

2.4 Preparation of industrial waste for use in the construction industry

Future prospects for the development of enterprises in the construction materials industry are at the stage of radical revaluation due to the acute shortage of energy resources. To solve the problem of reducing the cost of final construction products and reducing the cost of natural raw materials, fuel and energy and other resources, a special role is given to expanding the use of industrial waste. With this resource source, as confirmed by research, there are significant reserves for the rise of production and its further intensification [72-79].

The main task of builders today should be the introduction of new advanced and economical technologies for the production of building materials using industrial waste and local raw materials. It should be borne in mind that the development of ways to solve the problem of environmental pollution by heavy tonnage waste - ash-removal of thermal power plants and environmentally hazardous waste from the chemical industry - phosphogypsum, desulfogypsum [80-83].

Up to 10 million tons of ash and slag waste are generated annually in Ukraine, and more than 50 million tons are accumulated in dumps. Such waste should be considered not only as a factor of environmental pollution, but also as a source of additional resources for a wide range of construction materials. In the Vinnytsia region alone, about 20,700,000 tons of ash and slag waste have been accumulated at the Ladyzhyn TPP [83-84], and about 800,000 tons of phosphogypsum are stored on the territory of the former Khimprom plant [85-86]. About 300 thousand tons of dispersed metal waste - metal sludge - have been accumulated at the enterprises of metal processing enterprises of the region [87-88].

Increasing the strength of construction products can be solved by technological methods - through the integrated use of chemical and active mineral additives and activation of raw materials [89-91]. To obtain natural mineral supplements requires additional costs for their extraction, transportation and production. At the same time, Ukraine accumulates a huge amount of industrial waste annually, the share of their use in the technology of building materials is 5-8 times less than in foreign

countries [92-93].

A comprehensive solution to the problem of economy and environmental friendliness of construction products is possible by developing new effective composite binders and concretes using industrial waste that would meet basic construction requirements, namely such products must have sufficient strength, high water resistance, fire resistance and frost.

Currently, the development of the concept of maximum use of industrial waste (ash-removal, phosphogypsum, red bauxite sludge and other waste) as raw materials to obtain new modern building materials and products that are not inferior to traditional, but are more efficient in environmental and economic points of view.

In accordance with modern world trends, composite binders (composite cements, binders based on industrial waste) are becoming increasingly important, which should be considered as an alternative to traditional binders, with the greatest attention being paid to binder systems containing limited amount of Portland cement clinker (up to 20%). Therefore, ash as an aluminosilicate substance should become one of the main components of modern binders.

The structure and composition of ash depends on a complex of simultaneously acting factors: morphological properties of fuel combustion, fineness of grinding in the process of its preparation, fuel ash content, chemical composition of the mineral part of the fuel; temperature in the combustion zone; time spent in the combustion zone [94-95], etc.

A characteristic feature of the fly ash is a smooth fused glassy surface and approximately the correct spherical shape of the particles. Due to this particle shape, the ash increases the plasticity of the mixture and is therefore used in the technology of preparation of concrete as a plasticizer [96].

The density of fly ash from the combustion of different fuels ranges from 1800 to 2400 kg /m³; the average porosity of the ash is 4.8-7.4 %; bulk density - from 600 to 1100 kg/m³. The main component of the fly ash is a vitreous aluminosilicate phase, which is 40-65% of the total mass, its particles have a spherical shape with a size of up to 100 μm.

Analysis of scientific research and practical experience in the use of fly ash, indicates the economic feasibility of using waste thermal power plants 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 previous [97-98] research, it was found that to improve the physico-chemical and physico-mechanical characteristics of construction products, it is most appropriate to use the fly ash of Ladyzhyn TPP. Its chemical composition is one of the main evils, which will have a positive effect on the processes of structure formation. Table 1 shows the chemical composition of the ash removal of Ladyzhyn TPP.

Table 1

Chemical composition of fly ash from Ladyzhyn TPP

The content of oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	At_2O	SO_3	
Ash slag Ladyzhyn TPP	49.26	23.00	19.35	3.53	1.79	2.11	0.40	0.10	1.40
Ash-removal of Ladyzhyn TPP	52.1	23.1	15.6	3.16	1.08	0.4	1.2	0.57	0.7

Analysis of the experience of using fly ash shows that when it is introduced into the concrete mixture, it performs several functions, has multifunctional properties. However, it should be borne in mind that an excessive amount of ash in the ash-containing materials leads to increased porosity and reduced rate of strength over time, impairs performance, including frost and corrosion resistance. To prevent such undesirable processes, complex additives with multifunctional action are introduced into the concrete mixture, which not only determine the kinetics of strength, but also form the appropriate structure of the material, which significantly affects the physical and mechanical properties and durability of artificial stone [99-100].

