Means of optimizing coal combustion product utilization

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1. Introduction

As we develop new technologies for the production of energy and materials, we also have to implement environment protection laws; thus, we need a plan for a responsible, large-scale utilization of coal combustion products which are valuable mineral resources. Currently, we obtain CCPs from solid fuel power plants and from landfills. In a number of countries where coal combustion has been reduced, the CCPs already stored at landfills have become a valuable source of soil, aggregates, binders, etc.

In the last 20 years we have been efficient in utilizing coal combustion products and implementing new technologies of CCP utilization, which we owe to the influence of Polish scientists, engineers, economists and industrial managers. The results have also been affected by the implementation of a new system of CCP utilization, which encompasses not only the transportation of CCPs but also the development of new, state-of-the-art technologies of ash beneficiation and refining. Another significant reason for increased utilization of coal combustion products, fly ash in particular, is the fact that our scientists have conducted in-depth analyses of their physiochemical properties and are now able to take advantage of these properties when designing new products.

When optimizing the process of burning coal-based fuels and co-combusting coal and biomass, as well as other products, it is necessary to research the influence that introduced changes have on the usability of fly ash and its environmental impact. Publishing the data, assessments and results of implementation is no less important.

To improve on CCP utilization, we need to consider using it on a mass scale to produce classified, activated and hydrophobic fly ash. In order to design new, high quality products, it is necessary to improve on the production of cenospheres from dry flue gas desulfurization, ore concentrates, as well as micro- and nanofills and carriers. Since the utilization of fly ash from landfills increases, it is possible to make profit from a comprehensive depletion of the lode. The following paper discusses the issue.
Analyses of what amounts of CCPs are being used and how, prove that the problem of their utilization is still a valid one. Simultaneously, though, both in Poland and abroad, new technologies are being developed and new research is conducted, which may eventually result in an efficient use of CCPs, as well as bring economic and ecological profits.

Among many new developments in the discipline we can mention research and implementation of new means for:

- increased recovery of fly ash cenospheres from power plants and landfills;
- increased production and utilization of activated fly ash;
- resuming production of hydrophobic fly ash;
- ore concentrates recovery;
- usability and production of nanoproducts from fly ash;
- using fly ash as an active component of binders, concrete and plastic fillers.

2. Physiochemical properties of fly ash

Knowing the chemical composition, physical properties and mineralogy of fly ash and slag enhances their usability. A number of commonly recognized uses have been further developed by new publications, such as [1] and [2].

While fly ash obtained from burning bituminous coal in conventional boilers meets a number of requirements and can be used in cement, binders, concrete and ceramics, its properties can be enhanced through particle size separation, which creates new possibilities for its use.

Research into the relation between physiochemical properties of fly ash and fine particle content, shows that as the latter increases:

- particle surface area expands;
- pozzolanic activity increases;
- amount of light metal compounds increases;
- rheological properties of cement paste, grouting, etc. improve;
- gas and water permeability decreases;
- amount of components with loadstone characteristics increases periodically.

Preliminary classification is sometimes performed by extracting fly ash from particular sections of electrofilters. Fly ash procured in this way has a globular shape and larger surface
Adding such ash to concrete increases its workability, strength and durability [3].

According to the Institute of Ceramics and Building Materials (ICiMB) in Opole, fly ash demonstrates a similar, and at later stages of hardening even better pozzolanic activity than other known additives, such as metakaolin or silica fume. Unlike silica fume, though, fly ash does not increase hydrophilicity, nor does it decrease workability [5].

Ash collected from bituminous coal combustion has been used in cement and concrete industry for a long time, but only recently has it started to be processed and refined to meet the increased expectations of its properties.

There are a number of processing techniques that can modify the properties of fly ash. Separation of fly ash particles with grain size of less than 30 μm is usually performed in mechanic vibrating sieves. Mass classification of any grain size is usually done in cyclone separators (air classifiers).

Pulverization of fly ash not only expands its surface area, but also increases its hydraulic activity and decreases its permeability, including water permeability of concrete to which such fly ash was added.

