Technologies of complex processing of the ash-and-slag wastes of thermal power stations

The increased number of thermal power stations operating with local fuels, in particular peat, makes important for Belarus to resolve the issues related to the disposal of the ash-and-slag wastes. In this context, the experience of other countries in reusing these by-products for the production of high added value products is of great technical and commercial interest. The average level of utilization of the ash-and-slag wastes in developed countries is about 50%, with France and Germany reusing – 70% and Finland about 90% of their current output.

The main commercial interest is the extraction of aluminosilicate microspheres, silica (SiO_2), alumina (Al_2O_3), oxides of rare and rare-earth metals.

Aluminosilicate microspheres are one of the components of the ash-and-slag wastes of coal-fired thermal power stations (TPS), which are formed when coal is burned in power plant boilers as a result of granulation of the melt of the mineral part of the coal and blowing of the crushed fine droplets with internal gases. As a result of this process, hollow aluminosilicate microspheres of almost perfect spherical shape are obtained. The diameter of the particles averages from 10-20 to 500 microns. This material has several unique properties: low density, high mechanical strength, chemical inertness, good heat resistance, low thermal conductivity [1].

Many technological solutions have been developed for the production of aluminosilicate microspheres from ash and slag wastes

from thermal power plants. In the first method, according to the patent No. 2263634C1RU [2], the aluminosilicate microspheres are separated from the ash-and-slag waste by immersion in a liquid, collecting the aluminosilicate microspheres from the surface of the liquid and drying. The drying is carried out in two stages, with the aluminosilicate microspheres maintained at a temperature of above 20°C in the first drying step until they reach a residual relative humidity less than 30%, and in the second drying stage, the aluminosilicate microspheres are heated to a temperature of 100-300°C in a drum-type furnace by direct contact drained and heated aluminosilicate microspheres by external drum walls of said furnace to achieve a relative humidity less than 3%.

Disadvantages of this method are: firstly, a long period of natural evaporation of moisture with the difficulty of implementing a continuous technological process; secondly, at the above temperatures in a drying oven, it is virtually impossible to obtain a microsphere humidity of less than 3%. At the same time, the required moisture content of the microsphere for commercial use is below than 0.5%.

The second method known for collecting microspheres from fly ash (patent No. 2257267C2RU) [3], includes the steps of hydroseparating an aqueous suspension, extracting and dehydrating the microspheres, and collecting microspheres using floating booms.

The device corresponding to this method includes bonded polypropylene booms of about 30 m in length and about 0.5 m in width, with a weight holding device in the lower part, a pulling winch and a centrifugal motor pump.

In addition this device is known for separating hollow microspheres from ash-and-slag pulp (patent No. 2047379 C1RU) [4] represents a hinged beam on the body.

The high level of utilization of the ash-and-slag wastes in European countries was ensured by the wide introduction of technologies for integrated processing of the ash-and-slag wastes from TPSs.

The company «Zolanewtechnology» (Russia) offers a complete technological process for the treatment of the ash-and-slag wastes,

which includes several stages [5].

In the first stage, by flotation, the unburnt fraction is extracted from ash and slag waste, which after drying can be used as secondary fuel in charcoal TPSs.

Second stage extract aluminosilicate microspheres of different fractions. Ash as raw material enters hydrocyclones, which in turn foams this mass (raw materials) at low speeds and sends the collected foam to special centrifuges with the help of pumps. Further, in a centrifuge through a special screen, the microspheres are separated into different fractions and at a certain temperature the water evaporates, while the microspheres, in dry form, are scattered into bags in different types and then sent to the consumer.

At the third stage by magnetic separation, the ash is divided into magnetic and non-magnetic fractions. Magnetic concentrate from the ash-and-slag wastes can be used for the production of ferrosilicon, cast iron and steel. It can also be used as raw material for powder metallurgy. The cost of the magnetic concentrate obtained from the ash-and-slag wastes of TPS by magnetic separation is much lower than the ore concentrate.

In the fourth stage: the purified ash-and-slag wastes in a dry state are mixed in a mixer with a reagent and enter a furnace where, under certain temperature conditions, the process of opening the ash occurs. As a technological method of opening ash, it was chosen to fuse it with soda, which allows the transfer of a significant part of the silica to water-soluble silicates (sodium and potassium silicates). Fusion with soda makes it possible to convert to a solution of up to 70% silica in aqueous leaching of the melt.

The fifth step: the cooled speck is mixed with a solution of hydrochloric acid. The deionized solution enters the redistribution of rare metals production, and the cake is used to produce the silicon compound.

The sixth stage: the production of rare-earth metals determines the already known technological processes from a ready-to-use concentrate solution.

High-quality commercial products from ash are obtained on the basis of technologies of OmegaMinerals Group (Germany). The

technology of extraction of microspheres is based on the mechanized extraction of light ash fractions (LAF) from the surface of the hammable maps of the ash-and-slag disposal sites. The LAF produced is packed in accordance with the requirements for the transportation of such goods and is transported to the processing plant for further processing. Processing LAF for the purpose of obtaining conditioning microspheres includes several partially compatible stages:

- removal of organic impurities and underburning;
- non-destructive drying and separation of garbage;
- classification of the material by particle size, density, strength;
- magnetic separation of the product, removal of iron-containing particles;
- calcination of the material (if necessary);
- dehydration of the material to the moisture content of less than 0,25% and ensuring its free flow;
- regulation of acid-base properties of the material (pH level);
- sterilization of the material (if necessary - for paint manufacturers) [6].

The technology firm RockTron (UK), based on the method of froth flotation, allow a complex solution of the problem of fractionation of ash from ash-and-slag repositories. Developed by experts of the company RockTron unique technology of ash-and-slag enrichment, which has been successfully used in Europe for more than 20 years, it makes it possible to receive from waste a number of eco-mineral products with unique characteristics. These mineral products can be used in various industries, including the production of building materials, polymers, elastomers, coatings, adhesives, can replace expensive raw materials and will allow producers to obtain economic benefits from use. The most interesting for the construction industry is the Alpha product, the use of which as an additive in the production of ready-mixed concrete, reinforced concrete structures and others concrete products, allowing to save 25-30% of cement in volume without compromising the strength and durability of the concrete. Taking into account the lower cost of Alpha in relation to cement, this will allow the producers of concrete and reinforced concrete

structures to reduce the cost of their products. The uniqueness of RockTron technology lies in the fact that it allows 100% reuse of ash-and-slag into useful eco-mineral products RockTron [7].

The technology of electrostatic separation, developed by Separation Technologies (USA), allows to reduce the carbon content in coal fly ash, which results in ash with a low content of carbon, which can be used to replace part of the cement. From fly ash with a loss on ignition (loi) > 25%, an ash with a controlled burndown content of about $2 \pm 0.5\%$ was obtained. The separation is based on the fact that in the electric field the ash particles are charged negatively, and the coal particles are positively charged. In addition to the high-quality commercial product with low carbon content, which is known under the ProAsh trademark (the ProAsh ash), which is used in the production of concretes, as a result of ST separation processes, high-carbon ash with the EcoTherm brand (the EcoTherm ash) is also released. The EcoTherm's ash has a significant energy value and can be easily used on TPSs to improve fuel efficiency using the EcoTherm ash return system in the fuel delivery system [8].

2.2 The application of ash-and-slag wastes as mineral additives

The reuse of the ash-and-slag wastes in the production of building materials is one of the most promising areas of utilization. The greatest use of the ash-and-slag wastes is found in the concrete and mortars technology, allowing to produce complex binders. In the complex binder the ash-and-slag wastes perform the role as a mineral additive.

The classification of active mineral additives according to State Standard 24640-91 [9] subdivides the additives-components of the material composition by the role in the process of hydration and hardening of cement for the active mineral additives and fillers. In turn, active mineral additives are classified according to the activity type to those having hydraulic and pozzolanic properties. Basic and acidic ash are active mineral additives with pozzolanic properties. In [10], the effective classification is proposed taking into account the

genesis and role of mineral additives in the process of hydration and hardening. As noted, this classification makes it possible to predict the effectiveness of the action of both a single mineral additive and in combination with other additives in the material composition of composite cements. According to this classification, the ash-and-slag wastes of thermal power plants by origin are technogenic, which are also subdivided into active mineral additives, possessing hidden hydraulic properties and possessing pozzolanic properties, and fillers.

