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Fly ash – a valuable material for the circular economy

Introduction

Electricity generation in Poland and in most countries around the world is still based on coal. This results in originating large amounts of energy waste. In order to emphasise its raw material potential, that kind of waste is often called coal combustion by-products (CCPs). It includes i.a.: fly ash, slags, ash and slag mixtures from furnace wet waste disposal, fly ash microspheres, or mixtures of fly ash and solid waste from waste gas calcium desulphurisation methods. The storage of these waste products is associated with their negative impact on the environment. This is why research has been undertaken worldwide on the implementation of the concept of a circular economy, where the final amount of waste would be minimal due to multiple use of coal combustion by-products. This is particularly important considering the fact that approx. 150 million tonnes of coal combustion by-products are produced annually in Europe alone, of which over 20 million tonnes are generated in Poland (Szczygielski 2019). The management of such a huge amount of material can bring benefits for both the natural environment and the economy. Although research on the utilisation and effective management of waste has been carried out in many institutions

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for many years, further scientific research into new directions of CCPs use remains a top priority. One of the most valuable types of energy waste in Poland is fly ash, obtained mainly from exhaust gases in dry electrostatic precipitators (Uliasz-Bocheńczyk et al. 2015). Due to the different composition of the fuel, as well as the use of different combustion technologies, the ash grains exhibit a high degree of variability in their chemical, phase, or morphological composition. The selection of the appropriate direction of applying these coal combustion by-products forces the need to conduct research not only on their composition, but also on their physico-chemical properties. A number of such studies was performed in order to meet the requirements of applicable standards and application approvals (Hycnar 2009).

In European standards, the factors determining the further use of fly ash are primarily the chemical composition, which is determined, among others, by the type of mineral substance present in the coal and the type of coal burned. The main components of hard coal fly ash are silica SiO_2 and alumina Al_2O_3. Ashes resulting from the combustion of brown coal are generally richer in calcium and magnesium oxides, with a lower content of silica SiO_2. Such composition implies their properties. Siliceous ashes exhibit pozzolanic properties, and calcium can additionally exhibit hydraulic properties (Giergiczny 2013). A different chemical composition is characteristic for ash from fluidised bed boilers, and yet another for ash and slag mixtures from wet waste disposal. Thus, the way of managing them must necessarily vary. In order to efficiently utilise raw materials and reduce the negative environmental impact of combustion by-products, it is necessary not only for the scientific institutions to conduct research, but also for coal-based energy companies to become active in this area (Bielecka 2017). As shown in the paper (Bielecka and Kulczycka 2020), the current priority of power plants is the use of combustion technologies that ensure air protection.

According to the authors (Hycnar et al. 2017), the introduction of a circular economy in the management of energy waste forces the need for a new approach to the development of power industry. When building new power units, the production of mineral products should be taken into account apart from the production of heat and electricity. Correcting the chemical composition of the burned coals with appropriate additives and controlling the thermal parameters makes is possible to plan the creation of new products with added value. The creation of raw materials/products on the basis of coal combustion by-products will ensure achieving the desired economic effects. The latest studies on the readiness of the seven largest power plants in Poland to change in the direction of circular economy, conducted by Bielecka and Kulczycka (Bielecka and Kulczycka 2020), indicate, however, that the greatest obstacle in the implementation of CE (circular economy) is the lack of precise guidelines in this regard. According to the authors of the paper (Bielecka and Kulczycka 2020), in order to capture the economic effects, it is necessary to present the environmental effects in the form of measurable indicators showing the value that can be obtained by creating a product instead of waste. Companies need such indicators to be able to plan appropriate activities. This can be achieved by introducing a circular business model and its indicators.