As far as high-calcium fly ash from lignite coal combustion is concerned, when thick fractions are pulverized, they release active particles that are globular in shape from inside. As they are round, they decrease the hydrophilicity of such activated ash, despite the expanded surface area and fineness, especially if lumps of incombustible matter are separated simultaneously (figure 3).
Such separation can increase the activity of fly ash under consideration, which has been proven in research.

Pozzolanic activity index has reached a high rate after 28 days of conducting a hydration reaction (well beyond 100% of standard cement strength). Beneficiating fly ash by further pulverization, after coal particles have been extracted, has proven to increase its strength compared to unpulverized ash (figure 4). It needs to be emphasized that these improvements have been achieved using fairly simple technological solutions.

After further pulverization, when the grain reaches the size of nanometers, fly ash develops new properties, which is a result of destroying the original microstructure of the grain and, frequently, releasing certain elements from the particle.

Pulverized ultrafine ash has more grains, larger surface area and is more reactive, thus it manifests new properties. It has been widely used as a resource for producing new high-strength materials and for other purposes. It can also improve the quality of concrete.

Nanotechnologies are a promising means of effective utilization of fly ash and slag, although at the moment they are energy-intensive and thus require particular consideration as far as profitability is concerned.

A change in physiochemical properties of fly ash and separation of particular compounds can also be achieved through various kinds of treatment, such as:

- hydrophobization, which causes hydrophilic or weakly hydrophobic grain surface to become hydrophobic when covered with mineral and synthetic oils as well as active organic compounds (amines, silicones). As a result, the surface treatment of grains makes the fly ash impermeable to water; it also levels the surface tension between ash and oil, as well as ash and organic materials, which renders the ash more usable in deoiling water and wastewater; it can also be used as a plastic and rubber filler as well as a carrier for plant protection products;
- magnetic separation, which separates non-magnetic fractions from the magnetic fractions. As a result, fly ash with lower specific gravity is produced, as well as an iron oxide concentrate that can be used as an element of heavy liquids for mining industry, drilling fluids for drilling industry and as concrete shielding against radioactivity;
- electrostatic separation, which takes advantage of different reaction of various materials to the triboelectric effect in the electric field. This way coke breeze can easily be separated from fly ash;
- thermal treatment. Depending on tempera-
ture, we can dry a wet mixture of ash and its products, dewater gypsum, burn coke breeze in fly ash and slag and conduct a desublimation of light metal oxides, but first and foremost bake (lightweight aggregates) and melt (slag wool, cast metal resistant to abrasion) fly ash and slag;
- flotation separation takes advantage of the wetting ability of fly ash components and can be used to remove grains of coke breeze while releasing cenospheres;
- chemical treatment of grain surface removes absorbed elements (ammonium compounds, mercury, etc.) and produces zeolites and lightweight metal concentrates (germane, gallium). These methods are also used in chemical extraction of aluminium and titanium compounds, as well as any aluminosilicate compounds found in fly ash.

As we develop new technologies for coal combustion and new means of fly ash treatment and utilization, it is necessary to conduct further research on the composition and properties of CCPs and react properly to any problems that may arise. Changes in composition of fly ash that is being produced at the moment are due to the new requirements of environment protection and the need to adjust to these requirements — this concerns especially the co-combustion of coal and biomass and other materials.

Presently, the problem that draws the most attention is the presence of ammonia and compounds of mercury in fly ash [11, 12]. An effective solution to that problem can be found in the EU REACH project.

3. Technologies for extended utilization of fly ash

The assessment of coal combustion product use and changing demands of the market, as well as the necessity to reduce CO2 emission, prove that it is reasonable to produce more of the products already described and develop new products from CCP. As far as the former is concerned, there is a need to recover more cenospheres from fly ash, develop production of activated fly ash and fertilizers. As for the latter, it is advisable to consider producing classified ash (with particular grain size), hydrophobic fly ash, ore concentrates, etc.

Using cenospheres

Cenospheres are superfine grains found in fly ash and slag obtained from conventional coal combustion. They have lower density and thermal conductivity index than fly ash.

