Ministry of Education and Science of Ukraine
Black Sea Universities Network

ODESA NATIONAL UNIVERSITY OF TECHNOLOGY

International Competition of Student Scientific Works

BLACK SEA SCIENCE 2022

PROCEEDINGS

ODESA, ONUT 2022

Ministry of Education and Science of Ukraine

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Odesa National University of Technology

International Competition of Student Scientific Works

BLACK SEA SCIENCE 2022

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Proceedings of International Competition of Student Scientific Works «Black Sea Science 2022» contain the works of winners of the competition.

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Odesa National University of Technology, 2022.

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INTRODUCTION

International Competition of Student Scientific Works "Black Sea Science" has been held annually since 2018 at the initiative of Odesa National University of Technology (formerly Odesa National Academy of Food Technologies) with the support of the Ministry of Education and Science of Ukraine. It has been supported by Black Sea Universities Network (the Association of 110 higher education institutions from 12 countries of the Black Sea Region) since 2019, and by Iseki-FOOD Association (European Integrating Food Science and Engineering Knowledge into the Food Chain Association) since 2020.

The goal of the competition is to expand international relations and attract students to research activities. It is held in the following fields:

- Food science and technologies
- Economics and administration
- Information technologies, automation and robotics
- Power engineering and energy efficiency
- Ecology and environmental protection

The jury includes both Ukrainian and foreign scientists. In the 4 years that the competition has been held, the jury included scientists from universities of 24 countries: Angola, Azerbaijan, Benin, Bulgaria, China, Czech Republic, France, Georgia, Germany, Greece, Israel, Italy, Kazakhstan, Latvia, Lithuania, Moldova, Pakistan, Poland, Romania, Serbia, Slovakia, Switzerland, Turkey, USA.

At the same time, every year the geography has expanded and the number of foreign jury members has increased: from 46 jury members representing 25 universities from 12 countries in 2018, to 73 jury members of the 46 universities from 19 countries in 2022.

More than a thousand student research papers have been submitted to the competition from both Ukrainian and foreign institutions from 25 countries: China, Poland, Mexico, USA, France, Greece, Germany, Canada, Costa Rica, Brazil, India, Pakistan, Israel, Macedonia, Lithuania, Latvia, Slovakia, Romania, Kyrgyzstan, Kazakhstan, Bulgaria, Moldova, Georgia, Turkey, Serbia.

The interest of foreign students in the competition grew every year. In 2018, the students representing 15 institutions from 7 countries have submitted 33 works. In 2021 the number of submitted works increased to 73, authored by the students of 40 institutions from 18 countries.

The competition is held in two stages. In the first stage, student research papers are reviewed by members of the jury who are experts in the relevant fields. In the second stage of the competition, the winners of the first stage have the opportunity to present their work to a wide audience in person or online.

All participants of the competition and their scientific supervisors are awarded appropriate certificates, and the scientific works of the winners are included in the electronic proceedings of the competition. Every year the competition receives a large number of positive responses from Ukrainian and foreign colleagues with the desire to participate in the coming years.

4. POWER ENGINEERING AND ENERGY EFFICIENCY

INCREASING THE ENVIRONMENTAL SAFETY OF THERMAL POWER PLANTS BY COAL FLY ASH UTILIZATION

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Abstract. *The paper presents the results of hydrothermal zeolitization of fly ash from hard coal combustion in one of the Polish power plants and possible further applications of zeolites. The synthesis was carried out using various NaOH fly ash mass ratio and the effect of NaOH concentration in the activating solution on composition of synthesized sample was tested. The present work proves the benefits from development of fly ash utilization and further opportunities in the use of zeolites. There exist the need for research to expand options to reduce harmful impact derived from energy production.*

Keywords *coal fly ash, utilization, thermal power plants, fusion - hydrothermal treatment process, removal, zeolite*

I. INTRODUCTION

Coal is one of the most widely use type of energy carrier. Despite efforts it is impossible to completely eliminate the demand of using coal in power plants. Great example on this field can be Poland where there is no other opportunity caused by insufficiently diversified sources of energy. In this case, it is necessary to take into account the need to eliminate harmful factors arising in the processes of coal combustion.

