UDC 622.33: 621.311.22.002.84 DOI: https://doi.org/10.15407/geotm2024.169.045

PROCESSING OF ASH WASTE FROM THERMAL POWER PLANTS: FOREIGN EXPERIENCE AND UKRAINIAN REALITIES

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Abstract. Ash and slag wastes are man-made mineral formations that are produced in large quantities and pose a serious environmental hazard. On the other hand, it is a valuable mineral raw material for the production of various materials, housing, road, agricultural and industrial construction, agriculture, mining and oil industries. In accordance with the stated goal, foreign and Ukrainian experience in processing ash waste from thermal power plants was studied. The experience of ash and slag waste processing in world practice is analyzed. The factors preventing the large-scale use of ash and slag materials in Ukraine and the necessary measures to increase recycling volumes have been identified. Successful examples of the use of ash and slag in countries around the world are summarized. Promising directions for using ash and slag waste as additional raw materials have been identified. Thanks to the use of ash and slag materials, significant cost savings will be achieved compared to traditional options using natural raw materials. With existing methods of use and available technologies, ash and slag wastes become valuable materials that are used in road construction and in the production of: cement, concrete (heavy, porous, heat-resistant), reinforced concrete products and structures, bricks, lightweight aggregates for concrete, dry construction mixtures, asphalt concrete mixtures, etc., thermal insulation, abrasives, roofing materials, ceramic tiles. In Ukraine, road construction using ash and slag materials is being successfully implemented. The direction of selling microspheres (cenospheres) of fly ash on export markets is developing. Aluminosilicate microspheres are widely used in construction, oil, gas, chemical industries and other industries. The production of building materials is the main material base of the country's construction complex and has a significant impact on the pace of economic development. Ukraine can achieve a higher level of use of ash and slag waste thanks to a balanced environmental and economic policy. For this, it is necessary: to develop standards for ash and slag products; launch a system of "green" public procurement; to initiate the implementation of the cement concrete road construction program; apply financial instruments to stimulate waste processing; increase the rent for the extraction of crushed stone and sand; to approve the mechanism for compensating costs for the transportation ash and slag waste by rail. This will make it possible to obtain a significant profit from the sale of ash and slag waste processing products and significantly improve the ecological condition of the territories.

Keywords: coal, ash waste from thermal power plants, coal combustion products, recycling, recycling experience, fly ash, bottom ash, boiler slag, phosphogypsum.

1. Introduction

Generation of electricity through the use of fossil raw materials is an important component of energy security. Therefore, given the presence of powerful deposits on the territory of Ukraine and the lack of alternatives to the role of thermal power plants (TPPs) and combined heat and power plants (CHPs) in power generation, coal will be one of the sources of the energy fuel base for many years to come [1, 2]. At the same time, its use also has negative consequences, both for Ukraine and other countries.

As a result of the combustion of solid fuels, ash and slag waste (ASW) is formed, which, as practice has shown, firstly, is produced in large quantities, and secondly, poses a serious environmental hazard. With physical and moral wear and tear of equipment, this problem becomes especially acute. Therefore, on the one hand, the objects of the fuel and energy complex the TPPs and the CHPs are one of the main sources of environmental pollution. The impact of toxic substances contained in the ASW storage areas on the environment and the human body was analyzed in [3].

On the other hand, ash and slag waste can be used as secondary raw materials. Based on an analysis of a review of global experience in processing the ASW [3], the main direction of their use, until recently, was the construction sector: construction products, primarily concrete and wall slabs, clinker (raw materials for the production of Portland cement), roofing granules, road fillers materials and asphalt fillers, etc. In Ukraine, the utilization of ash and slag waste is about 10% (mainly road construction), which is 5–7 times less compared to countries such as the USA and the EU [3].

It is necessary to search for new directions and areas of use of ash and slag waste. Despite the large number of publications, insufficient attention has been paid to the extraction of associated elements, including rare earths, from waste. At the same time, the global experience of processing the ASW is useful and very relevant for Ukraine, given the huge volumes and low degree of their recycling in our country.

To further improve and develop the processing of the ASW, it is necessary to generalize global experience and the necessary measures to increase the level of their recycling in Ukraine, to search for promising areas of their use and new markets. The integrated use of waste from the energy complex is an urgent need not only for Ukraine, but also for any economically developed state.

2. Methods

The following methods were used in this study: analytical review of literature sources, comparative analysis; monitoring and assessment of the impact of ash and slag waste storage sites on the environment and population; analysis of the composition of the ASW; analysis of the possibilities and prospects for the use of ash and slag materials in the world. When analyzing the state of the ash microspheres market, information resources of the Internet were used.

The purpose of the work is to study and compare foreign and Ukrainian experience in processing ash waste from thermal power plants and identify promising areas for their use.

Object of study: disposal of ash and slag waste from thermal power plants.

To achieve this goal, the following **tasks** were solved:

– the volumes, properties, composition of the ASW, economic incentives for their processing in international practice, as well as the results obtained are analyzed;

– the factors preventing the large-scale use of ash and slag materials in Ukraine, and the necessary measures to increase the level of recycling of the ASW have been identified;

– the successful examples of the use of ash and slag in world practice are summarized;

– the promising directions for their use as additional raw materials have been identified.

3. Theoretical and experimental parts

The problem of waste disposal involves the involvement of various types of waste in new technological cycles or their use for other useful purposes. In the countries of the European Union, as well as the USA and other industrialized countries of the world, recycling of the ASW is an integral component of the technological process of coal-fired thermal power plants. Therefore, great attention is paid to these issues [4–31].

The main range of the ASW products (in foreign publications – coal combustion products CCW or CCPs) include [4, 5]: bottom ash; boiler slag; phosphogypsum (FGD gypsum); fly ash; semi-dry absorption product (SDA Product).

Analysis of the volumes, properties, composition of the ASW, levers for economic stimulation of their processing in international practice, as well as the results obtained.

Every year, the European Coal Combustion Products Association (ECOBA) prepares statistics on the production and use CCPs in the association's member countries. In 2016, the volume of CCPs produced at power plants in Europe (EU-15) amounted to 40 million tons, including: Fly Ash – 63.8%; FGD Gypsum – 23.6%; SDA Product – 1.0%; Bottom Ash – 9.0%; Boiler slag – 1.2% [4].