Analysis of scientific papers on the use of fuel ash and slag in the composition of binders and concrete, shows the feasibility of activating the ash in different ways. The choice of activation method depends on the chemical and mineralogical

composition of the ash, the method of its production, as well as the composition of the binder system. Since the ash performs several functions when introduced into the concrete mix, its amount can be increased both through the use of different types of activation and due to multifunctionality. Moreover, the introduction of ash not only in the binder, but also as a microfiller and fine aggregate, will contribute to the formation of a stronger contact zone by increasing the degree of crystal chemical similarity of tumors and relict residues that are not subject to hydration.

The amount of ash used in the complex binder of the concrete mixture can be increased by activating it in various ways. The authors in works [101-106] established the relationship between the types of fuel ash and slag, methods of their activation and the possibility of their use in building materials and products. Table 2 shows the different names of waste, the method of their activation and the recommended scope of use in the construction materials and products.

The possibility of using fly ash in the binder system is determined by pozzolanic activity, which ensures the stability of the properties of artificial stone over time. Pozzolanic activity depends on many factors, the most important of which are the chemical composition of pozzolana, its mineralogical composition and specific surface area. As a result of research, the authors in their works [108-111] came to the following conclusion:

- the efficiency of the use of ash in the composition of cement-sand compositions subject to heat treatment (TVO) is higher not only in quantity but also in quality, the coefficient of pozzolanic ash in the studied systems after TVO is 2-2.5 times higher than samples that harden under normal conditions;
- the optimal amount of ash, which increases the strength of cement-sand compositions depending on the chemical and mineralogical composition and specific surface area and is 20-40 wt. % of the amount of filler. When using fly ash and fluid ash, the amount of pozzolanic component is 35-40 wt.%, The pozzolanic coefficient is more than 1.7. In the case of using ash removal, the pozzolanic index is 1.3-1.7;
- fluid ash and removal ash are highly active, and water removal ash is a medium activity additive. In the study of the activity of energy wastes of different

origins in the initial state, the maximum value of the pozzolanic coefficient is achieved when using the ash-removal Ladyzhinskaya TPP;

- mechanical activation of ash and slag waste increases the pozzolanicity coefficient by 11-37%. Thermal activation (heat-wet treatment or autoclaving) has the most noticeable effect on this indicator;
- the use of complex activation of ash and slag waste partially eliminates fluctuations in their chemical and mineralogical composition.

Table 2

Relationship between types of fuel ashes and slags, methods of their activation and possibilities of their use as a part of building materials and products [107]

Name of energy waste	Type of activation	Building materials and products	Scope of use
Fly ash	chemically (alkaline earth)	binders modified by plasticizing additives with an ash content of up to 35 wt.%	commodity concrete mixes
	mechanochemical (alkaline + mechanical activation in the speed mixer)	binders and concretes based on them, including those with improved thermophysical properties, containing up to 60 wt.% ash	three-layer expanded clay concrete wall panels
Hydro-removal ash	mechanochemical (alkaline + grinding)	effective binders (with an ash content of up to 60 wt.%) and concretes based on them	single-layer pavements of III and IV category roads
Fluid ash	mechanochemical (sulfate + grinding)	binders and concretes based on them, containing up to 85 wt.% waste	single-layer pavements of III and IV category roads

The use of mechanical, chemical and complex activation of ash and slag waste allows to produce materials with improved strength characteristics and high performance properties, and the use of certain types of activation of ash and slag waste affects the phase composition of tumors, which can positively affect the durability of mortars and concretes [112].

The authors in their works [113-114] developed the principles of compositional construction of ash-filled artificial materials, which increase the amount of ash-slag component in the concrete mixture without compromising the properties of the synthesized artificial stone:

- taking into account the composition, structure of ash and slag waste and the choice of appropriate the method of activation of ash, which causes a change in both the physical state and the chemical composition of the raw material;

- mandatory introduction of ash-filled binder systems plasticizing or complex additives containing, in addition to the plasticizing additive, an active microsilica or aluminosilicate component that prevents the formation in the late stages of hardening of secondary ettringite and taumasite;

- the choice of the type of plasticizing additive should be made taking into account the chemical and mineralogical composition of the ash and modifying mineral additives.

