DOI: 10.46299/ISG.2024.MONO.TECH.4.1.3

1.3 Perspectives on the use of technogenic raw materials in the production of low-clinker composite binders

At present, approximately 3 billion tons of binders are produced globally, the majority of which is accounted for by Portland cement. Its production consumes about 400 million tons of conventional fuel, while CO_2 and dust emissions into the environment amount to approximately 2.5 billion tons (table 1) [14-15]. In light of these environmental concerns, the construction materials industry has recently shifted towards concretes with reduced cement consumption. In the United States and Europe, this category includes concretes in which cement usage is reduced by 50 –60%. This reduction is mainly achieved through the use of blended binders, where a portion of the cement is replaced by fly ash, slag, or silica fume.

Table 1

Production Indicators of Binders Worldwide

№	Type of binder	Total production worldwide, million. t	Energy consumption, kg/unit production		Harmful emissions			
					CO_2		Dust	
			per 1 t	Total (million t)	(kg/t)	Total (million t)	(kg/t)	Total (million t)
1	Portland Cement	2540	150	381	850	2159	21	53,34
2	Lime	286	204	58,34	528	151	5	1,43
3	Gypsum	112	47	5,264				
Total:		2938		444,6		2310		54,77

According to current global trends, composite binders (including composite cements and binders based on industrial waste) are gaining increasing importance as alternatives to traditional binders. Of particular interest are binder systems containing a limited amount of clinker [16-18].

The potential for resource conservation through comprehensive raw material processing and waste utilization is significant. Capital investments required for processing secondary raw materials are approximately four times lower than those needed for products derived from primary raw materials [19-20]. It is evident that investments should focus on waste-free technological processes that conserve raw and energy resources while ensuring high product quality [21-22].

The construction materials industry is the largest consumer of industrial waste, with raw materials accounting for 50% or more of the production cost. Many types of waste have compositions and properties similar to those of natural raw materials [23]. Studies have shown that the use of industrial waste can meet up to 40% of the construction sector's raw material needs and reduce the cost of building materials production by 10 – 30% compared to production using natural raw materials. Additionally, new construction materials with high technical and economic performance can be derived from industrial waste [24-28].

Traditionally, in modern recycling technologies for industrial waste, the primary direction of processing phosphogypsum stockpiles is the production of construction materials. The technologies for producing phosphogypsum-concrete construction materials involve the preparation of multi-component raw material mixtures. These mixtures typically include cement, lime, tripoli, slags, ash, expanded clay dust, and other components containing silicates, aluminates, and alumoferrites.

The hydration products and their interaction with calcium sulfate form water-resistant compounds within the structure of the resulting material. An essential requirement for the development of phosphogypsum-containing binders and mixtures is the creation of chemical and technological conditions that prevent the formation of highly basic calcium hydroaluminate sulfate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) [29-30]. Slags, ashes, opoka, and tripoli are considered reactive silica-containing fillers because, in the presence of phosphogypsum, they interact with lime and cement to form hydrated compounds and complex hydrous phases that differ from the typical cement hydration products known as hydrosilicates [31].

The accumulated scientific and practical experience of using industrial waste in Ukraine and abroad allows it to be regarded as a valuable raw material for the production of construction materials [32-33]. Industrial waste can be divided into two main groups: mineral and organic, with the former being more advantageous due to its abundance, better research, and significant importance in construction material production.

When developing economically viable approaches to utilizing industrial waste for construction materials, several factors must be considered: the initial state (chemical activity, dispersity, and aggregate state), and the choice of technology with minimal preparation and processing [34-35]. It should also be noted that the selection and justification of utilization methods are tasks for technologists, while ecological and sanitary services are responsible for conditioning and compliance with storage regulations. The key parameters characterizing any industrial waste include: chemical-mineralogical composition; aggregate state; volume. Each type of waste must undergo multiple levels of evaluation based on these criteria to determine its potential applications [36].

In practice, virtually all primary construction materials can be produced from waste or a combination of waste and natural mineral raw materials [37-38]. High-volume waste from the energy and chemical industries (e.g., phosphogypsum, titanogypsum, fluorogypsum, citrogypsum, desulfogypsum) can be used to manufacture construction materials, products, and structures for residential, industrial, agricultural, and infrastructural projects. Therefore, Ukraine's current focus on using industrial waste and local materials for construction promises significant benefits [39].

An analysis of scientific studies and practical experience with ash-slag waste indicates the economic feasibility of using thermal power plant (TPP) waste in cement and complex multi-component binder production. The content of SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO significantly affects the basic physicochemical properties of construction products. Research has shown that the fly ash from Ladyzhynska TPP is particularly suitable for improving the physicochemical and physico-mechanical characteristics of construction products [40-41]. Due to its chemical composition, it is classified as a basic ash, positively influencing structure formation processes. Table 2 presents the chemical composition of the fly ash from Ladyzhynska TPP.