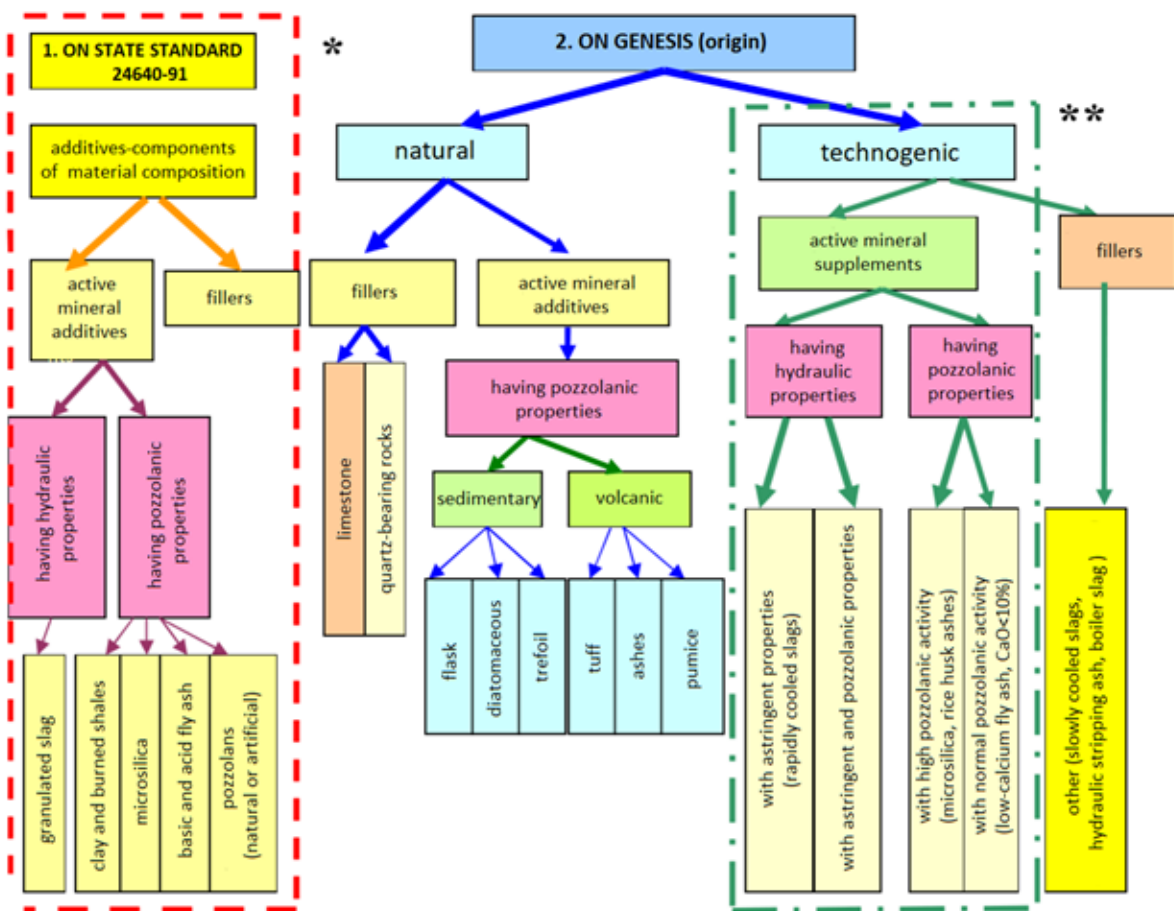


Figure 2.1. – The classification of mineral additives by genetic characteristics:

*The red frame indicates the existing classification in accordance with State Standard 24640-91;

**The classification of the RILEM Committee for Mineral Additives of Technogenic Origin

Mineral additives are powders of different mineral nature, obtained from natural (mountain rocks) or technogenic raw materials (ash, ground slag, microsilica, etc.). Mineral additives differ from the aggregate with small grain sizes (less than 0.16 mm), and from chemical modifiers in that they do not dissolve in water. Being

located together with cement in filler voids, they compact the structure of concrete, in some cases allow to reduce the consumption of cement [11].

Mineral additives are divided into active and inert. Active mineral additives are able in the presence of water to interact with calcium dioxide at ordinary temperatures, forming compounds that have astringent properties [12]. When introduced into concrete, they interact with $\text{Ca}(\text{OH})_2$, which is released upon hydration of Portland cement [11]. Some active mineral additives, for example, ground blast furnace slags, are capable of self-hardening, which is activated by the addition of lime. The properties of mineral additives are significantly influenced by their grain composition, which determines the specific surface and, accordingly, the reactivity or the possibility of compacting the structure of the concrete.

Inert additives, for example, ground quartz sand, do not react with cement components at normal temperatures, but under certain conditions these additives may exhibit reactivity (for example, in autoclaving) [11]. In most cases, inert additives are used to regulate the grain composition and voidness of the solid phase of concrete: aggregate-cement-mineral additive, in order to control the properties of the concrete mixture and concrete.

Natural mineral additives are obtained by finely grinding various volcanic rocks (tuff, ash, rhyolite) or sedimentary (diatomite, tuff, flask) origin [13]. Mineral additives of volcanic or sedimentary origin consist mainly of silica and alumina (70-90%), which to a certain extent determine their pozzolanic activity. These additives are widely used in the production of cement. Their disadvantage is the increased water demand.

Mineral additives from technogenic raw materials: ash, ground slag, microsilica and others have different mineralogical composition and dispersity, which determine the effectiveness of their use in cement and concrete.

Microsilica is a waste product of silicon-containing alloys: ferrosilicon, crystalline silicon, etc. During the melting of the charge and the recovery of quartz at the temperature above 1800°C , gaseous silicon is formed, which upon cooling and contact with air is oxidized to SiO_2 and condensed in the form of ultrafine silica

particles. The SiO_2 content in the microsilica is 85-98%.

From other active mineral additives microsilica differs very small particle size (0.1-0.5 microns) and high specific surface (18-25 m^2/g). Used in concrete to fill the pores of the cement particles arrangement, microsilica helps to increase the density and accordingly strength, impermeability and durability of concrete.

According to the mineralogical composition and properties of ash can be divided into two types: acid (rich in quartz - SiO_2) or basic (rich in calcium oxides - CaO). The former exhibits pozzolanic properties, the latter additionally exhibits the properties of an independent binder.

According to the content of calcium oxide, ash is divided into high-calcium ($\text{CaO}>10\%$) and low-calcium ($\text{CaO}<10\%$) [14]. High-calcium ash has some astringent properties and can be used to replacement of the part of cement in concrete, which does not have high requirements for strength and durability. In these solids, part of CaO can be in the free (burnt) state, which leads to uneven volume changes and certain difficulties in their application.

Low-calcium ash does not possess astringent properties [11], but in the presence of lime and water they actively participate in the formation of hydrosilicates and calcium hydroaluminates, the basic structure-forming components of the cement stone. These ash by 80% or more consist of aluminosilicate glass, which predetermines their pozzolanic activity. Low-basic ash is widely used as the active mineral additives.

It was shown in [15-17] that the main characteristics of the chemical composition of ash-and-slag wastes were the basicity module M_0 (hydraulic module) - the ratio of the mass fractions of the main oxides to the total content of acid oxides; silicate (siliceous module) M_0 shows the ratio of the amount of silicon oxide reacted with other oxides to the total content of aluminum and iron oxides; coefficient of quality K , showing the ratio of oxides that increase the hydraulic activity, to oxides that reduce it.

For basic sols and slags $M_0>1$, for weakly acidic - $M_0= 0.9-1.0$, for acidic - $M_0=0.6-0.9$, and for super acids - $M_0<0.6$.

The calculations of the main characteristics of the chemical

composition of fly ash from the burning of peat of some of the republic's energy enterprises, carried out in [18, 19], showed that the basicity modulus varies from 0.27 to 0.78; the silicate module is in the range of 1,08 to 6,27; the quality factor K is in the range from 0.38 to 1.08. Thus, the peat ash of the Belarus energy enterprises are related to acidic and super-acid latently active ash.

The studies carried out by E.A. Stroiteleva [20], confirmed the high efficiency of the use of acid ash for replacing part of the fine aggregate in fine-grained concrete in order to increase the strength parameters. It is shown that the application of heat and moisture treatment at the optimal dosage of the filler leads to an intensification of the pozzolan type reaction and to the production of concretes that are superior in strength to similar compositions of normal-moisture hardening. A decrease in the capillary porosity of cement stone due to improved particle size distribution and pore colmatation with additional calcium hydrosilicates formed by the interaction of ash with Portland cement hydration products is established. It was found that ash acts as a substrate on which formation of crystalline hydrates during hydration of cement is activated.

2.3 The effect of mineral additives on the processes of hydration and structure formation of the cement stone

The pozzolanic activity of mineral additives is primarily determined by the presence of amorphous silica in their composition, which interacts with $\text{Ca}(\text{OH})_2$ to form highly disperse calcium hydrosilicates with increased binding properties. This contributes both to an increase in strength and to a decrease in pore size, the latter reduces the permeability of concrete [21].

Ash is characterized by the late onset of pozzolanic reaction (on average at 7-day old age) and its slow flow during the first month of hardening. The main part of it falls at the age of 30-90 days, the high intensity of hardening of concrete with ash persists at its sufficient humidity and at the later date. Most fully this effect is used when it is

possible to assign the standard age of concrete for more than 28 days. But in the normal situation, it is useful, because will also give an additional margin of strength, and reduced permeability, and, consequently, increased durability of such concrete. However, there should not be a complete binding of $\text{Ca}(\text{OH})_2$, which would violate its passivating effect on steel reinforcement. Therefore, the amount of ash introduced into the concrete is limited [42].

When using mineral additives in Portland cement, their effect on the processes of hydration and structure formation can be different.

Solidification of binding systems is a complex physicochemical process that can be considered as a set of two interacting elementary processes [22]:

- hydrate formation (x) - the chemical reaction of binding of the mixing fluid to the phases of binders and aggregates with the formation of reaction products;

- structure formation (h) - the formation of a spatial framework of the hardening structure and its hardening.

Both of these processes are closely related to each other, that is, the formation of artificial stone in binder systems is determined by the kinetics and quantitative characteristics of hydrate and structure formation, their mutual influence on each other.

When the binders are hardened, several chemical reactions occur, which is due to the different hydraulic activity of the constituent components. At the same time, in any isolated volume of the solidifying system, only one structure-forming process can take place, which has a purely physical nature [22]. In this case, each chemical reaction that takes place in the hardening mixed binder is associated with the same process of structure formation, and the number of stages of their coupling depends on the hydraulic activity and the content of the mineral additive.

In work [23], the modification of the structure of the cement stone was studied by using a filler from the fly ash of Khabarovsk TPP-3, which is acid ash and has a high water demand. To identify the current processes of modifying the structure, studies were carried out using differential thermal analysis (DTA). To study the effect of hardening conditions on the microstructure of the cement stone with the filler from the fly ash of TPP-3 in Khabarovsk, samples were prepared that

hardened under normal-humid conditions and with the use of thermal-moisture treatment.

The given qualitative analysis of DTA thermograms of the cement stone is presented in Figure 2.2, where 1 - the control composition at the age of 28 days with normal hardening, 2 - the control composition at the age of 28 days at HMT, 3 - the composition with ash (B/C=const) at the age of 28 days at normal hardening, 4 – the composition with ash (B/C=const) at the age of 28 days with HMT, 5 – the composition with ash with constant plasticity at the age of 28 days with normal hardening, 6 – the composition with ash with the constant plasticity at the age of 28 days at HMT.