Phosphogypsum waste is a by-product of phosphoric acid production by extraction. Depending on the temperature-concentration conditions of 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 attributed to gypsum raw materials, as they consist of 80-95% of calcium sulfate. The chemical composition of phosphogypsum of Vinnytsia VO "Khimprom" is shown in table 3.

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

Table 3

Chemical composition of phosphogypsums of Khimprom Vinnytsia

The main components	Content,% by weight	
	phosphogypsodihydrate	phosphogypsum hydrate
Total 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
Crystal hydrate water	19-21	5.5-6.5

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

Residues of free phosphoric and sulfuric acid, solutions of salts - monocalcium phosphate, dicalcium phosphate and others are present in phosphogypsum, slow down hardening and reduce the strength of cement binders [115]. The release of fluoride gases during heat treatment complicates the technology of production of building materials. High acidity of raw materials leads to corrosion of equipment. 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 efflorescence. Therefore, the use of unwashed phosphogypsum makes it difficult to obtain gypsum binder with satisfactory mechanical properties. The concentration of acid residues can be reduced by washing. Pre-washing of phosphogypsum raw materials requires additional costs and leads to new types of waste - acid effluents, which must be disposed of.

Phosphogypsum has been studied as a raw material for the production of gypsum binder, as well as in the manufacture of cement as an additive to regulate the setting time of cement paste. However, due to the fact that phosphogypsum cannot be used from a technological point of view without special preparation (drying and briquetting), this method of disposal has found use only in those countries that do not have natural gypsum stone. So in Japan, all phosphogypsum is used in the cement industry.

Before using phosphogypsum, it is necessary to remove or neutralize harmful impurities and reduce the concentration of acid residues. You can neutralize acidic residues with quicklime. The amount of lime is selected based on the cost of phosphogypsum neutralization and additionally to maintain a highly alkaline environment. Lime interacting with H_3PO_4 , CaHP_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, H_2SiF_6 and HF , forms insoluble compounds of $\text{Ca}_3(\text{HPO}_4)\text{F}$, $\text{Ca}_5(\text{HPO}_4)\text{OH}$, $\text{Ca}_3(\text{PO}_4)_2$, CaSiF_6 , and CaF_2 [116- 118]. However, this technology involves the use of high-energy substance - building lime only to neutralize acidic and harmful residues. It should be noted that the cost of lime is currently higher than the cost of cement, which is illogical, as cement is fired at $1450\text{-}1500^\circ\text{C}$ and lime - $1000\text{-}1200^\circ\text{C}$, so the cost of lime should be zero due to less use of energy component.

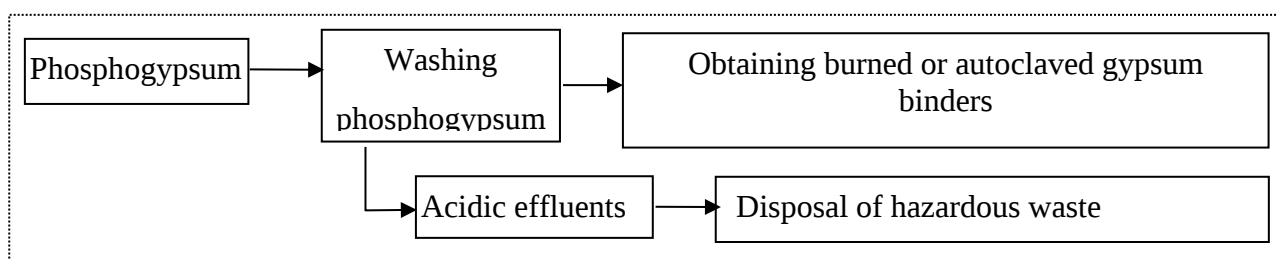


Figure 1. Scheme of production of fired and autoclaved gypsum binders from phosphogypsum.

The concentration of acid residues can be reduced by washing. Flushing phosphogypsum with water also allows you to wash away harmful water-soluble impurities and obtain raw materials for the production of gypsum binders. This requires at least four times the volume of water relative to phosphogypsum. Figure 1 shows the scheme of production of fired and autoclaved gypsum binders from phosphogypsum. The disadvantage of this technology is the production of acidic aqueous solutions with an acid concentration of 2 to 6% wt.