Table 2

Chemical composition of Ladizhin TPP fly ash

Oxide content	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	P.P
Ash slags from Ladizhin TPP	49,26	23,00	19,35	3,53	1,79	2,11	0,40	0,10	1,40
Fly ash from Ladizhin TPP	52,1	23,1	15,6	3,16	1,08	0,4	1,2	0,57	0,7

It is essential to consider that an excessive ash content in ash-based materials increases porosity, reduces the rate of strength development over time, and negatively affects performance characteristics, such as frost and corrosion resistance. To prevent these undesirable effects, complex multifunctional additives are introduced into the concrete mix. These additives not only influence the kinetics of strength gain but also shape the material's structure, significantly affecting the physical-mechanical properties and durability of the resulting artificial stone [42-43].

The amount of ash used in the composition of complex binder concrete mixes can be increased through activation. The choice of activation method depends on the chemical-mineralogical composition of the ash, its production process, and the binder system composition. Since ash serves multiple functions in concrete mixes, its quantity can be increased by using various activation methods and exploiting its multifunctionality. Incorporating ash as a binder component, microfiller, or fine aggregate contributes to forming a stronger interfacial transition zone. Studies [44] have established a relationship between types of fuel ash and slag, activation methods, and their potential use in construction materials and products. Table 3 provides the names of various thermal energy production wastes, their activation methods, and recommended applications in construction materials and products.

Phosphogypsum waste is a byproduct of phosphoric acid production via the extraction process. Depending on the temperature-concentration conditions of phosphate raw material decomposition, the solid phase of calcium sulfate can exist in one of three forms: dihydrate, hemihydrate, or anhydrite. Phosphogypsum waste is classified as a gypsum raw material since it consists of 80–95% calcium sulfate. The chemical composition of phosphogypsum from the Vinnytsia Chemical Plant "Himprom" is presented in Table 3.

Table 3

Chemical Composition of Phosphogypsum from the Vinnytsia Chemical Plant "Khimprom"

Main components	Content, % by mass	
	Phosphogypsum dihydrate	Phosphogypsum pentahydrate
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
Hygroscopic water	21-29	18-22
Crystalline water	19-21	5,5-6,5

The bulk density of phosphogypsum is variable and depends on factors such as moisture content, particle size distribution, and degree of compaction. Phosphogypsum is a highly compressible material, and its compression results in reduced porosity and displacement or redistribution of moisture. The total moisture content of phosphogypsum is approximately 66%. Its maximum molecular moisture, about 15–16%, reflects the material's ability to retain water through molecular adhesion between phosphogypsum particles and water.

Several specific characteristics hinder the widespread use of phosphogypsum: its physical state, high moisture content, the presence of phosphoric and sulfuric acids, and water-soluble harmful phosphorus and fluorine compounds. Residual free phosphoric and sulfuric acids, as well as soluble salts like monocalcium phosphate and dicalcium phosphate, delay setting and reduce the strength of cementitious binders [45-46]. The emission of fluorine gases during thermal processing complicates the production technology of construction materials. The elevated acidity of raw phosphogypsum contributes to equipment corrosion, and newly formed sodium, potassium, and calcium sulfates tend to crystallize on the surface of products as efflorescence during drying. Consequently, the use of untreated phosphogypsum complicates the production of gypsum binders with satisfactory mechanical properties. Acid residue concentrations can be reduced by washing, but this requires additional resources and generates acidic wastewater that must be treated.

Phosphogypsum has been studied as a raw material for gypsum binder production and as an additive for regulating the setting time of cement paste. However, due to its technological limitations, such as the need for drying and briquetting, phosphogypsum utilization has primarily been adopted in countries lacking natural gypsum deposits. For example, in Japan, all phosphogypsum is utilized in the cement industry.

Theoretically, zero-waste phosphogypsum utilization can be achieved through complete thermal decomposition of calcium sulfate into CaO and SO_2. The resulting SO_2 can be used for sulfuric acid production, while CaO can be applied as quicklime or in Portland cement clinker production. However, this process requires extremely high temperatures exceeding 1450°C, which is a significant drawback of the technology [47-48].

Among the existing methods for improving the efficiency of hydraulic interactions between components of molding solutions and active mineral additives, mechanical activation through preliminary grinding is the most common. The presence of free acids in phosphogypsum allows for their use in chemical activation, primarily of fly ash, as a component of low-clinker phosphogypsum-fly ash cementitious binders. The destruction of glassy films on the surface of fly ash will significantly enhance its hydraulic activity.

It is well known that the application of active mineral additives in the production of hydraulic binders is driven by several critical reasons: the need to impart special properties to cement, saving fuel and energy resources, and improving the ecological balance of processing industries through recycling industrial waste. In the existing production technologies of building materials, natural additives and products derived from industrial waste contribute to the intensification of certain physical and technological processes. Active mineral additives, such as ground tripoli, opoka, marl, tuff, liparite, diatomite, volcanic ash, fuel ash, blast furnace slag, burnt clay, and others, can interact with calcium hydroxide hydrates, improving specific properties of binders while simultaneously reducing their production costs [49-50].

