COMPLEX BINDER BASED ON INDUSTRIAL MAN-MADE WASTE

Lemeshev Mykhailo[1], Bereziuk Oleg[2], Cherepakha Dmytro[1], Kovalskiy Viktor[1]
[1]Department of Construction, Urban Economy and Architecture, Vinnytsia National Technical University
[2]Department Security of Life and Pedagogic of Security, Vinnytsia National Technical University

At present, about 3 billion tons of binders are produced in the world, the main share of which is Portland cement. At the same time, about 400 million tons of conventional fuel are spent on its production, and emissions of CO_2 and dust into the environment amount to about 2.5 billion tons [1-4]. In connection with this, in recent years there has been a reorientation of the building materials industry towards concrete with reduced cement consumption. In the USA and Europe, these types of concrete include concrete in which cement consumption is reduced by 50-60%. This is achieved mainly through the use of mixed binders, in which part of the cement is replaced by fly ash or microsilica.

According to modern world trends, composite binders (composite cements, binders based on industrial waste) are becoming increasingly important, which must be considered as an alternative to traditional binders, and binder systems containing a limited amount of clinker [5-7].

The reserves of resource saving in the complex processing of raw materials and the use of waste are very significant. The capital investments required for the processing of secondary raw materials are approximately four times less than when obtaining products from primary raw materials [8-10]. Obviously, funds should be invested in waste-free technological processes that conserve raw materials and energy resources and at the same time ensure high product quality [11-12].

Of the industries that consume industrial waste, the construction materials industry is the most capacious, the share of raw materials in the cost of production reaches 50% or more. Many wastes are similar in their composition and properties to natural raw materials [13-15]. It has been established that the use of industrial waste allows to cover up to 40% of the construction needs in raw materials, as well as to reduce the costs of manufacturing building materials by 10-30% compared to their production from natural raw materials. In addition, new building materials with high technical and economic indicators can be obtained from industrial waste [16-19].

The accumulated scientific and practical experience of using industrial waste in Ukraine and abroad allows us to consider it as a valuable raw material for the production of construction materials [20-21]. All wastes are divided into two large groups, mineral and organic, the former have an advantage, as there are more of them, they are better studied and are of great importance for the production of building materials.

During the development of an approach to the selection of economically feasible directions for the utilization of industrial waste in the production of building materials, it is necessary to take into account: the initial state (chemical activity, dispersion and aggregate state); the choice of technology with minimal preparation and processing [22-23]. At the same time, it should be noted that the direction of disposal is chosen and justified by technologists, and the task of bringing it to condition and complying with the rules of storage should be entrusted to environmental and sanitary services. The main parameters characterizing any industrial waste are: - chemical and mineralogical composition; aggregate state; and their volume. To choose the direction of waste use, each type of waste must pass several levels of evaluation according to various criteria, taking into account the main parameters [24].

As practice shows, almost all basic building materials can be made from waste or waste in combination with natural mineral raw materials [25-26]. Almost all construction materials, products and structures used in the construction of residential and industrial buildings, agricultural facilities, road structures, etc. can be made from large-tonnage waste of energy and chemical enterprises (phosphogypsum, titanium gypsum, fluorogypsum, citrogypsum, desulphogypsum). Therefore, the guide taken today in Ukraine for the production of building materials, products and structures from industrial waste and local materials promises significant benefits [27].

Analysis of scientific research and practical experience of using ash and slag waste indicates the economic feasibility of using TPP waste in the production of cement and complex multicomponent binder. The amount of SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO significantly affects the basic physical and chemical properties of construction products. As a result of the conducted research, it was established that to improve the physico-chemical and physico-mechanical characteristics of construction products, it is most expedient to use fly ash of the Ladyzhynskaya TPP [28]. According to its chemical composition, it belongs to the main evils, which will have a positive effect on the processes of structure formation. Table 1 shows the chemical composition of the fly ash of Ladyzhynskaya TPP.

Table 1

Chemical composition of fly ash of Ladyzhynskaya TPP

The content of oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	П.П.
Ash slag Ladyzhinskaya TPP	49,26	23,00	19,35	3,53	1,79	2,11	0,40	0,10	1,40
Ash disposal of Ladyzhynska TPP	52,1	23,1	15,6	3,16	1,08	0,4	1,2	0,57	0,7

It should be taken into account that an excess amount of ash in the composition of ash-containing materials leads to an increase in porosity and a decrease in the rate of curing with time, and worsens performance characteristics, in particular, frost and corrosion resistance. To prevent the occurrence of such undesirable processes, complex additives of polyfunctional action are introduced into the composition of the concrete mixture, which determine not only the kinetics of strength development, but also form the corresponding structure of the material, which significantly affects the physical and mechanical properties and durability of the resulting artificial stone [29].