In the study of coal combustion by-products, much attention is also paid to their physical properties. Both the particle size distribution of the waste and the morphology of the particles directly affect the way of their disposal or management. Awareness of these properties allows to predict the mechanical and physical properties of materials obtained on the basis of these ashes. One of the stages that should be taken into account when working on the economic use of waste is the proper identification of its phase composition. Extensive microscopic and X-ray examinations of waste has allowed to distinguish glass and crystalline phases in coal combustion by-products. These include i.a.: mullite, quartz, magnetite, hematite, and in limestone ash, additionally, anhydrite, calcium oxide, portlandite, hannebachite, brownmillite, gehlenite, or akermanite (Jończy et al. 2012). On the basis of the obtained results, conclusions can be drawn regarding the combinations in which individual elements occur in the waste and the degree of weathering of individual components. Since the variability of fly ash manifests itself in the diversity of its chemical and mineral components, one of the methods of ash management may be to physically separate these components (e.g., electrostatic, triboelectric, foam, or gravity separation) and use them in various areas of economy and life.

This paper presents selected valuable components of fly ash (Figure 1), increasingly in demand in the industrialised world, as well as the potential possibilities for their use.

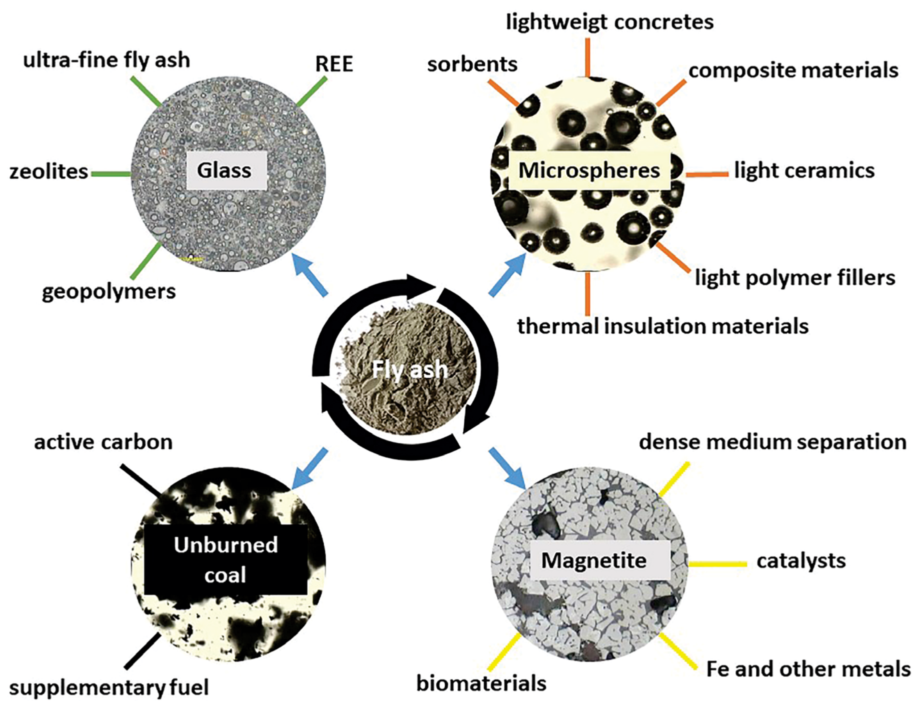

Fig. 1. Selected fly ash components and their possible applications

Rys. 1. Wybrane składniki popiołów lotnych i możliwości ich zastosowań

1. Materials and methods

This paper is based on a systematic review of Polish and English literature from 1997 to 2021, and is also partly based on the author's own research. The microscopic photographs of fly ash components from Polish power plants presented in the article were taken using a Zeiss Axioskop and Axioplan microscope for transmitted and reflected light at a magnification of 100, 200, and 500×.