The most widely used is fly ash. Advantages of fly ash and bottom ash [4]:

– fly ash can easily combine with calcium hydroxide to form the required compounds during the cementation process, providing a cheaper substitute for clay, sand, limestone and gravel;

– fly ash produces strong, durable concrete that is resistant to aggressive chemicals.

According to ECOBA, fly ash has the following environmental benefits [4]:

– the use of fly ash eliminates the need to mine primary materials and saves limited land and material resources;

– fly ash does not require burning and therefore does not emit carbon dioxide; For every ton of fly ash used to replace traditional cement, one less ton of carbon dioxide enters the Earth's atmosphere;

– fly ash requires very little water compared to traditional cement.

To increase the level of utilization of ash and slag waste, developed countries at the state level stimulated their use, which had a positive effect on the results [2].

In the United States, builders are legally required to use thermal power plant ash in concrete and cement mortars. Violators are subject to economic sanctions from the state. Typically, the TPPs pay extra to the consumer for ash selection [14]. There are five regional ash distribution centers in the Great Britain [2]. In Bulgaria, the ash itself is free [2]. In Poland, powerful economic levers are used to encourage consumers to use ash and slag. The price for ash dumps has been increased, so thermal power plants pay extra to consumers of ash in order to reduce the costs of storing and processing them [2, 17, 18]. China takes a rational approach to the disposal of ashes and waste, considering them as a real source of artificial raw materials in various sectors of industry and agriculture. In China, ash and slag from thermal power plants are sold and delivered to consumers free of charge [2, 17, 18].

In recent years, in developed countries, up to 70–95% of ash and slag is processed as a percentage of its output. More and more attention is being paid to expanding the scope of their use as useful materials. The level of ash utilization in the EU is more than 50%, in France, Germany – 70%, in Finland – about 90% [2].

Tightening environmental legislation in developed and developing countries is forcing the recycling of ash and finding rational uses for ash. In developed countries, recycling rates are 5–7 times higher than in developing countries. The world leaders in recycling are: USA, EU, Japan, India, China (Table 1 shows the volumes of production and recycling of the ASW for 2010 and 2016) [9, 19–21].

Table 1 – Volumes of generation and disposal of the ASW in the world for 2010 and 2016 [9, 19–21]

Country/Region	2010			2016		
	ASW was formed, million tons	ASW recycled, million tons	Share of recycled ASW, %	ASW was formed, million tons	ASW recycled, million tons	Share of recycled ASW, %
USA	118	49.7	42.1	107.4	60.	56.0
EU	52.6	47.8	90.9	40.3	38	94.3
Canada	6.8	2.3	33.8	4.8	2.6	54.2
Japan	11.1	10.7	96.4	12.3	12.3	100.0
Australia	13.1	6.0	45.8	12.3	5.4	43.9
India	105	14.5	13.8	197	132	67.0
China	395	265	67.1	565	396	70.1
Middle East and Africa	32.2	3.4	10.6	32.2	3.4	10.6
Total	733.8	399.4	50.1	971.3	649.8,6	62

In the USA, the volume of use of ash and slag waste in 2013 amounted to 51.6 million tons or about 45% of the production (114.7 million tons) [4]. 50% of the fly ash produced in the United States was disposed of in various areas of the economy. In India, the leader in terms of the amount of ash used, 70% of the ASW (~ 100 million tons) of high-ash coal combustion was used for construction and reclamation [8]. In the **EU** countries and Japan, ash dumps at thermal power plants are prohibited, or their operation is subject to a fine [15]. They have been replaced by tanks located next to the main buildings of the thermal power plant, in which dry ash is collected. In the Netherlands and Denmark, 100% of ash and slag was used.

In Germany, almost 100% of coal fly ash (3–4 million tons/year) was utilized domestically and abroad. Of these, more than 75% were used for the production of cement-based building materials. Many thermal power plants in Germany have reservoirs with a capacity of up to 40–60 thousand tons, usually small with daily and two-day capacity. From them, samples are taken for analysis of ash in the laboratory, then using mixing and volumetric dosing, a product is created, which, in terms of its fractional composition, acquires characteristics that meet regulatory requirements. At the end of the process, the ash is transferred for storage to appropriate tanks. The largest company in Europe for processing thermal power plant ash – Bau Mineral (BM), which is a subsidiary of the energy system, operates in Germany. This company serves as a link between the construction industry and thermal power plants. BM was formed in Herten in 1989 as a result of the merger of two companies, which by that time already had almost 30 years of experience in the use of by-products from power plants [22, 23].

BM uses its own system for transporting and storing by-products of thermal power plants. Delivery is carried out by road, sea vessels and trains. One of the main advantages of the company is timely transportation. The BM Company has branches in 8 regions, employing more than 100 employees, a total storage capacity of 200 thousand tons, and has more than 50 special vehicles with a transportation capacity of 600 thousand tons. The company sells more than 3 million tons of by-products per year the TPP products. BM products comply with DIN (German Institute for Standardization) standards and instructions, which is confirmed by building materials testing institutes. Product quality is ensured through continuous monitoring in our own construction materials testing laboratories, equipped with the latest technology [22, 24]. There are no intermediaries between thermal power plants and builders, except BM. The basis for the prosperity of the BM Company is: technical competence, economic indicators, and innovative ideas for using the by-product of thermal power plants.

For many years now, the Technical Union of Users of Thermal Power Plant By-Products has been functioning in Germany. According to his data, in 2011, 25 million tons of by-products from thermal power plants were produced in Germany, of which 15 million tons belonged to thermal power plants operating on brown coals; 10 million tons belonged to thermal power plants operating on hard coals. Annual by-products of thermal power plants using brown coal are: 7.9 million tons of fly ash, 1.8 million tons of furnace sand, 5.3 million tons of gypsum, etc. At thermal power plants operating on hard coal, their quantity and composition vary: 4.3 million tons of fly ash, 0.53 million tons of furnace sand, 0.20 million tons of gypsum, 4.97 million tons of granular slag. Of the total fly ash volume of 4.3 million tons, 3.5 million tons correspond to the European fly ash standard [2, 24].