The amount of ash used in the complex binder concrete mixture can be increased by activating it. The choice of activation method depends on the chemical and mineralogical composition of the ash, the method of its production, as well as on the binder system. Since ash performs several functions when introduced into the concrete mixture, its amount can be increased both through the use of various types of activation and through multifunctionality. Moreover, the introduction of ash not only into the composition of the binder, but also as a microfiller and fine aggregate will contribute to the formation of a stronger contact zone. The authors in works [30-31] established the relationship between the types of fuel ash and slag, the methods of their activation and the possibilities of their use as part of building materials and products.

The use of mechanical, chemical and complex activation of ash slag waste makes it possible to produce materials with improved mechanical characteristics and high operational properties, and the use of certain types of activation of ash slag waste affects the change in the phase composition of new formations, which can positively affect the durability of the resulting construction mortars and concretes [32-35].

The authors in their works [36-38] developed the principle of composite construction of ash-filled artificial materials, which allow to increase the amount of ash-slag component in the concrete mixture without deteriorating the properties of the synthesized artificial stone, for this it is necessary:

- taking into account the composition and structure of ash and slag waste and choosing the appropriate method of ash activation, which causes a change in both the physical state and the chemical composition of the raw material;
- mandatory introduction of plasticizers or complex additives into the composition of ash-filled binding systems, containing, in addition to the plasticizer, an active microsilica or aluminosilicate component, which prevents the formation of secondary ettringite in the later stages of hardening;
- the choice of the type of plasticizing additive should be carried out taking into account the chemical and mineralogical composition of ash and modifying mineral additives.

Phosphogypsum waste is a by-product in the production of phosphoric acid by the extraction method. Depending on the temperature and concentration conditions for the decomposition of phosphate raw materials, the solid phase of calcium sulfate can be represented by one of three forms: dihydrate, hemihydrate or anhydrite.

Phosphogypsum waste can be classified as gypsum raw material, as it consists of 80-95% calcium sulfate. The chemical composition of phosphogypsum of Vinnytsia VO "Khimprom" is given in Table 2.

Table 2

Chemical composition of phosphogypsums of Khimprom

The main components	Content, % by mass	
	phosphohypsodihydrate	phosphogypsum hemihydrate
General P_2O_5	0.5-1.5	1.2-1.5
Water soluble P_2O_5	0.1-0.7	0.7-2.0
CaO	22-23	25-28
SO_3	38-39	45-47
F	0.1-0.2	1.2-1.5
Water is hygroscopic	21-29	18-22
Crystalline water	19-21	5,5-6,5

The bulk density of phosphogypsum is a variable value and depends on moisture, fractional composition and degree of compaction. Phosphogypsum is a material that is very easily compressed. When it is compressed, there is a decrease in porosity, displacement or movement of moisture. The total moisture content of phosphogypsum is approximately 66%. The maximum molecular humidity is 15-16% and is characterized by the property of phosphogypsum to retain moisture by the forces of molecular adhesion between the particles of phosphogypsum and water.

The large-scale use of phosphogypsum is hindered by its specific features: aggregate state, high humidity, presence of phosphoric and sulfuric acid and water-soluble harmful compounds of phosphorus and fluorine.

Remains of free phosphoric and sulfuric acid, solutions of monocalcium phosphate, dicalcium phosphate, and others present in the composition of phosphogypsum slow down hardening and reduce the strength of cement binders [39-49]. The emission of fluorine gases during heat treatment complicates the production technology of building materials. Increased acidity of the raw material leads to equipment corrosion. Newly formed sulfates of sodium, potassium and calcium tend to stand out on the surface of the products when they dry, in the form of precipitates. Therefore, the use of unrefined phosphogypsum makes it difficult to obtain a gypsum binder with satisfactory mechanical properties. It is possible to reduce the concentration of acid residues by washing. Preliminary washing of phosphogypsum raw materials requires additional costs and leads to new types of waste - acidic effluents, which must be disposed of.

In our opinion, the most effective way to use phosphogypsum in construction is to develop and obtain clinker-free phosphate, metal phosphate and metal ash phosphate binders. For this type of binder, it is not necessary to spend significant energy resources and perform preliminary cleaning of phosphogypsum from harmful substances.

The main process in the synthesis of a phosphate binder is the dissolution of oxidizing compounds in phosphoric acids. The regulation of this process consists in choosing the concentration of the acid, the chemical composition of the compound containing the cation, its optimal solubility modification, as well as the method of its introduction into the reaction mixture and the temperature regime of the synthesis. In addition, the speed of the interaction processes can be regulated by changing the reactivity of the filler by compaction, thickening of its parts, using dispersions of oxidized metal filler, passivating components that react excessively actively [41-42].