Cenospheres are one of the most valuable products obtained from fly ash and are in high demand, as they can be used in thermal insulation, light weighing agents for drilling fluids, plastic fillers, light concrete and other building materials, abrasive tools, catalyst supports and plant health products. Cenospheres have practical applications in:
- automotive industry (composites, tires, casting flasks),
- energetics and technology (drilling fluids, aircraft propeller blades, shells and composites for spaceships),
- recreation business (boats, surfboards, kayaks),
- plastics industry (nylon, polyethylene),
- ceramics industry (fire resistant materials, thermal insulation materials),
- construction industry (façade panels, special cements, grouting and mortars).

Increasing utilization of fly ash has caused the resources for obtaining cenospheres to diminish significantly because less ash is stored in wet landfill sites and consequently, in many cases, these landfills have been closed down. Because of that, different methods of obtaining and refining cenospheres in our possession are insufficient.

Currently cenospheres are produced in a number of countries, the biggest producers being China, Russia and Kazakhstan. Research and implementation in these countries have significantly improved our knowledge of cenospheres [17, 18, 19]. Increased utilization of dry fly ash has depleted the resource base for the production of cenospheres. The amount of fly ash stored in wet landfills has been significantly reduced and in many cases they had to be closed down.

In Poland, as far as obtainment and beneficiation of cenospheres from fly ash is concerned, there have been no significant improvements, so it advisable to take a much closer look at the issue. Figures 5 and 6 demonstrate the structure
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of a cenosphere and the results of the composition analysis of the surface glaze of a cenosphere (point 1) and the insides of the cenosphere (point 2) [20].

The analysis of physiochemical properties of fly ash and cenospheres (composition, granulation, density, aerodynamic properties) proves that they differ significantly, which can easily be used to obtain, beneficiate and produce several types of cenospheres from dry fly ash [21]. Moreover, it is advisable to look into obtaining cenospheres from closed-down landfills.

![Microscopic image of cenospheres](image1.png)

![EDS analysis of cenosphere grain](image2.png)

**Activation of fly ash**

Technologies for increasing chemical and hydraulic activity of fly ash have been known and, to some extent, used in Poland [22, 23, 26]. The forerunner in this discipline was professor A. Paprocki, but he met with resistance from local experts despite being otherwise acclaimed abroad [24]. These techniques include:

- surface modification, which exposes the surface of the aluminosilicate grains and pulverizes agglomerates with very little damage to the globular structure of the grain;
- volumetric modification, where the grain structure is broken to form smaller grains.
- Regardless of the method used, activated fly ash has greater fineness, larger surface area, higher reactivity (including hydraulic properties) and better resistance to fluids. Fly ash with modified surface also has better rheological properties.

Using activated fly ash for concrete reduces the need for cement and allows for a production of high-quality concrete (more impervious, resistant to penetration of chloride and sulfate irons); when used to produce binders, it increases the adhesion force, while used for wastewater and waste chemical treatment, as well as deoiling, it significantly reduces the amount of agent needed.

Using impact mills (figure 7), which compared to tumbling ball mills are smaller and more energy-efficient, can help popularize production of activated ash.
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Such activation involves not only mechanical breaking of grain microstructure, but also thermal treatment as the process generates heat and significantly increases the temperature inside the grain. Russian scientists have reached interesting conclusions when activating expired cement and steel slag in an impact mill [25]. Activation in impact mills can be used not only with fly ash, but also when mixing it with slag from production and landfills.

**Alkaline activation of fly ash**

Alkaline activation of fly ash is a chemical process which leads to the conversion of an amorphous, vitreous aluminosilicate phase to geopolymeric structure. Compounds that result in the synthesis of zeolites are both crystalline, semi-crystalline and amorphous, which is why they are difficult to identify [28, 29].

Research conducted in ICIMB proves that the properties of geopolymer binders from alkaline activation of fly ash depend predominantly on the type and amount of activator, temperature, duration of the reaction, type of ash and components. When 8 M NaOH solution was used in low pressure steam curing, the binder obtained had a zeolite structure of high durability. Studied was conventional fly ash from bituminous and lignite coal combustion, from co-combustion with biomass and FBC ash [30, 31]. A microscopic image of a hardened binder is shown in figure 8. It was obtained from alkaline activation of silica fly ash, 24 hours after the curing it had a high pressure resistance (50 MPa) (figure 9).