Complete recycling of granulated slag and furnace sand is carried out. Granular slag can be used as a sand substitute for sandblasting. The main requirement for them is the uniformity of the properties of the ash. Thus, the use of fly ash by enterprises serves as the most important indicator of the level of technical development of energy and construction. It can be used as an additive in concrete, mortar, cement, silicate products; for brick production; in underground and road construction. Still, the main promising area of use is cement replacement. In Germany, for example, at the Molke thermal power plant, the total volume of the reservoirs is 60 thousand tons, and the ash yield is 600 thousand tons/year [22, 25]. With thermal power plants, ash dumps do not accumulate. By-products of thermal power plants are successfully exported to neighboring countries. If fly ash is used in construction and the construction industry, then it must have a certificate [22].

The basis of consumer interest is, of course, the price range for cement and ash. No concrete production in Germany is complete without ash. In total, 3.1 million tons of cement is replaced with ash in Germany. Ash disposal is carried out using environmentally friendly methods. Let's list the main benefits of this process: saving resources and energy required for cement production, reducing CO_2 emissions by 3.1 million tons (considering that the production of 1 ton of cement produces 1 ton of

CO_2), which meets the requirements of the Kyoto Protocol for reducing emissions CO_2 [22, 26]. The costs of storage, transportation, and employee salaries pay off very quickly. Thus, we can say that a power plant in the modern world is a producer of valuable products, not waste [22].

Craig Benson, Wisconsin Distinguished Professor of Civil, Environmental and Geological Engineering at the University of Wisconsin-Madison and co-director of the Recycled Materials Resource Center at the University of New Hampshire, estimates that each year in the United States, CCW recycling saves about 160 trillion BTUs of energy (the amount of energy used by 1.7 million households), 11 million tons of CO2 equivalent (comparable to the average annual emissions of more than 1.8 million passenger cars), and 32 billion gallons of water (more than 121 billion liters) [5].

By stimulating the processing of ash waste in international practice, the following results were obtained: the degree of ash utilization is from 70 to 100%; In Western Europe and Japan, ash dumps at thermal power plants have been practically eliminated.

The work [5] shows promising areas for using CCW (Table 2–4).

Table 2 – Promising areas for using CCW in construction work [5]

Scope of use	Directions for use
Green roof and landscaping	Green roofs covered with plants reduce storm water runoff and provide insulation. Residual ash is used as bedding material, and flue gas desulfurization (FGD) materials and fly ash are used as additives to support plant growth and increase crop yields)
Outdoor furniture	Benches are made from lumber containing fly ash
Sidewalk	Concrete consists of Portland cement, aggregate (sand and/or stone) and water. Fly ash added to concrete can improve durability).
Carpet backing	The base of the carpet can be made from fly ash.
Backfill – foundation support	Backfill surrounds the building's foundation, supporting it and providing drainage. Recycled concrete, which may contain fly ash, can be used for drainage.
Structural pouring of the foundation	It is built in layers and compacted to the desired density. Fly ash, bottom ash and boiler slag can be used as structural filler. Recycled concrete can also be crushed and used as structural aggregate.
Poured concrete foundation	Concrete is used in many areas of construction, both indoors and outdoors. Fly ash can partially replace Portland cement, Portland cement itself can be made from fly ash and FGD gypsum, and concrete aggregates can include bottom ash and recycled concrete.
Masonry block	Masonry blocks are made from cement and aggregate. Fly ash can partially replace Portland cement, and fly ash and recycled concrete can replace virgin aggregate.
Main material	Recycled concrete is usually used as the main material.

Table 3 – Promising areas for the use of CCW in the production of construction products and materials [5]

Scope of use	Directions for use
Construction cladding material	Fly ash is used in the production of bricks and other artificial stone.
Ceiling tiles	Ceiling tiles may contain FGD gypsum and fly ash.
Floor tiles and tile underlay	Floor tiles and backing tiles can be made from fly ash.
Interior wall	FGD gypsum is used to make wall boards.
Mortar, plaster and stucco	Fly ash can partially replace Portland cement in mortar, stucco and stucco.
Pressing into bricks	Fly ash can also be mixed with water and pressed into bricks, which harden without the use of clay, heat or Portland cement.
Manufacturing of wall slabs	Approximately 33% of the gypsum used to make wallboard in the United States in 2008 was FGD gypsum.
Wood substitute	Fly ash makes up 50–85% of a wood substitute called LifeTime Lumber, manufactured by LifeTime Composites of Carlsbad, California. The material used for decking and fencing is inedible to termites and will not support mold growth, unlike wood substitutes made from sawdust.

Table 4 – Prospective directions for using CCW in road works [5]

Scope of use	Directions for use
Embankment	Topsoil on roadside embankments can be supplemented with FGD materials if soil conditions permit. FGD materials can improve soil health, enhance plant growth, and reduce runoff. Coal ash is suitable for filling embankments.
Retaining wall	Retaining walls retain soil and rocks and prevent erosion of roadside slopes; they are often made from concrete or modular blocks. Fly ash can partially replace Portland cement in concrete, making the concrete stronger and more durable. Portland cement may also contain FGD gypsum. Concrete aggregates may include bottom ash and recycled concrete, which may contain fly ash.
Asphalt pavement	Boiler slag can replace primary aggregate in the surface layer of asphalt.
Asphalt base	Fly ash, ash and recycled concrete can be used as aggregate in the asphalt base course.
Granular base and sub base	Various industrial materials are used as granular base and sub base, including bottom ash and recycled concrete. Fly ash is also used as mineral filler in asphalt base, granular base and sub base.
Subgrade – original soil	Fly ash can improve the structure and stability of the subgrade on which the road will be built.
Structural content	Structural filling supports and relieves pressure from retaining walls. Fly ash and recycled concrete can be used as backfill for retaining walls.
Swamps	Vegetation ditches provide road drainage and help improve water quality. Recycled concrete can be used in place of traditional drainage materials such as virgin sand or gravel.
Soil stabilization under highway	Fly ash can stabilize soil under highways because... when mixed with the top 300cm of soil, “it creates what is called lean concrete and creates a good working platform” that can replace the one meter layer of crushed stone typically used under major highways.