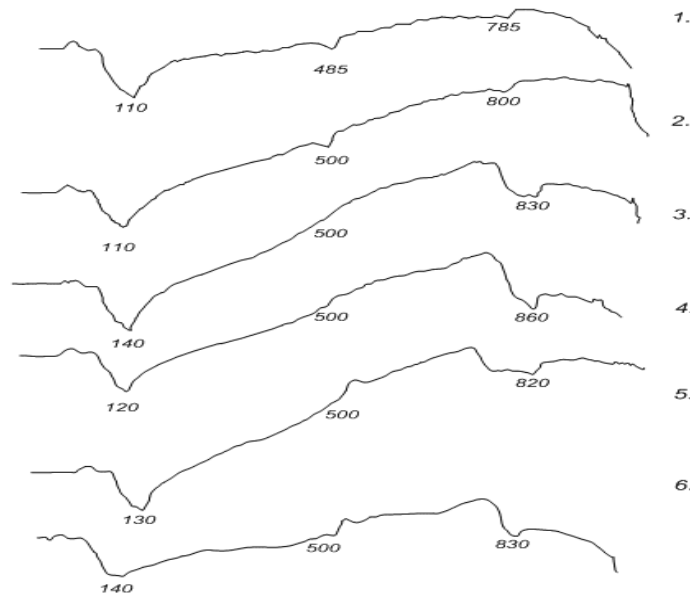


Figure 2.2. – DTA - thermograms of the cement stone for 28 days

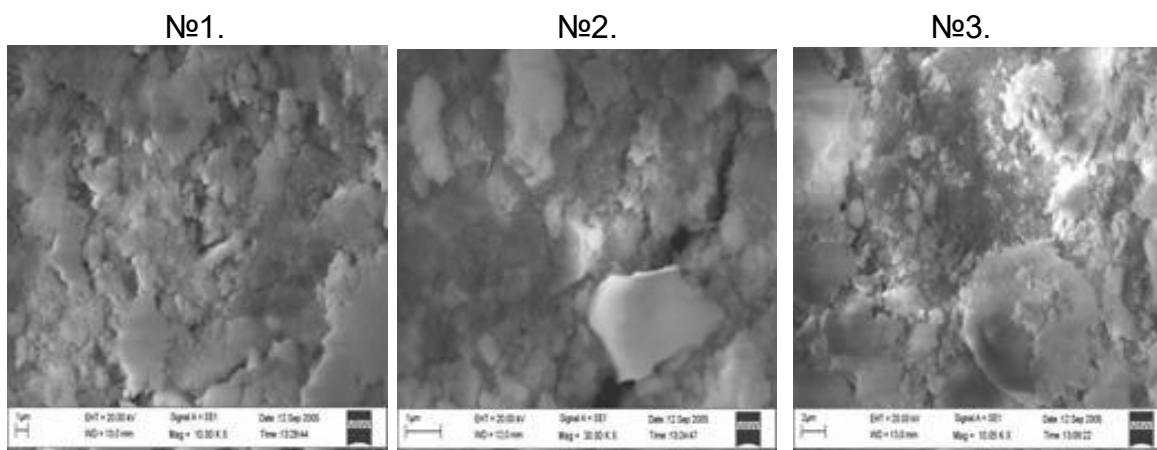
The samples of the cement stone with ash content (No. 3-6) are characterized by an increase in the amount of adsorption-bound water, since the endothermic peaks shift from 110°C to 130-140°C.

The endothermic effect inherent in the presence of $\text{Ca}(\text{OH})_2$ is evidently observed on the samples of the cement stone without ash, and in the samples containing ash this effect is not observed. This fact indicates the hydraulic activity of ash, expressed in the binding of free lime to low-basic calcium hydrosilicates (range 700-800°C).

In the compositions No. 3 and No. 4, these effects are absent, possibly due to some superposition of endothermic and exothermic peaks corresponding to $\text{Ca}(\text{OH})_2$ and unburned organic residues, in view of their similar temperature ranges.

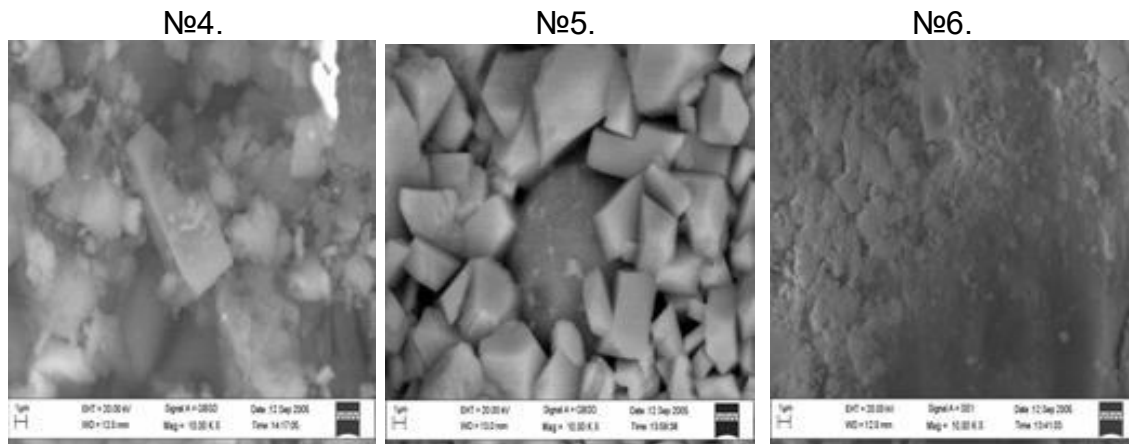
The maximum effect is noted when using the HMT. This can be explained by the fact that when steaming, more hydration products react with ash.

In [23], conclusions were drawn on the hydraulic activity of ash, for which the chips of the cement stone samples with or without filler were examined under an electron microscope.



1 – NHC, ash 0%; 2 – NHC, ash 30% (W/C=const); 3 – NHC, ash 30% (W/C≠const)
Figure 2.3. - The microstructure of the cement stone and the stone with the content of ash filler when hardened in normal-humidity conditions, an increase of x10000

Analysis of the fresh cleavage of the cement stone and the stone containing the ash filler in the amount of 30% of the mass of cement shows the features of microstructure development depending on the conditions of hardening. Under normal-moisture conditions of hardening, cracks are observed in the samples with the constant water-cement ratio (No. 2), and the samples with constant ductility (No. 3) have practically no cracks, as well as the samples of the cement stone without ash (No. 1) (Figure 2.3). When using heat and moisture treatment (HMT) in the samples with the constant water-cement ratio (No. 5) and with constant plasticity (No. 6), new formations of low-basic hydrosilicates are seen when the cement stone does not have them (No. 4) (Figure 2.4).



4 – HMT, ash 0%; 5 – HMT, ash 30% (W/C=const); 6 – HMT, ash 30% (W/C≠const)
Figure 2.4. - The microstructure of the cement stone and the stone with the content of ash filler when hardened with heat and moisture treatment, an increase of x10000

In specimens No. 5 (the rigid mixture), when the HMT is used, neoplasms do not have a regular shape, whereas in the samples under No. 6 (the mobile mixture), crystals of regular shape are formed which form on the surface of fly ash, which is clearly seen with an increase of x10000 (Figure 2.4).

It has been established [23] that ash is an effective microfiller that has hydraulic activity, especially with increasing water flow. The use of heat and moisture treatment increases the efficiency of ash, since they contribute to the additional formation of low-basic calcium hydrosilicates.

2.4 Durability of concrete with complex binder from Portland cement and mineral additives

Acidic ash as the mineral additive in the composition of cements [24], as well as in concrete, is used to bind $\text{Ca}(\text{OH})_2$, which is formed during the hydration of Portland cement. In addition to increasing the strength and saving binder, with the introduction of acidic ash by Reftinskaya state district power station, the authors of [25] achieved the reduction in water separation and delamination of the concrete mix, increased corrosion resistance and frost resistance of concrete, improved surface of products.

In his works, A.V. Ukhanov [26] showed that the dump ash-slag

mixture can be used as the mineral additive for the production of concretes, mortars and dry construction mixtures. It is shown that fly ash can both reduce and increase the water demand, the viscosity and plasticity of concrete mixes, can lead to an increase in the strength of concrete, and also can cause significant linear expansion of the cement stone when it is hydrated. In this case, the chemical composition of the ash plays a decisive role.

In the studies of D.E. Kucherova [10] used such mineral additives as expanded clay dust, cork, Cherepovets slag, perlite dust, foundry slag, volcanic tuff. By the method of multifactorial experiment it was established that when concrete is hardened, the increase in strength of composite binders is achieved due to the synergistic effect of mineral additives with a different mechanism of action. It was established that the composition and volume fraction of the products of the neoplasms depends on the material composition of the astringent and the genesis of mineral additives. The most complex composition of hydration products are compositions containing up to three mineral additives. It has been shown [10] that in the presence of mineral additives of various effects, the hydration of clinker minerals, especially C₄AF, is activated, the formation of an additional amount of hydrocarbon aluminates and scotite, which compact and strengthen the structure of the cement stone. The results obtained make it possible to classify calcium carbonate in an amount of 5-10% by weight to the active components of composite binder. On the basis of complex studies, the mechanisms of action of each component of composite astringents and the factors determining the effectiveness of the action of additives in concrete are specified. Electron microscopic studies have established that the hydrate structure of cement concrete cement is represented by two varieties - primary and secondary structures. The primary structure is represented by amorphous products in the inter-porous space formed by a through-solution mechanism. Moreover, the composition of products in the pore space depends on the electro-surface potential of large particles surrounding the pore. The secondary structure arises from the topotactic mechanism around hydrated particles of a larger size (more than 10 μm). This structure does not have clear interfaces,

but appears on a substrate of topotactically altered crystals, in which either the features of the original structure remain, or their structure approximates the structure of a fully crystallized neoplasm of a more dense structure than the primary structure.