2. Microspheres

Microspheres are a by-product of coal combustion – one of the most valuable ones. Most often they are spherical, gas-filled ash particles with a density lower than that of water, which facilitates their wet separation (Figure 2). There are also attempts to recover microspheres via the dry method, using air as a "fluid" separation medium (Ramme et al. 2013). The content of microspheres in ashes is low, up to a maximum of 5% by weight (usually, however, less than 1%) and depends on the type and size of coal particles burned, as well as the applied combustion technology (Łączny and Wałek 2011). The diameter of the microspheres usually ranges from 5 µm to 500 µm, and their sphericity decreases with increasing diameter (Strzałkowska and Stanienda-Pilecki 2018). The wall thickness of the microspheres varies even within the same grain. It generally accounts for 2% to 12% of their diameter. It has been noticed that particles with thicker walls show greater porosity (Figure 2d) (Strzałkowska and Stanienda-Pilecki 2018). Based on the research, it was concluded that the highest content in the composition of the solid phase was demonstrated by silica SiO_2 and alumina Al_2O_3. There is a noticeable tendency for the SiO_2/Al_2O_3 ratio to decrease with the growing size of the microspheres (Strzałkowska and Adamczyk 2019).

The phase composition of the microspheres reflects their chemical composition. The walls of the microspheres are mainly composed of the amorphous phase with crystalline inclusions (Blanco et al. 2000). The amorphous phase may constitute as much as 90% of their composition (Ranjbar and Kuenzel 2017), and its content depends on the illite content in the combusted coal (Spears 2000). The main crystalline components of the microspheres are quartz and mullite (Blanco et al. 2000; Pichór and Petri 2003; Strzałkowska 2017). The mineral precursor to these components is kaolinite present in coal (Fomenko et al. 2011; Spears 2000). In addition to quartz and mullite, the following were also established in the microspheres: plagioclases, potassium feldspars, gypsum, hematite, magnetite, as well as calcite and dolomite (Vassilev et al. 2004a; Żyrkowski et al. 2016; Strzałkowska 2017). The last of the aforementioned phases arise as a result of later crystallisation during the wet separation of microspheres (Ranjbar and Kuenzel 2017). The special properties of microspheres resulting from their chemical and phase composition, i.e. high mechanical strength, refractoriness, frost resistance, as well as low density and absorbability, imply the directions of their potential application. In recent years, there have been many publications informing

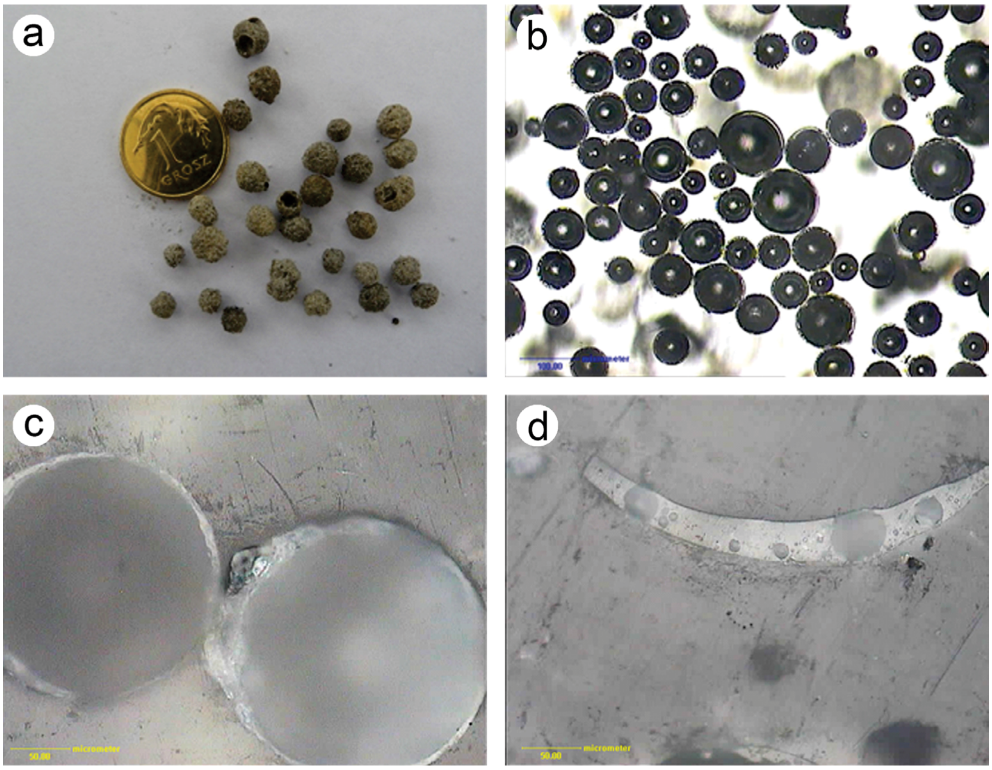

Fig. 2. Microspheres
a) macroscopic view; b) microscopic view in transmitted light; c, d) microscopic view in reflected light