India is one of the leaders in the generation and disposal of waste materials. [27] notes that there are many reasons to increase the amount of fly ash reused: disposal costs are minimized; a smaller area is allocated for export, which allows the land to be used for other purposes and reduces the requirements for export permits; financial profit from the sale of the by-product, or at least compensation for the costs of processing and disposal; by-products can replace some scarce or expensive natural products.

Table 5 shows the areas of use of fly ash considered by Indian specialists [27].

Table 5 – Directions for using fly ash [27]

Scope of use	Directions for use
Removing toxic metals from wastewater	Due to the main chemical components: oxides of aluminum, iron, calcium, magnesium, silica and carbon, as well as physical properties such as porosity, particle size distribution and surface area, it has potential applications in wastewater treatment. The alkaline nature of fly ash makes it a good neutralizing agent. Typically, to maximize the adsorption of metals to aqueous oxides, it is necessary to adjust the pH of the wastewater with lime and sodium hydroxide.
Removal of inorganic components from wastewater	Removal of inorganic pollutants such as phosphorus, fluorine and boron that is hazardous to human health. Phosphorus released into surface and ground waters from concentrated agricultural activities, including soil fertilization, feedlots, livestock and poultry farms, and causes water quality problems in rivers and lakes.
Removal of phenolic compounds	Phenols are organic pollutants released into the environment that cause unpleasant tastes and odors in drinking water. The main sources of phenolic pollution of the aquatic environment are wastewater from the paint and varnish, pesticide, coal processing, oil and petrochemical industries. Chlorination of natural waters for the purpose of disinfection leads to the formation of chlorinated phenols. There are several methods for removing pollutants from wastewater. Fly ash has good adsorption properties.
Removing dyes from wastewater	Dyes and pigments are discharged into wastewater from various sources, mainly from the dyeing and textile industries. There are various methods for treating dye wastewater. Among these is the adsorption process, which represents an attractive alternative for purification, especially if the adsorbent is inexpensive and does not require additional pre-treatment before use.
Fly ash leaching in water supply	Disposal of fly ash in water involves the potential leaching of some elements into the water. This creates the problem of secondary environmental pollution. The surface layer of ash particles, probably microns thick, contains a significant amount of easily leached material that settles during cooling after combustion. A significant role in leaching is played by the charge on the surface of the ash particles and the formation of a diffuse double layer.
Zeolite synthesis	Zeolites are crystalline aluminosilicates whose counterions are elements of group I or II. Their structure is a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, connected to each other at the corners by common oxygen. The tetrahedrons form a three-dimensional network with many voids and open spaces. It is these voids that determine many of the special properties of zeolites, such as the adsorption of molecules in huge internal channels.

continuation of Table 5

Scope of use	Directions for use
Construction work / industry	Uses of fly ash in cement industry: 1. replacement of cement in Portland cement concrete, 2. pozzolanic material in the production of pozzolanic cements, 3. cement retarding ingredient as a replacement for gypsum. Cement is the most expensive and energy-intensive component of concrete. The cost per unit of concrete is reduced due to partial replacement of cement with fly ash.
Lightweight aggregate	Use of fly ash as a by-product in the manufacture of lightweight construction products. The main advantage is savings for the manufacturer associated with lower costs for transporting the finished product compared to a heavy product, when weight is a decisive factor.
Road base	Use of fly ash in embankment soil stabilization as: subgrade material, aggregate, additive for bitumen road surfaces and mineral filler for bituminous concrete, soil stabilizer along embankments.
Backfilling of mines	Backfilling of mines and underground mines is technically vulnerable and is especially promising in areas where sand is scarce. Filling a quarry can be considered as land reclamation. The possibility of using a fly ash solution at a closed underground mining site is being considered. The injection process will reduce acid mine drainage.

Great attention is paid to the processing and use of the ASW in China. Slag and bottom ash (silicate part) are widely used in construction products and road works. Reasonable use of coal ash has great prospects for resource recovery and environmental protection: in construction, soil reclamation, ceramic industry, zeolite synthesis, catalysis, deep separation, extraction of valuable metals, etc. Coal fly ash has the advantages of replacing lime and dolomite, increasing plant nutrient availability, improving concrete workability, direct incorporation into ceramic pastes, use as catalyst or catalyst carriers, adsorbents, and increasing industrial synergy opportunities. The widespread use of fly ash limits the unburned carbon content, which has traditionally been in the range of 2–12%. According to the Chinese national standard GB/T 477-2008 (Fly ash used in cement and concrete), its amount should be less than 5%. This poses a major challenge to enrichment efficiency and equipment selection. Various separation techniques have been used to achieve higher efficiency in fly ash application by removing unburned carbon: flotation, electrostatic separation, oil agglomeration and gravity separation. However, due to the complex characteristics of fine ash, the beneficiation efficiency is unsatisfactory and faces many problems [10, 28].

For Kazakhstan, the growth of ash waste is of particular relevance and is one of the main government priorities. The annual output of ash and slag waste is about 19 million tons. To date, up to 430 million tons of waste have been accumulated in ash dumps [22, 29, 30]. In the large metropolis of Kazakhstan alone – in Almaty, as a result of the activities of the CHPP-1, the CHPP-2 and the CHPP-3 8 more than 2 million tons of ash and slag waste have been accumulated. In just one heating season, about 600 thousand tons of ash is added to the accumulated volumes from coal combustion. In the South Kazakhstan region, as a result of the activities of the Kentau Thermal Power Plant, a number of ash dump sites were formed, which removed huge areas from land use and have a negative impact on the environment (pollution of soil, air, groundwater) [21].

The chemical composition of ash depends on the type of coal burned and can vary widely in its main components. The alumina content in them can range from 5 to 35%, rare elements: Sr – 110 g/t, Zr – 2.30 g/t, Nb – 7 g/t, Ga – up to 9 g/t and rare earth metals: Y – 14 g/t, Eu – 0.68 g/t, La – 19 g/t, Pr – 7 g/t, Sm – up to 15 g/t. Despite the lower content of rare earth minerals (REM) in ash than in their known minerals (monazite: 264–280 g/t, loparite: 112–180 g/t), in the absence of explored sources, extraction of rare earth minerals (REM) from ash becomes attractive and relevant [21].