In the work of P.N. Kurochkin [27] for research as powdered mineral additives are accepted: ash; burnt rock; casting ceramics; silt of mine waters; graphite; soot [28]; ground quartz sand; silicate brick waste. The admixtures (except for the soot) were dispersed into fractions: <0.05 mm (sealers); 0.05-0.08mm (diluent); 0.08-0.14 (fillers). Strengthening additives, replacing 20% of cement consumption, contribute to the formation of a fine-porous structure of concrete. At the same time, its water resistance increases to B8-B10, and frost resistance is two or more times. The addition of 20% stabilizing additives to the standard consumption of cement provides a 100% probability of obtaining concrete of specified strength. After analyzing the results in [27], the additives studied were divided into three groups (Figure 2.5).

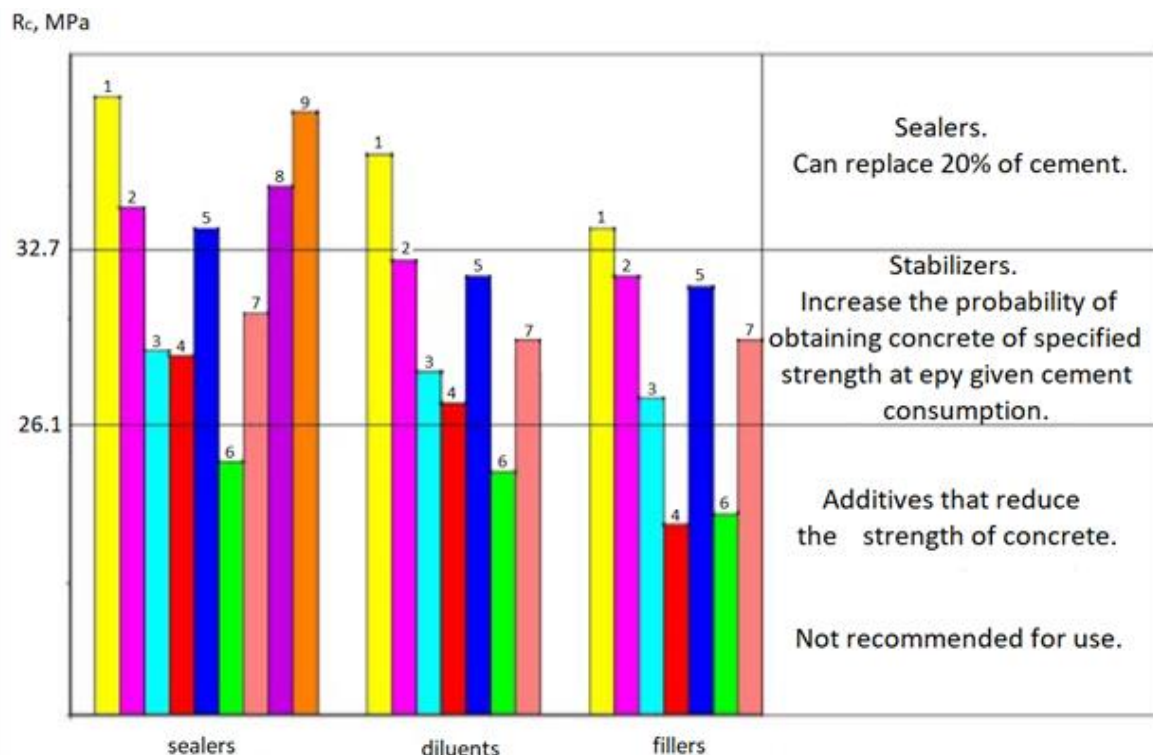


Figure 2.5 – The effect of the binder of cement and finely dispersed mineral additive (20% of the weight of binder) on the compressive strength of the concrete samples:
 1 - quartz sand; 2 - silicate brick; 3 - casting ceramics; 4 - burnt rock; 5 - ash;
 6 - mud of mine waters; 7 - graphite; 8 - soot; 9 - quartz sand (40%) + soot (60%).

When using fine sand in concrete mixes, the concrete strength without increasing the cement consumption can be provided by a complex binder consisting of a standard amount of cement and finely divided mineral additives. As additives, fine-grained quartz sand, fine powder from silicate brick, ash, soot, and also a mixture of soot with quartz sand are recommended. Stability of obtaining concrete of a given class at a certain cement consumption can be achieved by adding to the cement mineral additives specified in Figure 2.5.

Improvement of the mechanical properties of cement-ash stone can be achieved in later terms of hardening, since the hydration process slows down. It was shown in Ref. [29] that when the cement part in the composite ash complex is replaced by up to 30%, the compressive strength of the cement-ash stone is almost equal to the strength of the control sample without ash after 56 days of hardening.

Swaroop et al. [30] in the study is mainly limited to assessing the changes in compressive strength and density of five different compositions of concrete M30, namely: ordinary concrete; concrete with a reduced amount of cement by 20% and 40%; concrete when cement is replaced with ashes by 20% and 40%. The effect of 1% H_2SO_4 and seawater on the properties of concrete is determined by keeping the sample cubes for 7 days, 28 days, 60 days in the above solutions, and the corresponding changes in both the compressive strength and the reduction in density are noted. It can be concluded that concretes with replacement of a part of cement with ash have good strength and durable properties in comparison with a control sample when they are kept in an aggressive environment.

Alvin Harison et al. [31] conducted studies to replace cement with ash, respectively, in the range 0%, 10%, 20%, 30%, 40%, 50%, 60% by weight of cement for concrete M25 with the water-cement ratio of 0.46. Concrete mixtures were manufactured, tested and compared in terms of the compressive strength. It was noted that when cement is replaced with ash in the amount of 20%, strength increases by 1.9% and 3.2% after 28 days and 56 days, respectively. It was noted that when Portland cement is replaced by ash up to 30%, the strength is almost equal to the control sample of

concrete after 56 days. Samples of concrete with replacement of most Portland cement with ashes gain strength after 56 days of hardening due to slow hydration process.

R.R. Vanked and V.A. Fulyari [32] studied the effect of ash on the properties of concrete. The studies were carried out for concrete M25 at the age of 7 days, 14 days, 28 days of hardening. The cement was replaced with ash in an amount of 10%, 20% and 30% by weight of the binder. It was found that the reduction in strength of concrete is less significant with increasing water-cement ratio of concrete. Concrete with the cement replacement of 10% and 20% ash shows the high compressive strength at the age of 28 days at the water-cement ratio of 0.35. In the case of 30% replacement of cement with ash, the compressive strength of concrete decreases.

To increase the strength of concrete, mobility, reduce the labor intensity of concrete works, superplasticizers based on polycarboxylate ether are introduced into the concrete composition [33-35]. Foreign and domestic experience of their application has shown that superplasticizers based on polycarboxylate esters - PCE can reduce the water requirement of concrete mix to 30%, increase mobility to grade P4 to P5, significantly improve the design strength, frost resistance, water resistance, and self-compactness [36]. Also, unlike traditional superplasticizers of sulfonated melamine and naphthalene (SMFC and SNFC), whose action is based on electrostatic repulsion of cement particles, RFE uses a bulk polymer chain to create a steric effect. Depending on the type of cement, modern technologies make it possible to obtain polycarboxylates with a different polymer structure, which significantly expands their range of effective use [34].

2.5 Chapter summary

1. It is shown that for mass use of the ash-and-slag wastes in concretes, preliminary processing or enrichment is necessary, including fractionation with separation of coarse fraction, magnetic or electrostatic separation, flotation of ash.

2. Low-calcium ash on 80% and more consist of aluminosilicate glass, which predetermines their pozzolanic activity. Low-basic ash is widely used as active mineral additives, which when introduced into concrete interact with Ca(OH)_2 , released during the hydration of Portland cement, and form hardly soluble compounds.

3. The grain composition of mineral additives, which determines the specific surface and, accordingly, the reactivity, the chemical and mineral composition, the amount of the mineral additive and the hardening temperature, has a significant influence on the processes of the structure formation of the complex binders.

4. When used in concrete mixtures, depending on the chemical composition, the ash can both reduce and increase the water demand, viscosity and plasticity of concrete mixtures, and can also cause significant linear expansion of the cement stone when it is hydrated. When most of Portland cement is replaced with ash due to the slow process of hydration, concrete can gain control strength only after 56 days of hardening.

3. MATERIALS AND METHODS

3.1 Materials

To carry out the research, Portland cement was used by JSC «Belarusian Cement Plant», which meets the requirements of State Standard 31108-2003 [37].

The physico-mechanical characteristics of Portland cement are given in Table 3.1.

Table 3.1. – The physico-mechanical characteristics of Portland cement

Type of cement and name of the manufacturer	Specific weight, [kg/m ³]	Normal consistency, %	Setting time, [min]		Activity, [MPa]
			initial	final	
Portland cement CEM I, M500 (42,5N), Kostyukovich town	3200	31,0	190	290	45

As a fine aggregate, the sand of the quarry "Borovoye" was used, satisfying the requirements of State Standard 8736-2014 [38], its characteristics are given in Table 3.2.

Table 3.2. – The physico-mechanical characteristics of sand

Bulk density, [kg/m ³]	Density of grains, [kg/m ³]	The content of silty and clay particles, %	Voidness, %	Humidity, %
1567	2650	2,5	39,2	5,26

The quality of sand was evaluated according to State Standard 8735-88 [39]. The results of the determination of the granulometric composition are presented in Table 3.3.