Rys. 2. Mikrosfery
a) widok makroskopowy; b) widok mikroskopowy w świetle przechodzącym;
c, d) widok mikroskopowy w świetle odbitym

about the possibilities of using this coal combustion by-product. They include the production of plastic composites and a wide range of construction materials (acoustic, fire-resistant, and materials with improved thermal properties) (Pichór 2005; Wajda and Kozioł 2015). Their use in concrete technology may be an alternative solution for aerating fresh concrete mixes, which is extremely important considering the prices of aeration admixtures (Haustein and Kuryłowicz-Cudowska 2020). Microspheres have also been used in the production of light polymer fillers, as well as paints and varnish coatings. There are also promising attempts to use microspheres as sorbents, e.g. in the neutralisation of radioactive waste (Haustein and Quant 2011; Wajda and Kozioł 2015). Another advantage of aluminosilicate microspheres is the lack of any harmful effect on living organisms, which extends the scope of their application.

3. Magnetic fraction

One of the directions of using fly ashes may be the recovery of the magnetically susceptible phases they contain. The content of these phases in the ash ranges from 0.5 to 18% (Zyryanov et al. 2011) and varies depending on the type of coal and boiler operating conditions. The magnetic fraction in fly ash consists mainly of iron oxides in the form of magnetite and hematite (Vassilev et al. 2004b; Jończy et al. 2012). The content of quartz and mullite is usually low, lower than 3%. The magnetic fraction of brown coal ashes is characterised by a more complex phase composition, as the occurrence of the following has also been recorded: akermanite, anortite, free CaO, anhydrite, and syngenite (Strzałkowska 2021). Microscopic examinations allowed for the observation of the microstructure of these particles (Figure 3). Most magnetic particles are spherical and their diameter is generally 2±3 times smaller than that of the microspheres. The separation of this phase, similarly to the microspheres, can be carried out both dry and wet. The main factors limiting this process are the presence of iron-containing paramagnetic mineral and amorphous matter, and the