Many valuable metals that can be recovered technologically are irretrievably lost with ash. Ash and slag waste is a complex mixture, the properties of which depend on the type of coal and its combustion mode, boiler design and many other factors. This determines the need to conduct comprehensive studies of the composition and properties of the mineral part of various coals in order to use them as an additional source for extracting valuable metals and obtaining marketable products. Ash from coal thermal power plants is a potential raw material for the complex extraction of silica, aluminum oxide, iron and rare earth metals into commercial products [21].

Table 6 shows the material composition of the ashes of the main coal deposits in Kazakhstan [21].

Table 6 – Material compositions of ashes of the main coal deposits in Kazakhstan [21].

Field	Content, %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	P_2O_5	K_2O
Maikube	56.3	24.6	5.9	3.7	0.83	1.26	0.93	0.82	0.61
Ekibastuz	59.6	24.3	5.2	4.9	1.03	1.13	0.73	1.25	0.79
Karazhyra	54.8	29.6	4.2	2.7	1.92	2.85	1.56	1.37	0.92
Karaganda	49.8	21.3	5.2	3.0	1.22	2.15	1.06	1.12	0.87
Shubarkolskoye	50.4	22.7	4.8	3.7	1.55	1.39	0.64	0.98	0.90
Borlinskoe	52.3	25.1	5.0	3.2	1.01	1.82	1.43	1.07	0.98

The volume of ash and slag waste disposal in Kazakhstan was 5–10%. Limiting factors for using the ASW:

– unstable physical and chemical characteristics of the ASW as a raw material for the construction industry;

– there are no averaging tanks for 2–3 daily capacity and storage tanks for storage and shipment of ash to thermal power plants;

– consumers do not have devices for receiving and storing ash and slag;

– the country's infrastructure is not developed and, as a result, high transport costs for the transportation of chemical waste;

– there are no mandatory state technical and economic legislative documents and incentives for the use of ash by enterprises in the construction sector, agriculture and other industries;

– there is no regulatory framework for the use of thermal coal waste;

– there is no comprehensive program for the use of ash and slag from thermal power plants;

– seasonal gap between the peak production of the ASW and demand for them.

Recently, more and more specialists have been paying attention to studying the properties of ash and slag waste and the possibility of their use in various fields. Works [29, 30] present a program for the integrated use of ash and slag waste from the power plant of EEC JSC (Kazakhstan); classical methods of processing ash and waste are analyzed: acid-base technologies for the complex processing of ash and slag (sulfuric acid, nitric acid, hydrochloric acid, alkaline methods for processing self-disintegrating slag); technologies for processing the ASW for the production of cement and dry construction mixtures, production of aluminum sulfate, production of sand-lime brick, ceramic and fused materials, production of slag-ceramics, use of microspheres). As a result of complex processing of ash, it is possible to obtain the following high-quality commercial products: amorphous silica (“white soot”) with a higher developed surface compared to existing analogues produced in the CIS (Commonwealth of Independent States) countries, which is the raw material for “solar silicon” (SiO_2 extraction – 99 ,5%); commercial alumina (Al_2O_3 recovery – 98.6%); iron concentrate with Fe content above 65% (Fe_2O_3 recovery – 98.8%); The overall recycling rate is 99.4%. It is also possible to obtain liquid glass, wollastonite, gallium metal, and vanadium pentoxide.

The authors of the article [22] conducted research on the use of thermal power plant ashes as an active component of the composition of a dry adhesive and cement-based plaster mixture. According to experts, the composition of the mixture meets the requirements of the standard and can be used for plastering walls of residential and public buildings and structures. The possibility of significantly reducing the cost of dry plaster mixture by reducing the cement consumption in it by half has been shown.

More than 270 thousand tons of ash is produced annually in Kyrgyzstan. More than 170 thousand tons of wastes are provided by the Bishkek Thermal Power Plant and about 100 thousand by the private sector. Currently, more than 1.6 million tons of ash has accumulated in the dumps of thermal power plants, which occupies more than 192.7 hectares of fertile land. In Kyrgyzstan, ash is classified as waste hazard class four, and it is not subject to special disposal conditions. It is often stored in close proximity to heating facilities in ash dumps. The use of ash and its secondary use in Kyrgyzstan are not regulated in any way [31, 32].

According to the author [31], there are several options for solving the problem of waste generation from coal combustion. One of them is the improvement of production technologies, the use of modern ash collectors with a flue gas purification rate of up to 99.9% and boilers with pyrolysis fuel combustion. The second method is more economically attractive – involving the ASW in processing. Ash disposal can be beneficial from both an economic and environmental point of view. Firstly, this will reduce the areas that are currently being alienated for ash dumps and becoming uninhabitable. Secondly, heat supply enterprises will be able to make money from this – according to experts; ash processing can ensure an increase in the profitability of centralized heating supply by 10–20%. Thirdly, reducing this type of waste will also reduce the negative impact on the environment and public health. To implement this, it is necessary to create a guaranteed market for the sale of ash by making appropriate changes to the legislation. In addition, we need a current database on producers, consumers and processors of ash and slag waste, it is necessary to develop programs to support entrepreneurs, to increase the use of such waste when forming state and municipal orders in road and railway construction, in the production of building materials, etc.

In the European Union, the use of ash and slag is regulated by directives on integrated pollution prevention and control, industrial emissions and other documents. In most countries, the use of ash dumps is taxed – from 1 to 60 euros per ton. This stimulates the industrial use of ash, without its accumulation in dumps and negative impact on the environment [31].

Currently, there are more than 300 methods for recycling ash and slag in the world. The level of their use reaches 50–100%: ash is used as a raw material for the production of cement, concrete, dry building mixtures, paving slabs and others. Moreover, the cost of such building materials is 12–25% lower compared to those obtained by other methods [31].