Table 3.3. – The granulometric composition of sand

Dimensions of sieves, [mm]	2,5	1,25	0,63	0,315	0,16	less 0,16
Retained material, %	5,5	8,5	21,5	34,0	28,5	2,0
Accumulated material, %	5,5	14,0	35,5	69,5	98,0	100

According to the test results, this sand belongs to the group of medium, class II, the size modulus $M_s = 2.23$.

As a large aggregate used crushed stone produced by the State Enterprise "Granite" (Mikashevichi town), the maximum grain size of 20 mm, satisfying the requirements of State Standard 8269.0-97 [40]. The physico-mechanical characteristics of crushed stone (according to State Standard 8267-93 [41]) are presented in Table 3.4. The granulometric composition of crushed stone is given in Table 3.5.

Table 3.4. – The physico-mechanical characteristics of crushed stone

Bulk density, [kg/m ³]	Density of grains, [kg/m ³]	Content of lamellar and acicular grains, %	Absorption, %	Crushing, %	The content of silty and clay particles, %	Humidity, %
1399	2700	13	0,45	7,5	0,4	0,02

Table 3.5. – The granulometric composition of crushed stone

Dimensions of sieve holes, [mm]	20	15	10	5	less 5
Retained material, %	2,2	63,1	26	6,95	1,8
Accumulated material, %	2,2	65,3	91,3	98,2	100

According to the data in Tables 3.4, 3.5, it can be concluded that the crushed stone corresponds to State Standard 8267-93. The mark of the crushed stone is 1400.

As a mineral additive, the ash-and-slag mixture of the Belarusian state district power station of urban settlement Orekhovsk in the Vitebsk region. In the tests, a slag fraction was used, passed through a No. 008 sieve (hereinafter referred to as ash). The additive meets the

requirements of State Standard 25818-91 [42]. The properties of the mineral additive of peat-and-wood ash are presented in Table 3.6.

Table 3.6. – The characteristics of peat-and-wood ash

Bulk density, [kg/m ³]	Density of grains, [kg/m ³]	Normal consistency, %	Specific surface area, [m ² /kg]	Humidity, %
960	2300	37,3	200	6

The chemical composition of peat-and-wood ash (mass %) according to State Standard 10538-87 [43] is presented in Table 3.7.

Table 3.7. – The chemical composition of the ash-and-slag mixture of the Belarusian state district power station (mass %)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃	loi
87.62	4.39	1.08	3.08	0.55	0.61	1.79	0.24	0.19	<0.10	0.07

For tapping concrete mixes tap water was used, which complied with the requirements of Belarusian State Standard 1114-98 [44].

According to the chemical composition, the ash-and-slag mixture consists mainly of silicon and aluminum oxides (92%). According to the modulus of basicity ($M_b < 1$), the ash-and-slag mixture is acidic [42], the content of calcium oxide and magnesium oxide is 3.63%.

As the plasticizing additive, the hyperplasticizer Stakhement 2000M Zh30 (in liquid form) [45] is a product based on polycarboxylates. Opaque liquid of light brown color. The density varies from 1075 ± 30 kg/m³. The hydrogen index is $8 + 1.5$.

Stakhement 2000M Zh30 is an additive-superplasticizer (group I) of a new generation based on polycarboxylates. Stakhement 2000M Zh30 is used to produce high-mobility, including self-compacting concrete mixtures, for the production of thin-walled and thickly reinforced, vertically molded products, structures of complex configuration and high degree of factory readiness. Additive Stakhement 2000M Zh30 allows to produce high-grade concrete (M 600 or more) in compressive strength from high-plastic concrete mixtures; increase the mobility from P1 to P5 and more, increase the

initial and final strength of concrete, increase density; reduce cement consumption by 20% or more; improve the quality of concrete; reduce energy costs for heat and moisture treatment; reduce the time of vibration or exclude it, increase the turnover of forms and increase labor productivity.

As a lubricating agent was used the AT-5-B [46].

3.2 Methods

The studies were carried out using standard techniques. Cements were tested in accordance with State Standard 310.1-76 [47]. Normal density in accordance with State Standard 310.3-76 [48]. The quality of sand was evaluated according to State Standard 8735-88 [39], crushed stone according to State Standard 8267-93 [41].

The complex binder was obtained by replacing part of Portland cement with the peat-and-wood ash (Figure 3.1) in an amount of 10%, 20% and 30% of the binder by weight.



Figure 3.1. – Preparation of the complex binder

The normal consistency of the complex binder with replacing part of Portland cement with the ash in an amount of 10%, 20% and 30% of the binder by weight is presented in Table 3.8.

Table 3.8. – The normal consistency of the complex binder

Composition number	Component ratio of cement:ash, %	Normal consistency, %
1	90:10	33,3
2	80:20	35,0
3	70:30	35,7

To determine the strength of cement-ash stone, samples were prepared with cubes with an edge of 2 cm. The compressive strength of cement-ash stone was determined at the age of 7 and 28 days under normal-humidity conditions of hardening and at the age of 1 day after heat and moisture treatment.

Determination of the strength of the complex binder was carried out according to the procedure of Belarusian State Standard EN 196-1/PR [49]. The essence of the technique is to compare the compressive strength and flexural strength of mortars made from Portland cement (control composition) with the compressive strength and flexural strength of mortars made from Portland cement in the amount of 90%, 80% and 70% and ash content of 10 %, 20% and 30% of the binder by weight. To conduct the tests, measuring pieces 4×4×16 cm³ were made, which were hardened in normal-humid conditions for one day, then placed in a container with water, the temperature of which was 20°C, and stored there until the desired age was reached.

To determine the strength and deformation properties of concrete, sample cubes with a face of 10 cm were made. The strength was determined at the age of one day hardening under conditions of thermal treatment at normal pressure in the KUP-1 steaming chamber, Kraft LLC, №0157. Heat and moisture treatment mode:

- 2 hours - preliminary aging at t=15-20°C;
- 3 hours - rise t to maximum (up to 80°C);
- 8 hours - isothermal heating at the maximum temperature (holding

at $t=80^{\circ}\text{C}$);

2 hours - decrease to ambient temperature.

Tests of all compression and bending samples were carried out in accordance with State Standard 10180-2012 [50] on Testing bluhm & feuerherdt gmbh test machine model C089-04 with Servotronic control unit C104 (Figure 3.2), which provides fully automatic control.



Figure 3.2. – Test machine C089-04 with control unit C104

The dimensions of the finished samples were checked with a digital caliper of type I. The measuring range of the instrument is 0-150 mm, the measurement speed is no more than 1.5 m/s. The caliper corresponds to the requirements of State Standard 166-89 [51].

The mass of the samples was determined with the help of electronic scales VK-300. The laboratory scale VK-300 is designed for high-precision measurement of mass. This type of electronic balance is used in production laboratories where an increased measurement accuracy is required. Scales electronic laboratory VK-300 II accuracy class of production "Massa-K" can work with several units of weight and in different modes of weighing.

4. RESULTS

4.1 Binder paste strength

The results of studies of ash-cement binders, given in [10, 27], indicate an ambiguous effect on the strength of concretes and mortars of increasing the proportion of ash in the composition of mixed ash-cement binders. It is noted that the assessment of this influence should be carried out taking into account the water-binding ratio, the mobility of the mixture, the conditions of hardening, the time of the set strength, the dispersity of the used ash. It is known [20] that heat and moisture treatment accelerates the physicochemical processes of hydration and structure formation of complex binders.

In this connection, at the first stage of the research, the influence of the composition of the complex binder on the strength of the cement-ash stone under different conditions of hardening was studied: normal-humidity conditions (NHC) and heat and moisture treatment (HMT) at a steaming temperature of 80°C.

The samples-cubes with an edge of 2 cm (Figure 4.1) of the cement-ash stone were made with a water-binding ratio of 0.3; 0.4 and 0.5 and with the replacement of part of Portland cement with ash in an amount of 10%, 20% and 30%. The superplasticizer Stakhement 2000M Zh30 was introduced in an amount of 0.6% by weight of the binder.



Figure 4.1. – The samples of the cement-ash stone

The compositions of the complex binder are given in Table 4.1.

Table 4.1. – The compositions of the complex binder and the density of cement-ash stone

Composition number	Consumption of materials, g per 100 g of the binder			Additive Stakhement 2000M Zh30, % by weight of the binder	Density of the cement-ash stone, [g/m ³], after hardening in conditions	
	Cement	Ash	Water		HMT	NHT
1	100	-	50	-	1710	1550
2	90	10	50	-	1720	1500
3	80	20	50	-	1710	1490
4	70	30	50	-	1660	1460
5	100	-	40	-	1900	1690
6	90	10	40	-	1890	1660
7	80	20	40	-	1850	1630
8	70	30	40	-	1830	1570
9	100	-	30	-	2090	2030
10	90	10	30	-	2060	2030
11	80	20	30	-	2010	1950
12	70	30	30	-	1950	1880
13	100	-	30	0,6	2030	-
14	90	10	30	0,6	1990	-
15	80	20	30	0,6	1940	-
16	70	30	30	0,6	1920	-

The results of determining the strength of the cement-ash stone after heat and moisture treatment are shown in Figure 4.2.