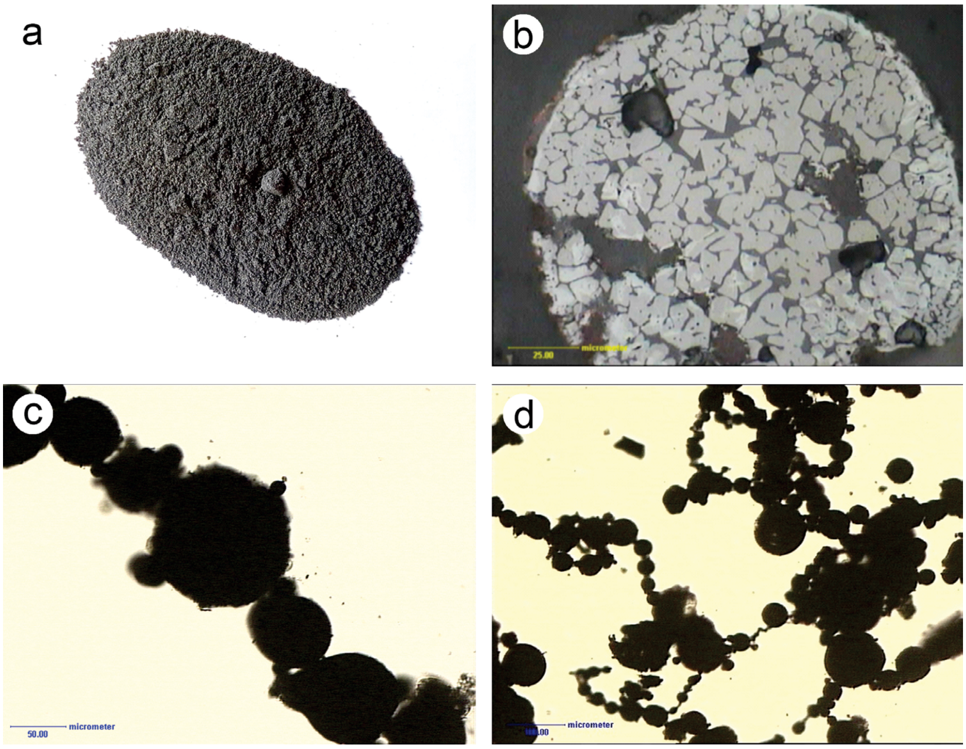

Fig. 3. Magnetite
a) macroscopic view; b) microscopic view in reflected light; c, d) microscopic view in transmitted light

Rys. 3. Magnetyt
a) widok makroskopowy; b) widok mikroskopowy w świetle odbitym;
c, d) widok mikroskopowy w świetle przechodzącym

existence of particles that are aggregates of magnetic and non-magnetic phases (Strzałkowska 2021). Ferrospheres present in ashes are characterised not only magnetic properties, but also high catalytic activity, thermal stability, and mechanical strength. Because of that, they can be used in many branches of the economy (Zyryanov et al. 2011; Sokol et al. 2002). The smallest magnetic particles, due to the strong development of the surface, can be easily modified. Combined with their magnetic properties, this opens a wide range of applications in biomaterial engineering. The literature also contains reports on enrichment of magnetic particles – not only with iron, but also with: Mn, Co, Ni, Cu, Zn, Mo, and Cd. The magnetic fraction can therefore be treated as an alternative source of other metals (Hycnar et al. 2015; Bielowicz et al. 2018; Strzałkowska 2021). Removal of the magnetically susceptible phases from the fly ash leads to iron-rich products on the one hand, and on the other hand it improves the properties of "refined ash." This is particularly important in applications of ashes where iron is an undesirable component or where there are limitations to its content in the end product. An example is the use of fly ash in the production of cement and concrete. The presence of large amounts of iron in the form of magnetite and hematite may adversely affect the course of the pozzolanic reaction (Giergiczny 2013).

4. Unburned coal

Unburned coal is an undesirable component of fly ash. It is concentrated mainly in the coarser grain grades. The grain size, chemical and technical properties of the burned coal determine the presence of unburned organic matter in the coal combustion by-products. The combustion technology itself also plays an important role here – including the combustion temperature, excess air, and the efficiency of the furnace (Misz 1999). Organic particles present in the coal combustion by-products exhibit very large diversity in terms of morphology (Figure 4). Because of this fact, attempts have been made for years to classify the morphological forms of unburned organic matter. The literature on this subject is very extensive (Misz 2002; Lester et al. 2010; Misiak 2015). As massive forms disappear with increasing burnout, porous forms with a strongly developed surface are dominant in the coal combustion by-products (Figure 4c). Fine spherical glass grains often accumulate inside these porous particles (Figure 4d). The presence of unburned coal in the ash determines its further use. It also indirectly indicates the course of the combustion process (Hower et al. 2017). The Polish standard for the application of these coal combustion by-products in concrete categorises ashes depending on their content of unburned coal, denoted as loss on ignition. This is due to the fact that along with the increase in loss on ignition, the water demand of ash increases, which may result in a lower durability of concrete (Giergiczny 2013; Hower et al. 2017). In coal fly ash obtained in commercial power plants in Poland, the value of loss on ignition usually ranges from 1 to 5% (Giergiczny 2013). Yet the loss on ignition is not only caused by the destruction of unburned coal, but it is also due to the breakdown of mineral phases and physically adsorbed water in samples. This is why the content of unburned coal