In Ukraine, as of 2021, about 30% of all electrical energy produced by enterprises of the fuel and energy complex came from thermal power plants [33–37]. However, they also account for about 27% of all particulate matter emissions in Europe. Eight Ukrainian thermal power plants (Kurakhovska, Burshtynska, Trypilska, Luhanska, Zmievska, Uhlegorska, Slavianska, Ladyzhinska) are among the ten power plants in Europe with the highest emissions of solid particles with a diameter of 10 microns or less [38]. For these thermal power plants using coal fuel of different grades, the concentrations of components in ash and slag waste vary widely, but in almost all cases the main ash and slag-forming components are oxygen compounds of silicon, aluminum, iron, calcium, magnesium [33–37].

When burning coal at thermal power plants in our country, slag and ash are formed every year in the amount of 7...9 million tons (50...200 grams per 1 kW of electricity produced) [17]. In the dumps of thermal power plants in Ukraine, 358.8 million tons of ash and slag have been accumulated on an area of about 3170 hectares [19]. About 40 million tons of ash has been accumulated in the dumps of the Burshtynska TPP alone [35]. On the territory of the Ladyzhinska TPP, located in the city of Ladyzhyn, Vinnytsia region, approximately 500 thousand tons of ash and waste are generated annually and currently about 30 million tons of ash and waste with a height of 35 m and a total area of 120 hectares have accumulated [40]. Today, ash dumps of domestic thermal power plants are filled by 50%, and in some cases – by 95% [37].

Coal combustion technologies at Ukrainian thermal power plants mainly provide for a hydraulic method for removing ash and slag with their further storage in ash dumps. To know in detail the properties of ash and slag, it is necessary to study the oxide and radionuclide, mineralogical, elemental composition of the waste, sorption and hydraulic activity, the structure of their surface and the behavior of minerals during the heating process. In terms of chemical composition, ash and slag are a complex mixture of various substances, mainly mineral. The content of various chemical compounds in the ASW directly depends on the type and composition of the fuel. For facilities of the fuel and energy complex of Ukraine, which use coal fuel of different grades, the concentrations of components in the ASW differ within certain limits, but in most cases the main ash-and-slag-forming components are oxygen compounds of calcium, magnesium, silicon, aluminum and iron. Also, a small part of the elements is present in the ashes in the form of sulfates $CaSO_4$, $MgSO_4$ and $FeSO_4$ [41].

In table 7 shows the average chemical composition of the mineral part of ash and slag from thermal power plants.

Table 7 – Average chemical composition of the mineral part of ash and slag waste from TPPs (CHPs) (Table taken from articles [41, page 61])

Thermal power enterprise	Mineral ash and slag-forming components, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
Starobeshivska TPP	44–50	24–30	8–6	2.5–4.6		–		1.2
Mironivska TPP	67.8	19.8	10.9	5.5		2.8		2.1–7
Uhlegorska TPP	16.7	40.6	23.0	8.4		–		0.02
Kramatorska CHP	49.4	22.5	17.1	10.05		–		–
Burshtynska TPP	48.6	23.3	15.3	4.4	2,2	0.5	1.6	0.47
Clarke content in the earth's crust	55.3	14.3	6.7	4.8	3,3	3.2	3.1	–

According to Table 7, the bulk of the ASW, on average, consists of silicon oxides – 45–60%, calcium – 2.5–9.6%, iron – 4.1–10.6%, magnesium – 0.5–4.8 %, aluminum – 10.1–21.8% and sulfur trioxide – 0.03–2.7% [41]. The qualitative chemical composition of ash and waste is quite close to the composition of sedimentary rocks, and it may seem that ash and slag do not pose an environmental hazard. However, it is not. The content of a number of the ASW components can significantly exaggerate their concentration in the earth's crust. For example, the content of MgO in ash and slag can be 2–3 times higher than the Clarke value, Al_2O_3 by 2 times, Fe_2O_3 by 1.5–3 times, CaO by 4–12 times, so storing such waste in natural conditions can lead to the disruption of the existing ecological balance [41].

In addition, ash and slag in its phase and mineralogical composition are quite different from sedimentary rocks: they consist of an amorphous-vitreous substance (formed by a number of free oxides, mainly CaO, aluminosilicates, silicates, ferroaluminosilicates) and a number of crystalline compounds (magnesium ferrites, quartz and others minerals) [41].

The results of research by the European Business Association (EBA) established that at the end of 2019 in Ukraine, about 360 million tons of ash and slag products had accumulated in the dumps of thermal power plants, approximately 0.5–0.7 million tons or 8.3–11.7% are recycled annually, which much less compared to other countries [42].

According to the coordinator of the EBA Committee on Ecology and Sustainable Development, Ukraine can achieve a higher level of use of waste thanks to a balanced environmental and economic policy. To do this, it is necessary to: develop standards for ash and slag products; launch a system of "green" public procurement; initiate the implementation of a program for the construction of cement concrete roads; apply financial instruments to stimulate waste recycling; increase rent for the extraction of crushed stone and sand; approve a mechanism for compensating the costs of transporting slag by rail [42].

Some of the listed points are already being implemented.

In Ukraine, there is a modern updated regulatory framework for the use of fly ash and slag in the production technology of various building materials: DSTU (State Standard of Ukraine) B V.2.7-205:2009 "Building materials. Thermal power plant fly ash for concrete. Specifications"; DSTU B V.2.7-128:2006 "Active mineral additives and filler additives for cement. Specifications"; DSTU B V.2.7-211:2009 "Building materials. Ash and slag mixtures of thermal power plants for concrete. Specifications"; SOU 42.1-37641918-104:2013 "Fly ash and ash-slag mixtures of thermal power plants for road works. Specifications"; GBN V.2.3-37641918-554:2013 "Automobile roads. Layers of road clothing from stone materials, industrial waste and soils reinforced with cement. Design and construction."; DSTU B V.2.7-46:2010 "Cements for general construction purpose. Technical conditions"; DBN V.2.3-4:2007 "Transport facilities. Automobile roads."; DSTU B V.2.7-30:2013 "Non-metallic materials for crushed stone and gravel foundations and road surfaces. General technical conditions."