The intensity of the interaction of components in phosphate systems of the "oxide-acid" type depends on the charge of the cation, the ionic radius and the electronic configuration. The curing time of such systems can be adjusted by using different compounds. To ensure the optimal temperature regime of a particular reaction, it is advisable to combine different oxides in one mixture, for example, CaO and FeO, Fe_2O_3, FeO, etc. [43-45].

Among the iron-containing dispersed wastes that must be used to create metal phosphate and metal ash phosphate binders are metal slurries from ball bearing production and red bauxite sludge.

Sludge of ball bearing production is practically not processed due to the high dispersion and content of lubricants and coolants. They are formed during the production of bearings from ShKh-15 steel. The percentage content of iron is 86.3 - 87.96%. The average size of sludge particles is 2×10^{-5} m. The specific surface of this powder reaches 0.5 2×10^3 m^2/kg. When sludge is stored in open dumps, deep oxidation of iron and drying of aqueous components of lubricating and cooling substances occur. The oxide layer consists of hematite (Fe_2O_3), magnetite (Fe_3O_4), justite (a solution of Fe_2O_3 in FeO), lapidocrite (FeO(OH)) [46-50]. The chemical composition of ShKH-I5 steel according to the results of X-ray fluorescence analysis performed at the Institute of Chemical Engineering of the Academy of Sciences of Ukraine is given in Table 3.

Table 3

Chemical composition of ShKh-15 steel sludge after heat treatment according to the results of X-ray analysis

Types of sludge	Content of elements %							
	C	O	Cr	Mn	Si	S	P	Fe і ін.
Sludge after treatment	1,34	2,14	1,06	0,25	0,31	0,06	<0,03	ост.
Sawing sludge	1,72	3,51	0,64	0,25	0,41	0,075	<0,03	ост.

The second important dispersed iron-containing waste for the creation of metal phosphate and metal ash phosphate binder is red bauxite slime. Bauxite red mud is formed as a by-product of processing during the production of aluminum from bauxite. The composition of the sludge depends on the bauxite being processed and the method of its processing. A characteristic feature of bauxite slurries obtained by Bayer's method is a high concentration of iron and aluminum oxides. The mineralogical composition of Bayer muds is mainly represented by iron compounds: hematite, as well as hydrogarnets and sodium hydroaluminosilicates.

The red sludge of individual alumina plants was studied as an additive that increases the mechanical strength of concrete. However, comprehensive studies of bauxite slurries in the composition of metal ash phosphate binder were not conducted.

Table 4

The content of oxides in the composition of red mud

Oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	P_2O_5	V_2O_5
Mass fraction of oxides, %	9,5-11,1	4,4-5,6	17,0-19,0	39,0-43,0	7,6-9,5	6,2-6,9	0,2-0,3	0,2-0,25

The high content of aluminum and iron oxides (Table 4) and the limited amount of calcium oxides do not allow it to be considered as the main raw material for binders. However, it can be used as an active additive for metal ash phosphate binder, taking into account its complex nature of influence on physical and mechanical properties.

Taking into account the above theoretical rationale for the use of ash sludge waste, phosphogypsum, metal sludge, the authors obtained an improved complex clinker-free metal ash phosphate binder based on phosphogypsum waste, metal sludge from bearing production, bauxite sludge and fly ash. Table 5 shows the physical and mechanical characteristics of samples of the complex metal ash phosphate binder.

Table 5

Physico-mechanical characteristics of samples of complex metal ash phosphate binder

Composition	Average density of samples, kg/m3	Compressive strength limit, MPa
Phosphogypsum + Recovered metal sludge of the Vinnytsia Bearing Plan	1875	6,3
Phosphogypsum + Recovered metal sludge + Fly ash	1920	5,5
Phosphogypsum + Recovered metal sludge + Red bauxite sludge	1980	6,8
Phosphogypsum + Recovered metal sludge + Fly ash + Red bauxite sludge	1970	7,2

Such a complex binder can be used for the production of heat-resistant concrete. As an oxide component of the binder, it is most expedient to use iron-containing wastes of the metalworking industry, which are finely dispersed metal sludge and red bauxite sludge with a high content of iron and aluminum oxides.

The obtained positive results of research on the physical and mechanical properties of the samples confirm the feasibility of continuing further scientific research. In particular, to increase the strength and improve the intensification of hardening, it is envisaged to add natural mineral additives to the composition of the metal-alloy phosphate binder mixtures. After optimizing the recipe and technological factors of the complex clinker-free binder, it is planned to study the special properties of the products obtained on the basis of such a binder.

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