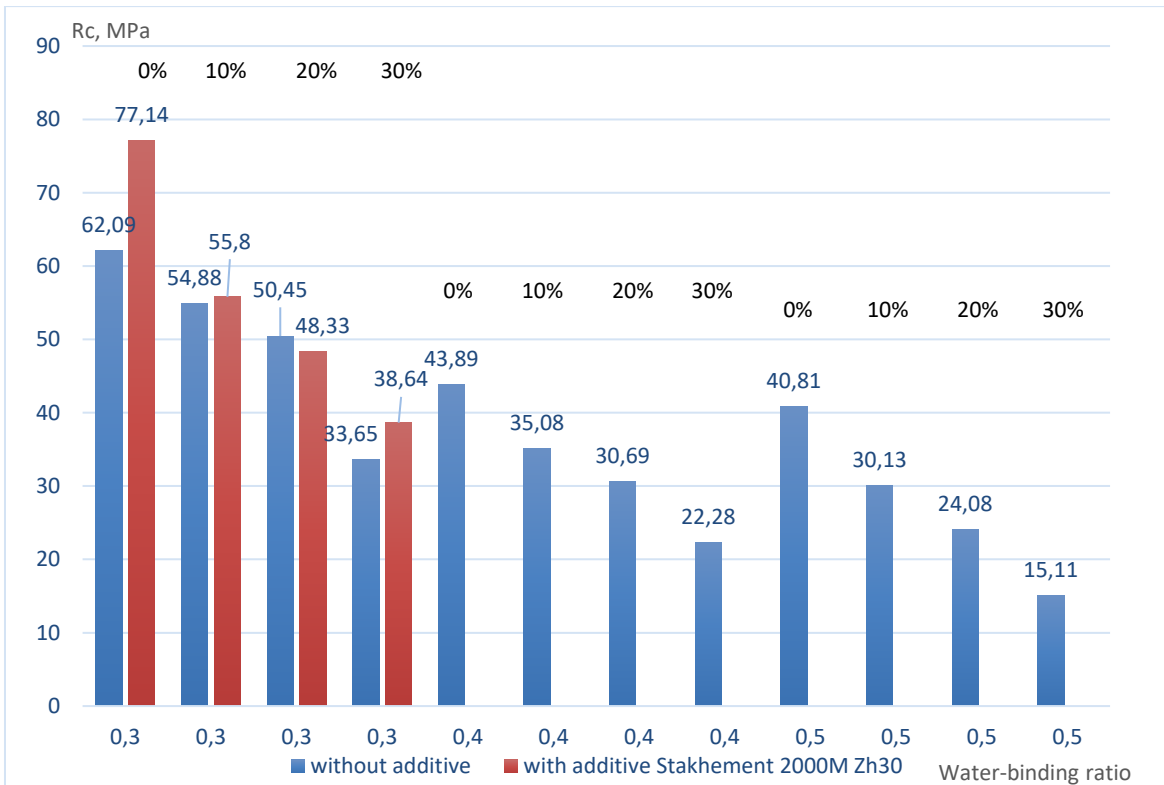


Figure 4.2. – Influence of the water-binding ratio and the proportion of ash in the complex binder on the strength of the cement-ash stone after heat and moisture treatment

It has been experimentally established that an increase in the percentage of cement replacement with ash at the constant water-binding ratio reduces the strength of the cement-ash stone. With the water-binding ratio of 0.4 the strength with the ash content of 10%, 20%, 30%, respectively, decreased by 20%, 30%, 49% compared to the control sample without ash. The water-binding ratio also affects the strength of the samples. At 10% of ash in the complex binder, the strength of the cement-ash stone decreased by 11%, 20%, 26%, respectively, with the water-binding ratio of 0.3; 0.4 and 0.5. The introduction of superplasticizer into cement-ash paste improved workability, but it didn't have a significant effect on the strength of the samples.

The change in the compressive strength of the cement-ash stone at different dosage of ash and water-binding ratio at the age of 7 and 28 days when hardened in normal-humid conditions is shown in Figure 4.3. The obtained results showed that when the percentage of replacement of Portland cement with ash is increased, the compressive strength of the cement-ash stone when hardened in normal-humid conditions is also reduced.

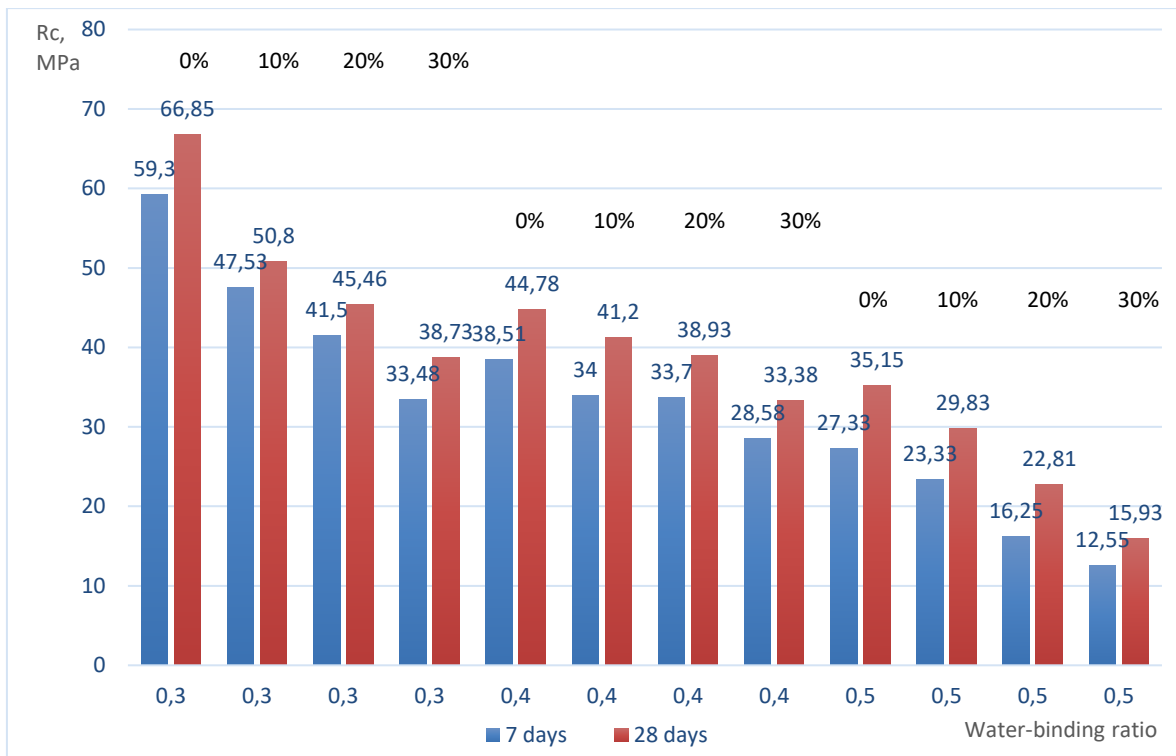


Figure 4.3. - Influence of the water-binding ratio and the proportion of ash in the complex binder on the strength of the cement-ash stone when hardened in normal-humid conditions

It was found that with the water-binding ratio of 0.3 the strength of the cement-ash stone with the 10%, 20%, 30% ash content, respectively, decreased by 24%, 31%, 42% compared to the control sample without ash. At 20% of ash in the complex binder, the strength of the cement-ash stone decreased by 31%, 13%, 35%, respectively, with the water-binding ratio of 0.3; 0.4 and 0.5.

The highest strength was obtained with the use of heat and moisture treatment for the modified cement-ash stone with the water-binding ratio of 0.3. In former studies [20], this effect was explained by the fact that when steaming, more hydration products react with ash.

In other work [10], it was proposed to use the efficiency coefficient as the criterion for evaluating the hydraulic activity of the additive used in the complex binder composition, which is the reciprocal of the percentage reduction in the strength relative to the control additive composition by 1% of the additive added. The coefficient of effectiveness of the additive was determined by the formula:

$$C_{eff} = \frac{\% \text{ additive content}}{(R_c - R_{add}) \times 100 / R_c} \quad (3.1)$$

where R_c - the strength of the control composition, MPa;

R_{add} - strength of the composition with the additive, MPa.

The results of the efficiency coefficient calculations are given in Table 4.2.

Table 4.2. – The coefficient of effectiveness of the additive in the complex binder

Composition number	Component ratio of cement:ash, %	Water-binding ratio	Coefficient of efficiency C_{eff} under hardening conditions	
			HMT	NHC
1	100:0	0.5	control	control
2	90:10	0.5	0.382	0.417
3	80:20	0.5	0.488	0.625
4	70:30	0.5	0.476	0.713
5	100:0	0.4	control	control
6	90:10	0.4	0.498	1.252
7	80:20	0.4	0.665	1.531
8	70:30	0.4	0.609	1.178
9	100:0	0.3	control	control
10	90:10	0.3	0.861	0.660
11	80:20	0.3	1.067	0.541
12	70:30	0.3	0.655	0.549
13	100:0	0.3	control	-
14	90:10	0.3	0.607	-
15	80:20	0.3	0.899	-
16	70:30	0.3	1.010	-

The tests carried out showed that the most effective is the addition of ash in the amount of 20% without a superplasticizer and in the amount of 30% with the addition of the superplasticizer at the water-binding ratio of 0.3 at the heat and moisture treatment ($C_{eff} = 1.067$ and $C_{eff} = 1.010$, respectively) 10%, 20%, 30% with the water-binding ratio of 0.4 for hardening in normal-humid conditions ($C_{eff} = 1.178 \div 1.531$).

4.2 Hardening rate of complex binder

The strength developing in time of the complex binder was determined in accordance of the Belarusian State Standard EN 196-1/PR [49] through two tests evaluating the flexural strength and the compression strength at the age of 3, 7, 28, 60 and 90 days. Samples of the beam measuring $4 \times 4 \times 16 \text{ cm}^3$ (Figure 4.4) were prepared from the mortar mixtures based on the complex binder with different percentages of ash and sand. The composition of the solution mixtures is given in Table 4.3. The beams were stored in a container of water.



Figure 4.4. – The samples-beams based on the complex binder

Table 4.3. – The compositions of the mortar mixtures on the complex binder

Composition number	Percent replacement of cement with ash, %	The consumption of materials, [g]			
		Cement	Ash	Sand	Water
1	0	450	0	1350	225
2	10	405	45	1350	225
3	20	360	90	1350	225
4	30	315	135	1350	225

The results in this study to obtain curing curve of these complex binders are presented in Figure 3.5 and Figure 3.6.