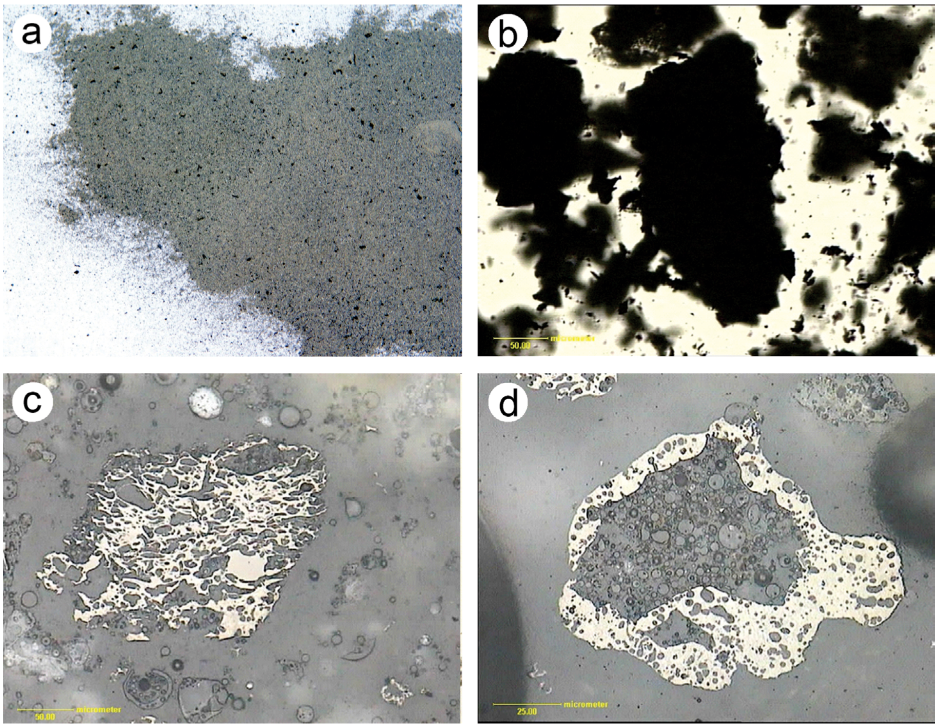

Fig. 4. Unburned coal particles in fly ash
a) macroscopic view, b) microscopic view in transmitted light; c, d) microscopic view in reflected light

Rys. 4. Niespalone cząstki węgla w popiele lotnym
a) widok makroskopowy; b) widok mikroskopowy w świetle przechodzącym;
c, d) widok mikroskopowy w świetle odbitym

might seem higher (Hower et al. 2017). The presence of unburned coal also affects the colour of mortars and concretes based on ash. Moreover, it changes their rheological properties. There is, therefore, a double benefit in separating these particles. It improves the properties of "purified ash", and on the other hand, unburned coal can be converted into activated carbon, or possibly used as a supplementary fuel (Batra et al. 2011). The technologies used worldwide to capture combustible substances from coal combustion by-products allow for almost 100% energy recovery from coal products and for obtaining mineral materials characterised by a high degree of purity (Olszewski et al. 2012).

5. Glass

Glass is the main component of fly ash. Its content ranges between 50 and 90% (Aughenbaugh et al. 2013; Ward and French 2006). The colour of the glass is usually yellowish, white, or brown and reflects its chemical composition (Figure 5). Due to the reactive silicon and aluminium present in the glass phase, fly ash is characterised by pozzolanic activity. Due to that, it is used mainly in construction as a cement component and additive.

These uses can reduce greenhouse gas emissions by minimising the consumption of primary resources, which is in line with the CE strategy.

The next stage of ash refinement may be the separation of ultra-fine particles containing more of the glass phase. These particles are characterised by a particularly high sphericity and a strongly developed specific surface (Figure 5d). Mortars based on these particles are characterised in the initial setting period by strength comparable to Portland cement and long-term strength exceeding the reference parameters by 10–23% (Nowak et al. 2018). Such ultra-fine ash can be used for the production of high-quality concretes and other specialist products in the cement and concrete industry as well as construction ceramics (Nowak et al. 2018).