Experimental data indicate that the use of thermal power plant ash (TPP) in concrete, when combined with modifying agents, can reach 200 kg/m³. At a content of 150–200 kg/m³, the utilization of TPP for concrete production alone could account for 22–30 million tons or 35–45% of its total production volume. Additionally, incorporating TPP into concrete reduces cement consumption by 5–15%, lowers the average concrete density, and enhances thermal protection properties of structures [51-53].

The most effective use of fly ash is achieved by substituting a portion of cement and sand while adhering to normalized component ratios. This approach maximizes cement savings and the total utilization of fly ash. This type of construction concrete requires less water during setting, exhibits reduced heat generation compared to pure Portland cement, and demonstrates lower shrinkage. Although the early strength of cement mixed with fly ash is lower, the difference diminishes with time and levels out in later stages [54-56].

Numerous studies have demonstrated that replacing up to 20% of sand with fly ash in the concrete mixture results in a 15–40% increase in compressive strength following heat-moisture treatment and a 12–15% increase at 28 days of age [57-58]. Fly ash serves as a micro-filler in the concrete mixture, improving its granulometric composition.

Cement solutions with 30% fly ash, ground to 10,500 cm²/g, exhibit compressive strength comparable to pure cement solutions at 28 days of age. Furthermore, cement solutions with 30% fly ash, ground to 6,450 and 10,500 cm²/g, exhibit significantly higher compressive strength than control samples over periods of 3 and 6 months. However, increased ash fineness requires significant energy consumption and higher material and labor costs [59-60].

The use of TPP allows for savings in cement, simplifies several production processes (such as concrete vibration and the use of expanded clay concrete mixtures), and substantially reduces production costs. Initially, ash was used as part of cement in commercial mortars and concretes. Subsequently, unground ash was introduced to improve the overall granulometric composition of the mixture, compensating for unsatisfactory natural sand properties. Utilizing both ground and unground ash types reduces cement consumption by significant margins, with ground ash being more cost-effective in cement savings.

The demand for low-clinker binders in Ukraine arises from several factors: their low energy consumption and cost, the need for low-strength binders in low-rise housing construction (where high-strength cements are economically unfeasible), increased utilization of TPP, and addressing ecological issues in certain regions.

A resource-saving technology has been proposed for developing composite building materials containing phosphogypsum and fly ash. This involves mechanochemical activation of fly ash with acidic residues from chemical industry waste. Preliminary mixing of phosphogypsum with fly ash ensures additional chemical activation of ash. The acids in phosphogypsum destroy glassy films on fly ash particles and interact with its alkaline oxides. When phosphogypsum interacts with fly ash, it breaks aluminosilicate glassy shells, forming calcium hydrosilicates and aluminum sulfates. This destruction of glassy films enhances the hydraulic activity of these materials when active mineral additives are used [61-64].

The most effective neutralization of acid residues in phosphogypsum-fly ash compositions can be achieved by incorporating active mineral additives, such as marl. Marl binds free lime in the composition, preventing the formation of ettringite, while its carbonate content neutralizes acid residues. Marl contains both carbonate ($CaCO_3$) and active silica (SiO_2) [65-67].

Preliminary mixing and holding of phosphogypsum and fly ash at room temperature in a 60:40 ratio for various durations (0, 3, 6, 9, 12, 24 hours), with the addition of active mineral additives and cement, results in increased strength of composite binders. The strength of these materials is also dependent on the time taken to neutralize the acids in phosphogypsum [68-71].

A resource-saving technological scheme has been proposed for producing low-clinker binders using phosphogypsum (dihydrate), fly ash, cement, and natural additives. This involves processing raw material mixtures in a three-section continuous mixer, ensuring the chemical and mechanical activation of fly ash and phosphogypsum. The technological scheme consists of the following stages: preparation of raw materials, preparation of the phosphogypsum-fly ash mixture to neutralize acids through intensive mixing, grinding of active mineral additives, and step-by-step mixing of the phosphogypsum-fly ash mixture with other components. Results of the tests are presented in Table 4.

Table 4

Characteristics of Building Material Test Samples

Composition of raw material mix, %				ρ, kg/m³	Strength, MPa		W, %	Softening Coefficient K_s
Phospho gypsum	Ash-uno	Portland cement	Marl		R_{comp}	R_{bend}		
50	30	20	—	1557	17,5	3,96	12,3	0,72
50	30	10	10	1642	19,8	4,78	9,39	0,84
25	43	11	21	1670	20,1	3,45	15,3	0,76
25	43	21	11	1697	29,7	2,95	11,8	0,85

The results of the physical and mechanical property studies of the samples, presented in Table 4, confirm that the increase in hydraulic activity and water resistance of the binder material, produced using phosphogypsum and fly ash, is achieved by the addition of active mineral additives, which promote the formation of calcium hydrosilicates. A rational method for neutralizing the acid residues from the phosphogypsum component with fly ash and marl as additives offers significant advantages compared to neutralizing phosphogypsum acid residues using lime or cement. The composition of raw material mixtures in the resource-saving technology, utilizing phosphogypsum, fly ash, marl, Portland cement, and fillers, meets the physical and mechanical requirements imposed on construction products. As shown in Table 4, the strength of the model samples ranges between 17.5 and 29.7 MPa.