The hardening of these complex binders in comparison with control samples based on Portland cement is significantly different. In the article [52] was shown that acid ash is characterized by the late onset of pozzolanic reaction (on average at 7-day age) [52] and its slow course during the first month of hardening. At the same time, the main part of the pozzolanic reaction occurs at the age of 30-90 days [52], the high intensity of hardening of concrete with ash persists at its sufficient humidity and at a later date. Accordingly, the increase in the strength of the cement-ash stone in later terms - up to 3-6 months and even up to 1 year - is more active than in non-additive samples.

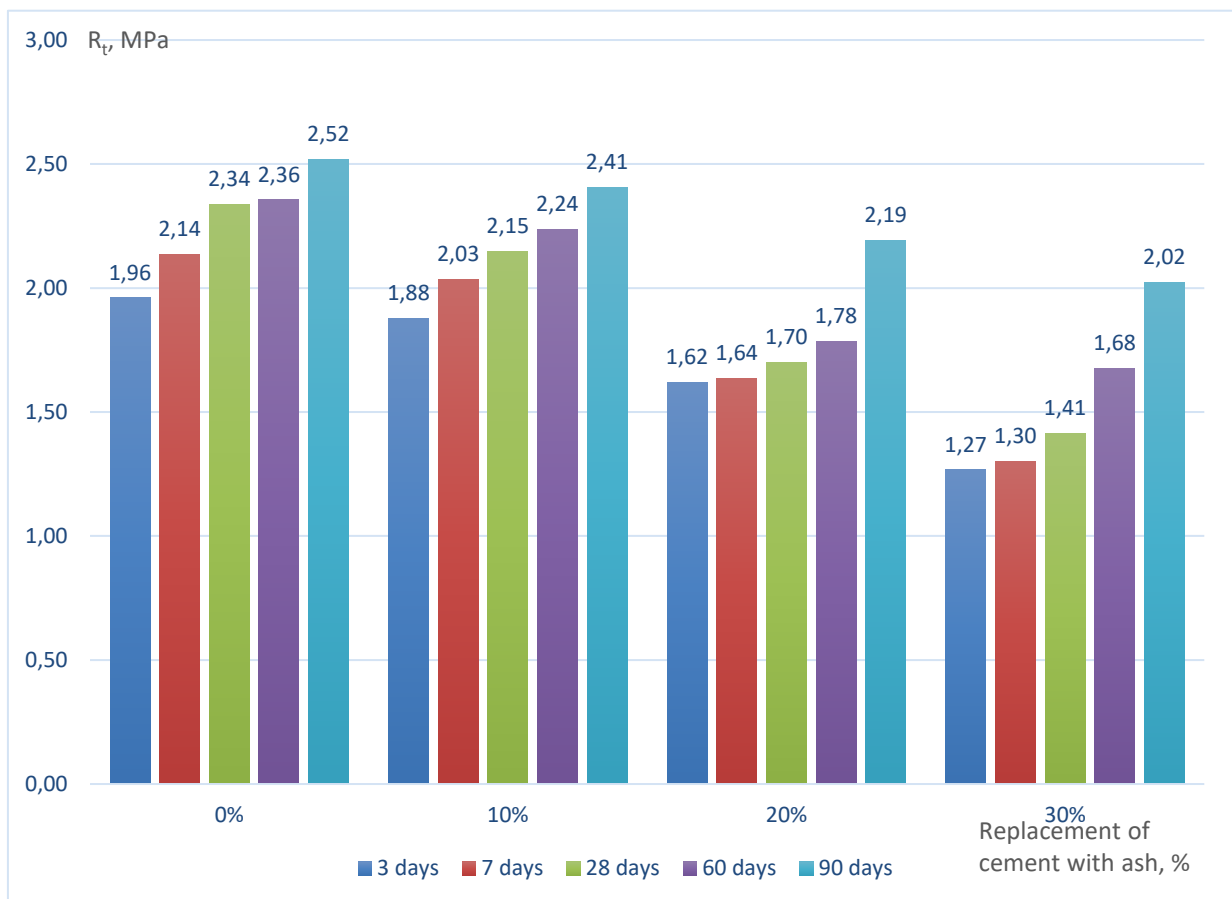


Figure 4.5. – Strength results in tension at bending at the age of 3, 7, 28, 60 and 90 days

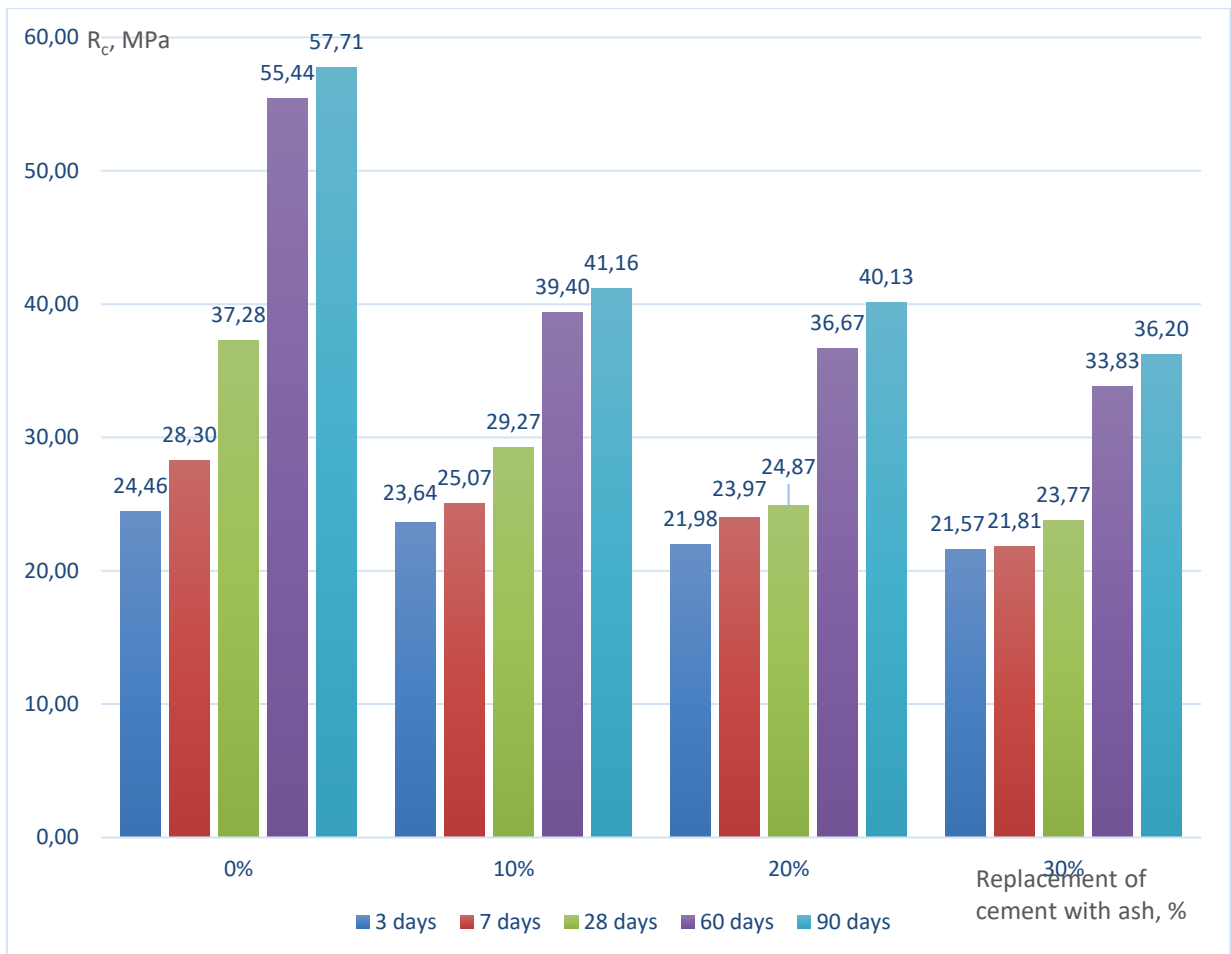


Figure 4.6. – Strength results in compression at the age of 3, 7, 28, 60 and 90 days

These results show the similar effect when peat-and-wood ash is used as part of the complex binder. The compression strength at the age of 3 days (Figure 4.6) decreased by 3%, 10%, 12% with the amount of ash in the complex binder content, respectively 10%, 20%, 30%. The compressive strength at the age of 60 days for the composition No. 2 already exceeds the strength of the control sample at the age of 28 days by 6%. At the age of 90 days, the compressive strength of the samples exceeds the strength of the control sample at the age of 28 days by 10% and 8%, respectively, when the ash content is 10% and 20% in the complex binder composition. At the ash content of 30%, the activity of the binder is reduced throughout the test periods of hardening. At the age of 90 days is 97% of the strength of the control sample at the age of 28 days.

The evaluation of the curing curve of the complex binder strength test shows that the efficiency of the complex binder is ensured when the amount of ash is not more than 20% of the weight of the binder.

4.3 The effect of the complex binder on the mechanical properties of concretes

It was found that ash reduces the level of activity of the complex binder in the early stages of hardening. The potential of ash, as an active component of concrete mixtures, can be realized by reducing the water-binding ratio and increase the consistency by the use of adjuvants like the superplasticizers.

To study the effect of the complex binder on the strength and deformation properties of concrete as a control was used the composition of Portland cement (composition 1, Table 4.4). The compositions of the concrete mixtures made with the complex binder with the ash additive in the amount of 10% of the binder mass (composition 2, Table 4.4), the complex binder and the superplasticizer additive Stakhement 2000M Zh30 in the amount of 0.2% of the binder weight with the water-binding ratio of 0.41 (composition 3, Table 4.4) and 0.37 (composition 4, Table 4.4).