Over 500 thousand are used annually in Ukraine tons of ash and slag (for the production of cement, concrete, etc.). In 2015, a road construction project was launched using ash and slag materials, in particular for excavation work: fly ash (for the construction of roadbeds, filling embankments and stabilizing soils, as a slow-hardening, independent binder or active hydraulic additive); slag crushed stone (for crushed stone bases and as a filler in road pavement structures); ash and slag mixture (for the construction of embankments of the roadbed – soil substitute 20–60 thousand m3 of ash and slag mixtures per 1 km of road; lower layers of foundations as drainage and frost protection layers – substitute for crushed stone-sand mixtures - 5–20 thousand m3 per 1 km of road). The advantages of using the ASW are obvious [16]:

– an effective substitute for natural materials – wear-resistant, universal, frost-resistant, has binding properties, complies with DSTU B V.2.7-205:2009, DSTU B V.2.7-211:2009, used in the production of building materials, in world practice – for the production of household items: doors, beds, etc.;

– cost savings (reduces the cost of production of building materials by at least 15–20%; on average, reduces the cost of road construction work by 30% - 300 thousand UAH per 1 km of road base);

– environmental friendliness (reducing the load on ash dumps of thermal power plants and increasing the environmental safety of the environment);

– availability throughout the country.

Another component of the ASW that is in consumer demand is microspheres (cenospheres) of fly ash. These are hollow ash balls with an average size of 20 to 500 microns with solid non-porous walls with a thickness of 2 to 10 microns, filled with a mixture of nitrogen and carbon dioxide under reduced pressure (about 0.3 atm). They are formed in the furnaces of thermal power plants during high-temperature flaring of coal. Depending on the composition of the coal, microspheres can be aluminosilicate or ferrosilicate. The latter have pronounced magnetic properties. The unique combination of such qualities of this product as an almost ideal spherical shape, low bulk density, high mechanical strength, thermal stability and chemical inertness, has provided a wide range of applications for cenospheres abroad in the production of thermal insulation materials, radiotransparent ceramics, fillers of composite materials and materials for oil and gas wells. Along with this, microspheres are also a promising raw material for the production of catalysts and adsorbents based on them, capable of functioning under conditions of aggressive environments and high temperatures. In 2015, the sales volume of ash and slag materials amounted to 348.2 thousand tons, and sales revenue was $5 million USA. At the same time, 31.5 thousand tons of ash microspheres were sold to customers in export markets. Aluminosilicate microspheres are widely used in construction, oil, gas, chemical industries and other industries. The production of building materials is the main material base of the country's construction complex and has a significant impact on the pace of economic development and the socio-economic state of society as a whole [36, 37, 42].

Considering the diversity of rocks hosting coal seams and their mineralogical composition, it is of practical interest to develop a technology for enriching the ash portion of slag and fly ash in order to extract useful minerals and metals. For example, it has been established that the slags of the Zelenodolska TPP have high iron content; the slags of the Prydniprovska TPP have a high aluminum content, etc. Thus, there is a need to quantitatively assess the chemical composition of ammonia and study the possibility of their enrichment [43, 44].

Fly ash is a valuable raw material for processing and subsequent disposal. Using the methods of chemical analysis and magnetic separation, the content of unburned carbon in certain classes of size (under-combustion) was established in its composition up to 20% [43, 44] and magnetically susceptible iron up to 30% (in aggregates) [43]. This indicates the feasibility of its complex processing in order to extract carbon, iron and silicate parts with further utilization of these products. Obviously, it is necessary to start such processing with dry ash to eliminate the replenishment of the ash dump, and the already accumulated dumps should be considered technogenic and suitable for subsequent complex processing.

There is positive experience in extracting unburned carbon from fly ash by fine classification on screens [43–50], as well as in separating coal and quartz particles from fly ash at the Novo-Kramatorska Thermal Power Plant in a hydraulic apparatus [51]. With a daily consumption of about a thousand tons of coal at thermal power plants, the return of up to 20% of the carbon extracted from the ash allows us to reduce the amount of purchased coal and transportation costs for its delivery from the station. Considering that the products of complex ash processing have a fine fraction that is convenient for further use, this eliminates expensive raw material preparation operations. For example, the resulting iron and aluminum powders are suitable for producing parts and assemblies by the pressing method, as well as silicates for molding building structures [43, 44].

Despite the positive changes, the volume of the ASW recycling in Ukraine remains quite low, from 8.3–11.7% according to [41] to 35% [16].

Factors preventing the large-scale use of ash and slag materials in Ukraine: unformed market for consumption of ash and waste; conservatism of the road construction sector; insufficient funding for road construction programs; organizational changes in the structure of state management of road construction; lack of incentives for the use of ash and slag at the state level.

Processing of ash and slag waste from thermal power plants is an important environmental and scientific problem that requires an integrated approach, the solution of which requires:

– use the experience of developed countries in increasing the volume of utilization of fly ash, slag and other technogenic mineral impurities in various fields;

– develop new and improve existing standards for ash and slag products;

– launch a system of “green” public procurement;

– initiate the implementation of a program for the construction of cement concrete roads;

– apply financial instruments to stimulate waste recycling;

– increase rent for the extraction of crushed stone and sand;

– approve a mechanism for compensating the costs of transporting slag by rail.

Generalization of successful examples of the use of ash and slag in countries around the world [11, 16, 18].

In Germany, 3.1 million tons of cement are replaced with ash. For comparison, in 2020 Ukraine produced 9.7 million tons of cement. In Germany, ash and slag are used in unbound admixtures for embankment or dam construction. Recycling of the ASW in the USA accounts for 80% of its generation. In the UK, most ash and slag are used as admixtures in road pavement structures. In Poland, the use of the ASW is associated with minimizing the transport distance between the supplier of raw materials (thermal power plants) and consumers (road construction). In France, coal ash is widely used in a mixture with stones, sand, lime ash, lime admixtures and other impurities for road construction. In the Great Britain, Poland and China, fly ash is added to autoclaved aerated concrete production technologies. Autoclave technology for the production of silicate materials makes it possible to partially replace traditional binders, such as lime and especially Portland cement, which are constantly increasing in price, with non-scarce raw materials - solid fuel ash [42]. Since 1951, London has had its first aerated concrete plant, built next to a coal-fired power station. Due to the closure of coal-fired power plants, factories are switching to sand. In Ukraine, fly ash is not used in the production of autoclaved aerated concrete. This is due, on the one hand, to the availability of high-quality quartz sand, higher costs for transporting fly ash compared to quartz sand, and the lack of guaranteed stability of ash properties, which is extremely important and noticeable in the production of low-density aerated concrete [42].