Fly ash is a combustion by-product constituting about 60–88% of total combustion residues from coal-fired power plants. To meet increasingly stringent limits for air pollution, the power industry has progressively improved its coal firing technology. Circulating fluidized-bed combustion (CFBC), as an advanced and clean coal technology, allows solid fuels with wide range of qualities and sizes to be burnt at lower temperature (800 – 950 °C) with high combustion efficiency, which results in considerably reduction in NOx emission compared to PCC [1]. Around 90% - 95% SO_2 reduction can also be achieved by injecting limestone in the furnace to capture the sulphur in the coal. Given all these environmental and economic benefits, CFBC has been growing steadily all over the world since its commercialization in the late 1970s [1], resulting in large amount of waste fly ash (CFBFA) discharge. Although a portion of the generated fly ash is used as fillers in brick manufacturing and road or dam construction, a significant amount is still disposed in land-fills or ash ponds with serious environmental consequences.

Coal fly ash (CFA), a by-product of coal combustion, is one of the most abundant industrial solid wastes. The emission of CFA increases annually. According to the European standard EN 450–1, fly ash is a fine grained, loose material, which is predominantly composed of spherical aluminosilicate glass particles, formed as a result of coal burning. CFA contains heavy metals, polycyclic aromatic hydrocarbons, silica, and other toxic substances [1]. If not properly disposed of, it can cause water and soil pollution, disrupt ecological cycles and pose environmental hazards (Fig. 1) [3].

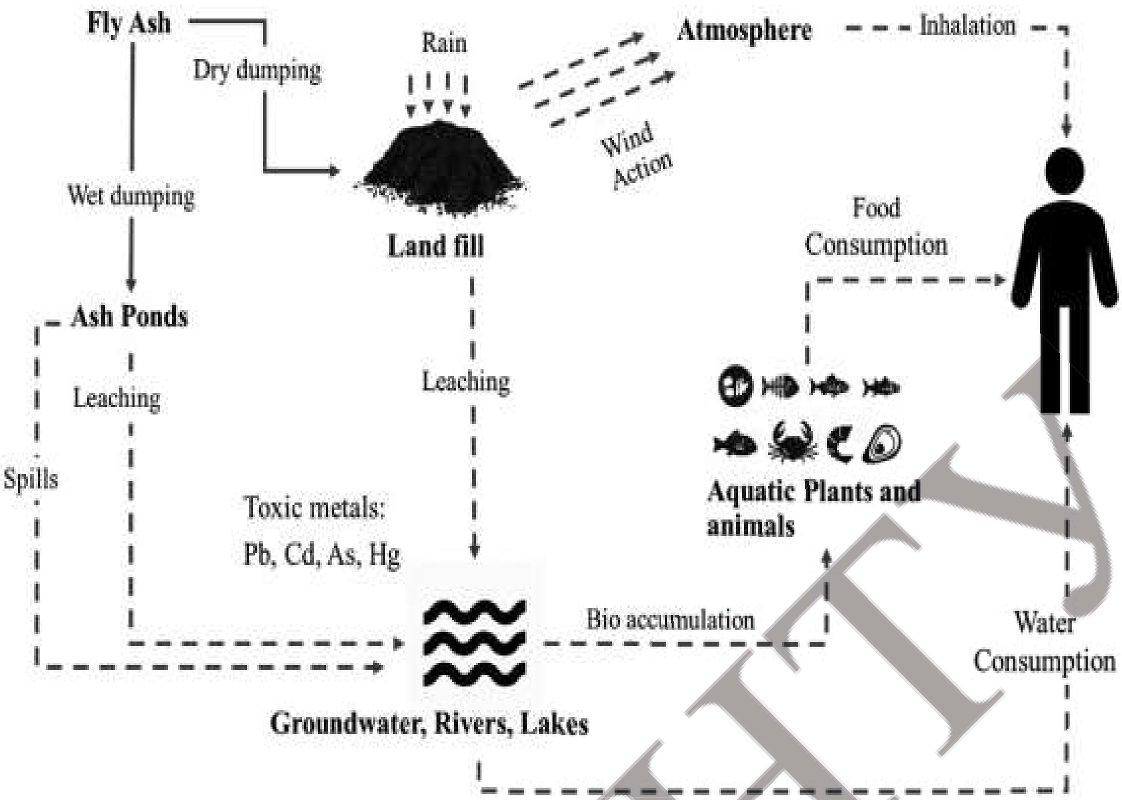

Fig. 1. Fly ash contamination pathways [3]

Carbon capture, utilization, and storage (CCUS) is one of the proposed technologies for reducing global CO_2 emissions, and it presents many opportunities for fly ash utilization. The use of cheaply available fly ash in various parts of the CCUS value chain could help reduce these costs while decreasing the environmental risks associated with fly ash disposal. In some cases, it might be possible to use the carbonated fly ash as a construction material or additive. All of which improve the economics of the capture process while benefiting the overall environmental impact of these processes. A schematic of the pathways for the application of fly ash in carbon capture, utilization, and storage (CCUS), is provided in Fig. 2 [2].