Figure 4.7. – The sample of concrete on the complex binder

Table 4.4. – Compositions of the concrete mixtures

Compo- -sition number	The consumption of materials					
	kg/1 m ³ of concrete					% by weight of the binder
	Cement	Ash	Sand	Crushed stone	Water	Additive Stakhement 2000M Zh30
1	500	-	530	1070	250	-
2	450	50	510	1070	250	-
3	450	50	600	1100	200	0,2
4	450	50	600	1155	185	0,2

The results of the determination of the consistency of the concrete mixture and the strength of concrete are given in Table 4.5. The tests were carried out 24 hours after the heat and moisture treatment.

Table 4.5 – The effect of the complex binder on the consistency of the concrete mixture and the strength of concrete

Compo- -sition number	Water- binding ratio	Density, [kg/m ³]		Consistency		Compressive strength, R _c , [MPa]	
		calculat- -ed	actual	cone draft, cm	class of consistency	24 hours after HMT	28 days after HMT
1	0,5	2350	2370	7,5	P2	38,06	42,14
2	0,5	2330	2373	9	P2	33,10	46,71
3	0,4	2400	2477	25	P5	43,75	50,32
4	0,37	2440	2472	6,5	P2	46,44	51,16

The analysis of the obtained results allows to establish that the replacement of Portland cement with ash in the complex binder in the amount of 10% (composition 2, Table 4.5) leads to the decrease in the strength of concrete by 13% compared to the strength of the concrete of the control composition, while the consistency of the concrete mixture with the complex binder slightly increased. The plasticizing effect of ash in combination with the plasticizing effect of the additive Stakhement 2000M Zh30 made it possible to increase the consistency of the concrete mixture from grade P2 to P5 and at the same time to reduce the water-binding ratio from 0.5 to 0.4

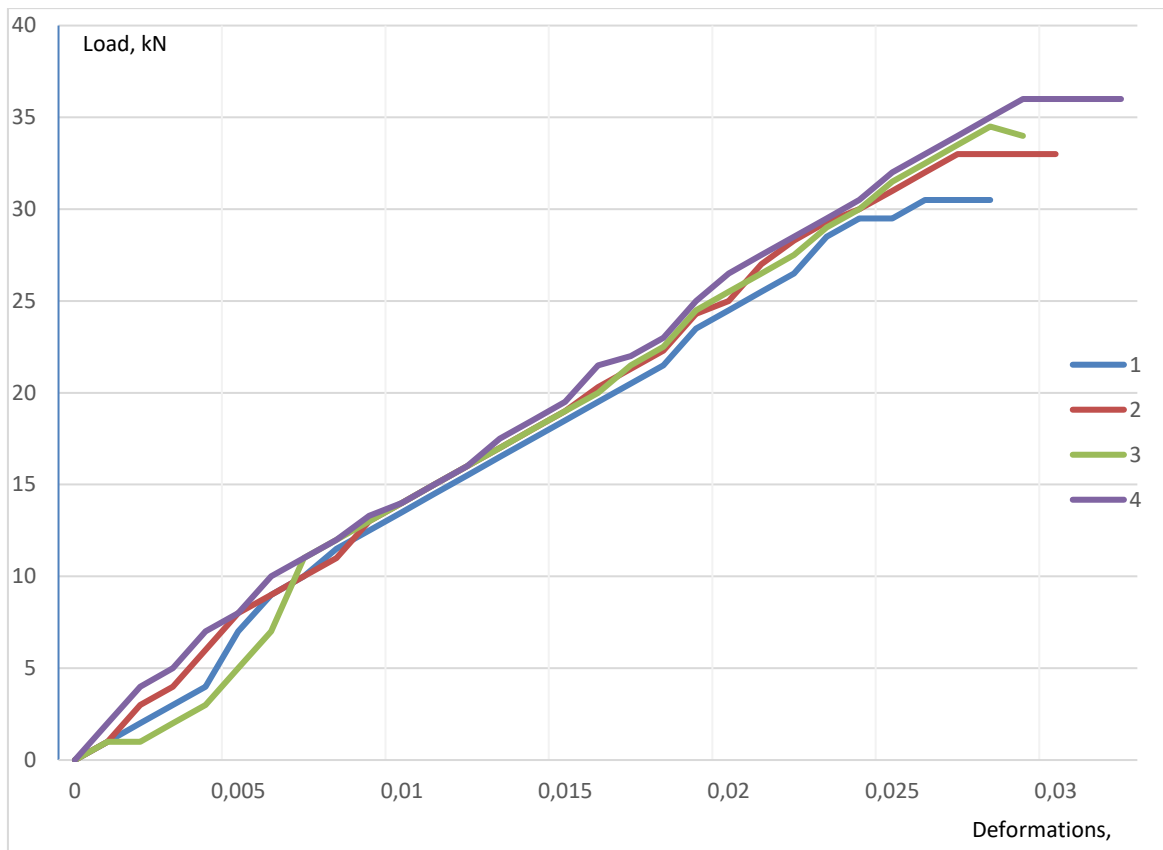
(composition 3, Table 4.5).

The plasticizing properties of ash in [53] are associated with a spherical shape and a smooth surface of ash grains. The presence of spherical particles with the smooth surface helps reduce the internal friction of the cement gel. At the same time, the sintered aggregated ash particles have spherical pores filled with a liquid phase, which prevents the particles from converging and prolongs the period of formation of the coagulation structure.

The composition 4 of the concrete mix exhibited the same consistency of the control mixture. The introduction of the plasticizing additive Stakhement 2000M Zh30 allowed to achieve the same consistency of the control composition although the decrease in the water-cement ratio from 0.5 to 0.37. The terms of strength, these mixture exhibit an increase of 22% in relation of the control composition.

The load-strain diagram was carried out according to a diagram reflecting the relationship between the value of the load and the value of deformations recorded under conditions of central compression during a short-time load on the test specimens (cubes with an edge of 10 cm) at a loading rate of 3 kN/sec. When testing concrete, the load was applied in steps. After each stage of the load increment, the concrete sample was kept for some time at a constant tension.

The experimental diagram of the state of concrete "load-strain" is shown in Figure 4.8. Compression deformations are conditionally taken as positive.



**1- on Portland cement; 2 - on the complex binder;
 3 - on the complex binder with the plasticizing additive;
 4 - on the complex binder with the plasticizing additive (equipotent mixtures)**
**Figure 4.8. The deformations in the case of the axial compression
 of sample-cubes from concrete**

The obtained results show that the concrete on the complex binder with the plasticizing additive (composition 4, Table 4.5) under smaller loads is less deformed. It should be noted that all concretes with the complex binder have higher deformative properties, which indicates the positive effect of the complex binder on the formation of the structure of concrete.

4.4 Chapter Summary

1. It was established that the strength of the cement-ash stone is reduced to 49% with an increase in the proportion of ash in the complex binder to 30%. It was determined that when the water-binding ratio decreases, the effect of reducing strength becomes less significant. The heat and moisture treatment contributes to the increase in the strength of the cement-ash stone, which indicates a more intensive reaction of the interaction of hydration products with ash.

2. The curing curve of the complex binder indicates a slowing down of the processes of structure formation during the 28 day hardening. At the age of 60 and 90 days the strength of the complex binder exceeds the strength of Portland cement at the age of 28 days to 10%. As part of the complex binder, the amount of ash that does not exceed 20% of the binder's weight is effective, since a significant slowdown in strength is observed at large values.

3. It has been established that the concrete mixture based on the complex binder is characterized by a higher value of consistency along the sediment of the cone. Addition of the plasticizing effect of the complex binder with the plasticizing effect of the additive Stakhement 2000M Zh30 allowed to achieve the maximum mark on mobility (from grade P2 to P5) with the decrease in the water requirement of the concrete mix by 20%.

4. The use of the complex binder with the ash content of 10% of the binder weight made it possible to increase the compression strength of concrete by 22% and reduce the deformability of concrete under the condition of using heat and moisture treatment and the plasticizing additive Stakhement 2000M Zh30, while reducing the water-binding ratio and obtaining the equiprobable concrete mixes.

5. CONCLUSIONS

1. The influence of the water-binding ratio, the hardening conditions and the plasticizing adjuvant on the strength and density of the cement-ash stone has been established. It is shown that heat and moisture treatment contributes to the formation of a more dense structure of the cement-ash stone. The effective dosage of ash-and-slag wastes in the complex binder also depends on the conditions of hardening and the amount of free water. When heat and moisture treatment is possible, the more effective dosage of ash-and-slag wastes is 20% without use of superplasticizer and 30% with use of a superplasticizer and a water-binding ratio of 0.3. In normal-humidity conditions of curing the more dosages of ash-and-slag wastes are 10%, 20% and 30% of cement replace for a water-binding ratio of 0.4.

2. The effect on the hardening of concrete of the cement replacement by ash-and-slag wastes was also evaluated. It was shown that the increase in the amount of peat-and-wood or ash-and-slag mixture of the Belarusian district power station as component of the complex binder from 10 to 30% of the binder weight leads to the decrease in the compressive strength at 3 days from 3% to 12%; at the age of 7 days from 11% to 23%; at nominal curing time (28 days) from 21% to 36% in relation of the control sample, only made with Portland cement. The complex binder actively continues to increase strength in later periods of 60 and 90 days of curing. At the age of 60 days, the compressive strength was 105% and 98%; at the age of 90 days was 110% and 108%, with the proportion of the ash-and-slag mixture correspondingly 10% and 20% relative to the compressive strength of the control sample at the age of 28 days. An essential slowing of the set of strength in the period up to 90 days is established with the amount of ash-and-slag mixture in the complex binder content of 30% of the binder mass.

3. The effect of the complex binder and the plasticizing additive Stakhement 2000M Zh30 on the strength and deformation properties of concrete was studied. The usefulness of using the complex binder together with the plasticizing additive Stakhement 2000M Zh30 was shown allowing to increase the strength of concrete in compression at the age of 28 days to 22%, to obtain concrete with the denser structure and to increase the consistency although the decrease of the water-cement ratio when compared with the control sample.

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