According to various estimates, a chemical synthesis of geopolymers is 2-3 times more energy-efficient than that of Portland cement and creates 4-8 times less carbon dioxide. Binders from alkaline activation of fly ash have a tendency to immobilize heavy metals, which is a result of their geopolymer and zeolite structure.

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Fig. 7. Impact mills for mechanical activation of fly ash

Fig. 8. Microscopic image of hardened geopolymer binder made of silica fume activated with 8 M NaOH solution. Zoomed in, the geopolymer structure around the grain.

Fig. 9. Results of strength tests on mortar made from different types of fly ash activated with 8% NaOH solution in low pressure steam curing in 80°C.
Classified ash

These are fly ash grains of particular sizes. The concept of classifying fly ash has been studied in a number of countries already in the 1970s, while mass production began in the Republic of South Africa [34].

In recent years the annual production of classified fly ash in RSA exceeded 3.5 million tons; Kendal Power Station in Mpumalanga alone produces 1.2 million t/year. The production of classified fly ash is done by means of air classifiers in the transportation and storing process — figures 10 [35, 36].

Growing interest in classified ash is a result of the awareness of the link between the fineness of the ash and the properties of concrete, that is: mechanical strength, decreased need for batching water, greater resistance to chloride and sulfate corrosion, better fluidity and rheological properties, etc. These properties allow for the production of self-consolidating concrete (SCC) and high performance concretes, including the type used in construction of skyscrapers [38, 39]. Even more interesting results have been achieved at the construction site of Freedom Tower in New York.

Figure 11 presents an instance of using classified fly ash at the construction site of the tallest high-rise in the world (828 m), Burj Khalifa Tower in Dubai [39]. The use of classified fly ash made it possible to pump concrete directly to the altitude of about 450 meters.

Analyses of the problem and preliminary tests show that it is possible to introduce a mass production of classified fly ash in Poland [41]. At the moment, we have access to materials with appropriate grain size, low content of incombustible matter and high pozzolanic activity; also we have operating research and implementation centers which can decide on the conditions of using classified ash in fillers and in construction, as well as estimate profits.

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**Literature:**

[16] Bai G., Teng W., Wang X., Zhang H., Xu P.: Processing and kinetics studies on the alumina enrichment of coal fly ash by fractalization silica dioxide as...
In the near future we can expect large-scale use of classified fly ash in hydraulic fracturing of shale gas wellbores. Presently, the conditions for using ceramic proppants [45] converge on the properties of classified fly ash from burning coal.

Hydropophbic fly ash

1960s through 1980s have seen researches, implementations and even a small scale production of hydrophobic fly ash. The hydrophobicity has been achieved through surface saturation with mineral oil, mazut or silicones in high temperatures [42].

Hydropofbic fly ash does not absorb water, nor does it combine with it, but at the same time i easily absorbs oil, etc. It can be used for example to insulate building foundations, make waterproof layers in hydrotechnical and engineering constructions, protect heat pipes from corrosion and loss of heat and in the so-called “floating roofs,” etc. The advantages to using hydrophobic fly ash are the simplicity of the technology and the possibility of large-scale production.

Ore concentrates

Up to date, Polish energetics have been successful in producing ore concentrates (Fe₂O₃, GeO₂ and Al₂O₃), but it needs to verify and develop new means of their recovery, minding that we possess large quantities of fly ash from production and landfills [42].

At present, electronics and technology involved in producing a number of devices, require small quantities of metals and compounds which are difficult to obtain. For a number of these, there is insufficient resource base. We assume that by segregating burned coal and fly ash, we could enlarge that base. This is why research is needed.

Burning fuels and flue gas treatment — as far as chemical, thermal and mechanical processes are concerned — is a process of mineral treatment of particular components (chemical compounds), the properties of which are established from samples of combustion taken at various stages of the process.