With existing methods of use and available technologies, ash and slag wastes become valuable materials that are used in road construction and in the production of: cement, concrete (heavy, porous, heat-resistant), reinforced concrete products and structures, bricks, lightweight aggregates for concrete, dry construction mixtures, asphalt concrete mixtures, etc., thermal insulation, abrasives, roofing materials, ceramic tiles [16, 52–55].

In Ukraine, road construction using ash and slag materials is being successfully implemented. The direction of selling fly ash microspheres (cenospheres) on export markets is being developed. Aluminosilicate microspheres are widely used in construction, oil, gas, chemical industries and other industries. The production of building materials is the main material base of the country's construction complex and has a significant impact on the pace of economic development.

Prospects for using the ASW as an additional raw material.

In the context of the energy crisis, environmental problems associated with territorial pollution, Ukraine should use the experience of developed countries in increasing the volume of use of fly ash, slag and other technogenic mineral impurities in various fields.

Table 8 shows promising areas for using the ASW.

Table 8 – Prospective directions for using the ASW

Scope of use	Directions for use
During construction work	Green roof and landscaping; Street furniture; building facing material; sidewalk; ceiling tiles; carpet backing; floor tiles and tile underlay; backfill – foundation support; structural pouring of the foundation; poured concrete foundation; mortar, plaster and stucco; masonry block; main material; pressing into bricks; production of wall slabs; wood substitute.
During road works	Embankments; retaining wall; asphalt surface and asphalt base; granular base and sub base; subgrade – original soil; structural content; swamps – swamps with vegetation; stabilization of soil under the highway.
Agriculture	Removal of inorganic components from wastewater.
Treatment of wastewater from various industrial sources	Removal of toxic metals from wastewater; phenolic compounds; dyes from wastewater; fly ash leaching in water supply.

Fly ash has great potential in environmental applications and is an interesting alternative to replace activated carbon or zeolites for air adsorption or water purification. The adsorption characteristics of fly ash are highly dependent on its origin and the chemical treatment used for activation. To date, most areas of use of the ASW have been implemented only on a laboratory scale and require additional research to move to industrial practice.

4. Conclusions

Thus, on the one hand, the ASW are technogenic mineral formations that are produced in large quantities and pose a serious environmental hazard, on the other hand, they are valuable mineral raw materials for the production of various materials, housing, road, rural and industrial construction, agriculture, mining and oil industry.

In accordance with the stated goal, foreign and Ukrainian experience in processing ash waste from thermal power plants was studied. The experience of the ASW processing in world practice is analyzed. Factors that hinder the large-scale use of ash and slag materials in Ukraine and the necessary measures to increase recycling volumes have been identified. Successful examples of the use of the ASW in countries around the world are summarized. Promising directions for their use as additional raw materials have been identified. Thanks to the use of ash and slag materials, significant cost savings will be achieved compared to traditional options using natural raw materials. The use of the ASW only in road construction reduces the cost of production of building materials by at least 15–20%; on average, the cost of road construction works is reduced by 30% – 300 thousand UAH per 1 km of road base. This will make it possible to extract significant profits from sales of the ASW processed products and significantly improve the environmental condition of the territories.

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ПЕРЕРОБКА ЗОЛОВІДХОДІВ ТЕПЛОВИХ ЕЛЕКТРОСТАНЦІЙ: ЗАРУБІЖНИЙ ДОСВІД І УКРАЇНСЬКІ РЕАЛІЇ

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Аннотація. Золошлакові відходи є техногенними мінеральними утвореннями, які виробляються у великих кількостях і становлять серйозну екологічну небезпеку. З іншого боку – це цінна мінеральна сировина для різних матеріалів, житлового, дорожнього, сільського та промислового будівництва, сільського господарства, гірничодобувної та нафтової промисловості. Відповідно до поставленої мети вивчено зарубіжний та український досвід переробки золовідходів теплових електростанцій. Проаналізовано досвід переробки золошлакових відходів у світовій практиці. Встановлено фактори, що перешкоджають широкомасштабному використанню золошлакових матеріалів в Україні та необхідні заходи для підвищення обсягів утилізації. Узагальнено успішні приклади використання золошлакових відходів у країнах світу. Визначено перспективні напрями їх використання як додаткову сировину. Завдяки застосуванню золошлакових матеріалів буде досягнуто значної економії коштів у порівнянні з традиційними варіантами з використанням природної сировини. При наявних методиках використання та доступних технологіях ЗШО стають цінними матеріалами, що використовуються у дорожньому будівництві та у виробництві: цементу, бетонів (важкі, пористі, жаростійкі), залізобетонних виробів та конструкцій, цегли, легких заповнювачів для бетону, сухих будівельних сумішей, асфальтобетонних сумішей і т.п., теплоізоляції, абразивів, покрівельних матеріалів, керамічної плитки. В Україні успішно реалізується будівництво дороги із використанням золошлакових матеріалів. Розвивається напрямок з реалізацією на експортних ринках мікросфер (ценосфер) летючої золи. Алюмосилікатні мікросфери знайшли широке застосування у будівництві, нафтовій, газовій, хімічній промисловості та інших галузях. Виробництво будівельних матеріалів є основною матеріальною базою будівельного комплексу країни та істотно впливає на темпи розвитку економіки. Україна може досягти більшого рівня використання золошлакових відходів завдяки виваженій екологічній та економічній політиці. Для цього необхідно: розробити стандарти для золошлакової продукції; запустити систему «зелених» державних закупівель; ініціювати реалізацію програми будівництва цементобетонних шляхів; застосовувати фінансові інструменти для стимулювання переробки відходів; підвищити ренту на видобуток щебеню та піску; затвердити механізм компенсації витрат за перевезення золошлакових відходів залізницею. Це дозволить одержувати суттєвий прибуток з продажу продуктів переробки золошлакових відходів та значно покращити екологічний стан територій.

Ключові слова: вугілля, золошлакові відходи теплових електростанцій, продукти згоряння вугілля, переробка, досвід переробки, летуча зола, котельний шлак, фосфогіпс.