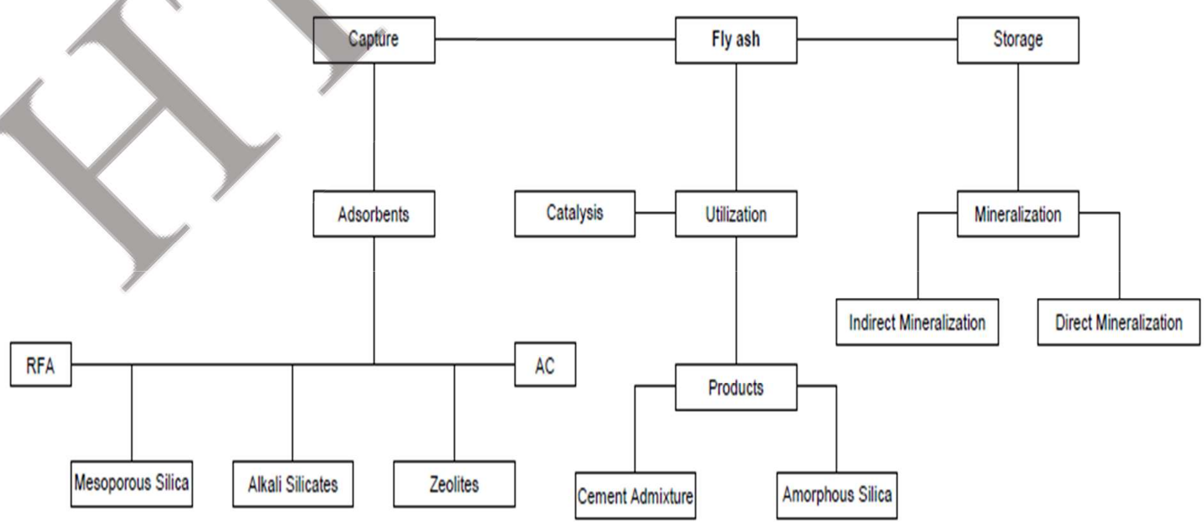

Fig. 2. Pathways for fly ash application in CCUS

Thus, there exist the need for research and development to expand options for fly ash utilization as this will result in higher utilization rates and ameliorate the harmful environmental impacts of its disposal.

II. LITERATURE ANALYSIS

2.1. Zeolite framework structures

Zeolite has broad application prospects due to its potential molecular sieving, high specific surface area, and good thermal and chemical stability. Zeolite is a kind of aluminosilicate molecular sieve crystal with uniform pores, and its skeleton contains Al, Si, and O. In Fig. 3 are illustrated common zeolite structures and in Fig. 4 are presented different zeolite structures result in distinct channels. These structural features provides a various characteristics for zeolites, of absorption selectivity, high specific surface and high ion exchange capacity [3].

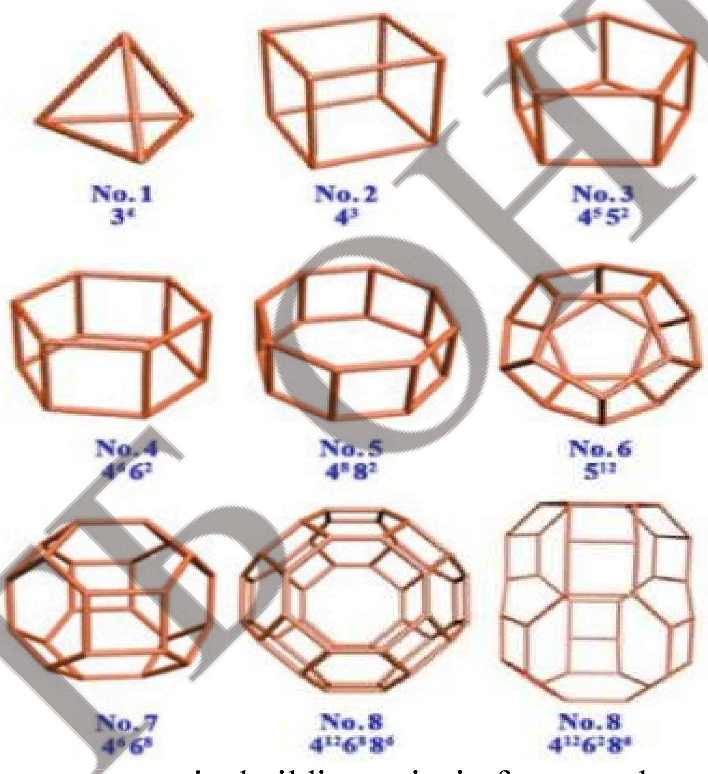

Fig. 3. Some common composite building units in framework structure of zeolite [3]