Calcium sulfate fertilizers

Fly ash obtained from burning lignite coal from Konin and Belchatów area has been continuously valued as a calcium and magnesium fertilizer [32, 33]. Nonetheless, the current use of high calcium fly ash in agriculture is insufficient.

As we have high calcium and FBC fly ash, it is possible to produce fly ash fertilizers which recently have been increasingly in demand. Considering current tendencies in agriculture, fly ash can easily be used as a granular fertilizer.

In recent years there have appeared fertilizers based on synthetic gypsum with magnesium. Many research centers study fertilizers made from fly ash obtained from biomass combustion and ammonium compounds from anthropogenic sources. The challenge now is to find inexpensive methods of granulating the ash and provide regular supply. Differences in opinion of various scientists as to the use of gypsum for soil amelioration and fertilizers can stand in the way of the process.

4. Conclusions

Coal combustion is not only a source of thermal and electrical energy, but also a me-

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Fig. 11. Photograph of the tallest high-rise in the world in construction. Classified fly ash was used for construction.
ans of obtaining gaseous and solid waste products. Initiated research and implementations have caused the waste to become a valuable and popular resource. The change has been motivated by economic and ecological needs.

Different methods of fly ash and other CCP production and utilization render it difficult to estimate the costs of their utilization and potential sales profits. Lack of consistency in this respect has been duly noted. However, it is important to point out that the cost of producing fly ash is directly related to the costs of producing energy. This is why the estimates should not include the costs of landfilling, which is beneficial for both sides. The economic benefits of using fly ash need to be determined by the producers who use it.

As far as energetics are concerned, the costs of using fly ash vary, depending on the flue gas emission regulations that apply and the guidelines for reduced use of resources, fuels and energy. These tendencies have a positive influence on both the economy and ecology of using fly ash.

Estimated benefits of pursuing fly ash beneficiation are related to the fact that enhancing the product will give it a new market value. Since the market value of fly ash depends on several factors — such as quality and legal status, norms and permissions — all research that will result in a better quality of fly ash and creation of guidelines for safe and efficient use, increases its market value.

Since there are no country estimates to establish the market value of fly ash, let us use data from the American Coal Ash Association, to be seen in [44], in which the market value of fly ash, depending on the use, was:
- for cement – 40/60 USD/Mg;
- for soil stabilization – 3/8 USD/Mg;
- as a filler in recultivation, etc. – 1 USD/Mg.

As can be seen from the data, it would be most profitable to implement new methods of improving the quality of fly ash and other CCPs to render them useful in the production of cement and concrete, as it is there that they have the biggest market value. At the same time, it is necessary to be aware of the dangers, possibilities and methods of their elimination, to pass on that knowledge to the producers, managing business and prospective users of fly ash.

Recently, it has become increasingly more important that using coal combustion products in many cases reduces the emission of carbon dioxide to the atmosphere, partly because it allows for reduced production and use of products that generate CO₂.

Analyses, researches and implementations here and abroad show that there are many possibilities of improving on current solutions for coal combustion products. To do that we need to encourage prospective producers by giving them a financial incentive in the form of proper allocation of funds obtained from environmental fees and fines, as well as facilitate access to special funds.

The experience of many countries, including Poland, shows that fly ash from energetics can be used in constructions as a component of many materials and products, which is economical and effective.

As the market economy in Poland developed, there appeared a number of managing businesses that use CCPs. Presently, there is a number of specialized entities that not only neutralize waste from coal combustion but also make use of and distribute them. ICIMB cooperates with several such entities, which employ either their own solutions, or these proposed by research centers, such as ICIMB, as a result of commissioned examinations. Examples of such entities include: EPO in Opole, Renevis in Wroclaw, Utex, Grinbet and others. These companies own recovery plants that produce innovative quality materials made from CCPs and play a significant role in the market. Their existence proves that using fly ash and other CCPs is profitable despite the obstacles.

As far as energetics are concerned, the costs of using fly ash vary depending on the flue gas emission regulations and the use of resources, fuels and energy. These tendencies have a positive influence on both the economy and ecology of using fly ash.

The economic aspect of using CCPs is only one of many, since unused they will generate losses, as they will need to be stored.