Due to the similarity of the chemical composition of the glass to some natural materials, fly ash can also be used as a raw material for the synthesis of zeolites or geopolymers (Mikuła and Łach 2015). Research on the synthesis of zeolites from fly ash has produced very

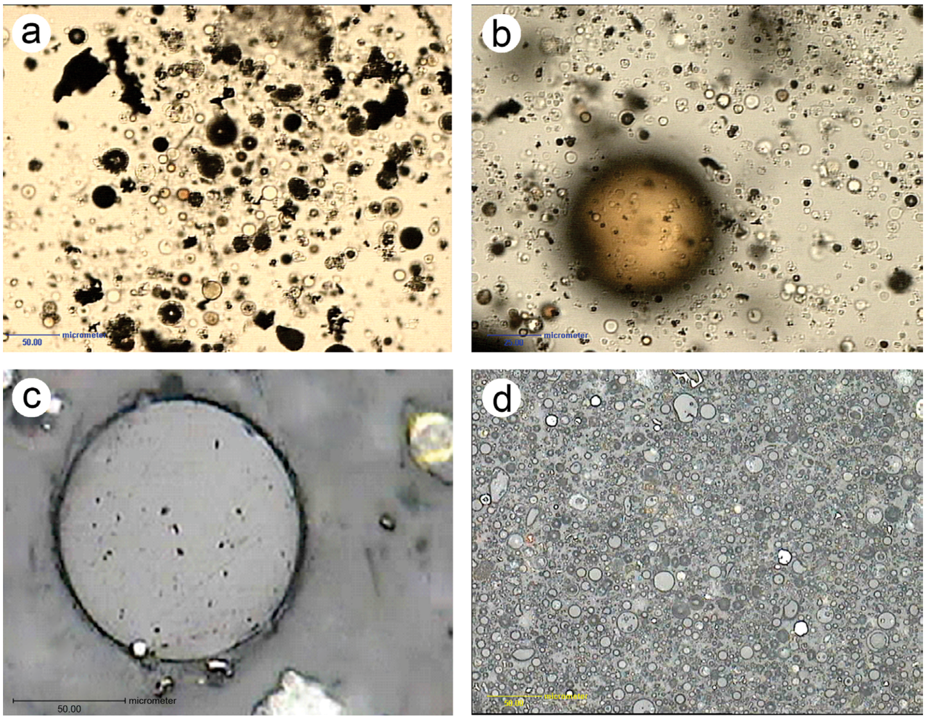

Fig. 5. Glass in fly ash
a, b) microscopic view in transmitted light; c, d) microscopic view in reflected light

Rys. 5. Szkliwo w popiele lotnym
a, b) widok mikroskopowy w świetle przechodzącym; c, d) widok mikroskopowy w świetle odbitym

encouraging results. Depending on the applied method (synthesis temperature and reagents used), different zeolites have been obtained (Adamczyk et al. 2005; Franus 2012; Bandura et al. 2015). Due to their adsorption, catalytic, and ion-exchange properties, the use of zeolites seems unlimited. Experiments on geopolymers are conducted mainly for their large--scale application in construction. On the basis of geopolymers obtained from fly ash, mainly geopolymer concretes are created. They are characterised by i.a. high compressive and tensile strength, as well as increased resistance to chemical corrosion and low temperatures (Tora 2019). Fly ash can also be regarded as an alternative source of both major and trace elements (Hycnar et al. 2015). Trace elements are commonly present as impurities in the glass phases (Vassilev 1997). In recent years, research has been initiated on the possibility of recovering rare earth elements from fly ash. This is considerably important, as the demand for these metals continues to increase, especially for those used in modern technologies (Mayfield and Lewis 2013; Hycnar et al. 2015; Kolker et al. 2017; Adamczyk et al. 2020).

Conclusions

Apart from the commonly known applications of fly ash, there are prospective directions of their use, including application as: sorbents, catalysts, raw material for the synthesis of zeolites, or innovative materials such as geopolymers. However, this requires the valorisation of the ashes through their earlier processing, in line with market needs. This will make it possible to obtain larger quantities of products characterised by high utility values, tailored to the requirements of various industries. After the separation of valuable components (microspheres, magnetic fraction, critical raw materials, etc.), the ash residue can be managed in the same way as before. On the basis of the information presented in the paper, it can be concluded that apart from the obvious benefits associated with activities aimed at environmental protection (avoiding land-filling of waste on the surface), the economic use of ashes has other benefits. Attention should be paid to the economic effects such as obtaining products while reducing the costs of their production, and to the social effects like, for example, the creation of new jobs.

This use of ash is a procedure conductive to actions not only supporting the lithosphere, but also the entire natural environment. Therefore, in the case of fly ash, we can intentionally consider a circular economy, since the waste generated in one process can be used as a raw material in the next.

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FLY ASH – A VALUABLE MATERIAL FOR THE CIRCULAR ECONOMY

Keywords

microspheres, magnetic fraction, glass, unburned coal

Abstract

Generation of coal-based electricity is always associated with the origination of large amount of combustion waste. The presented article is a review concerning the possibilities of innovative directions of management for one of the by-products of coal combustion: fly ash. The storage of these waste products is associated with their negative impact on the environment. This is why research has been undertaken worldwide on the implementation of the concept of a circular economy. This article includes the examination of basic physical, chemical, and mineralogical properties of the most valuable components of fly ash (microspheres, magnetic fraction, and glass). It contains the examination of methods of separating these components and indicates the prospective directions of their use, e.g. as light fillers for polymers, sorbents, catalysts, composite materials, light ceramics, lightweight concretes, thermal insulation materials, biomaterials, raw material for the synthesis of zeolites or geopolymers. The paper also presents the components of fly ash, which can be treated as an alternative source of valuable elements, including critical elements. Moreover, it points to the necessity of capturing flammable substances from combustion by-products in order to obtain raw material characterised by a high degree of purity. It has been demonstrated that this way of ash management can lead to high recycling rates and bring valuable materials back to the economy. Such actions fit perfectly into global efforts for sustainable development and the circular economy.

POPIÓŁ LOTNY – CENNY MATERIAŁ DLA GOSPODARKI O OBIEGU ZAMKNIĘTYM

Słowa kluczowe

mikrosfery, frakcja magnetyczna, szkliwo, niespalony węgiel

Streszczenie

Wytwarzanie energii elektrycznej opartej na węglu wiąże się zawsze z powstawaniem dużej ilości odpadów paleniskowych. Prezentowany artykuł ma charakter przeglądowy i dotyczy możliwości innowacyjnych kierunków zagospodarowania jednego z ubocznych produktów spalania węgla – popiołu lotnego. Składowanie tych odpadów wiąże się z ich negatywnym oddziaływaniem na środowisko, dlatego na całym świecie podjęto badania nad wdrażaniem koncepcji gospodarki obiegu zamkniętego. W artykule omówiono podstawowe, istotne dla oceny przemysłowej właściwości fizyczne, chemiczne i mineralogiczne najbardziej cennych składników popiołów lotnych (mikrosfer, frakcji magnetycznej i szkliwa). Omówiono sposoby wydzielenia tych składników oraz wskazano na perspektywiczne kierunki ich zastosowania np. jako lekkich wypełniaczy polimerów, sorbentów, katalizatorów, materiałów kompozytowych, lekkiej ceramiki, betonów lekkich, materiałów termoizolacyjnych, biomateriałów, surowca do syntezy zeolitów czy geopolimerów. Wskazano składniki popiołów lotnych, które mogą być traktowane jako alternatywne źródło cennych pierwiastków, w tym pierwiastków krytycznych. W celu uzyskania surowca o wysokim stopniu czystości zwrócono uwagę na konieczność wychwycenia substancji palnych z ubocznych produktów spalania. Wykazano, że taki sposób gospodarowania popiołami może prowadzić do wysokich wskaźników recyklingu i sprawić, że cenne materiały będą trafiały z powrotem do gospodarki. Takie działania doskonale wpisują się w globalne wysiłki na rzecz zrównoważonego rozwoju i gospodarki o obiegu zamkniętym.