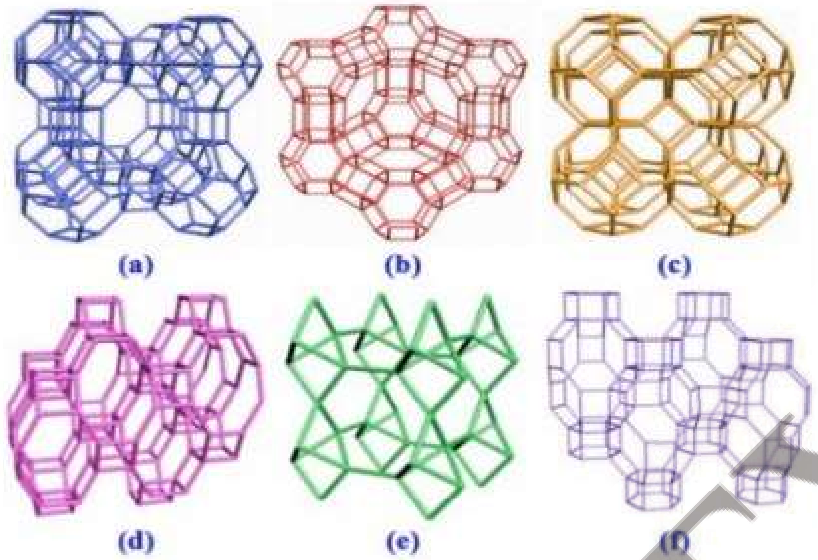

Fig. 4. Several common zeolite framework structures: (a) LTA, (b) FAU, (c) SOD, (d) GIS, (e) EDI, (f) CHA [3]

Zeolites have been widely used for air pollution control due to their excellent performance. Atmospheric aerosol is one of the main pollutants that affect the urban environment and human health, and it directly or indirectly causes haze, photochemical smog, acid rain, and other climate changes. Depending on the formation mechanism, atmospheric aerosols can be divided into primary and secondary aerosols. Primary aerosols refer to aerosol particles that are directly discharged into the atmosphere, and secondary aerosols are particles produced by the oxidation of certain gaseous pollutants (e.g., SO_x, NO_x, and hydrocarbons) in the atmosphere (e.g., from SO_2 to SO_4^{2-}).

2.2. Properties of Coal fly ash.

Fly ashes essentially consists of SiO_2 and Al_2O_3 (in both amorphous and crystalline form) [4], which have great similarity with the composition of zeolites, a valuable material widely applied in many fields related to radioactive waste management, petroleum refining, purification of gases, agriculture etc. [5]. Table 1 presents the typical chemical compositions of fly ash.

Table 1. Typical composition of fly ash from different coals

Component	Bituminous (%)	Sub-bituminous (%)	Lignite (%)
SiO_2	20–60	40–60	15–45
Al_2O_3	5 – 35	20–30	10–25
Fe_2O_3	10 – 40	4–10	4–15
CaO	1 – 12	5–30	15–40
MgO	0 – 5	1–6	3–10
SO_3	0 – 4	0–2	0–10
Na_2O	0 – 4	0–2	0–6
K_2O	0 – 3	0–4	0–4
LOI	0 – 15	0–3	0–5

Understanding the physical, chemical and mineralogical properties of coal fly ash is important, as these properties influence its subsequent use and disposal. The specific properties depend on the type of coal used, the combustion conditions, and the collector setup, among other factors. Fly ash normally occurs as fine, powdery particles with an average size of less than 20 μm, bulk density ranging from 0.54 to 0.86 g/cm^3, surface area varying from 170 to 1000 m^2 /kg band light texture. The color of fly ash is dependent on the content of unburned carbon left in ash, varying from yellow to grey to black [6]. The particle shape of fly ash also varies with the different combustion conditions applied. Fly ash produced from pulverized coal combustion (PCC), which usually operates at high firing temperature at 1300 – 1700 ℃ [7], is predominantly spherical in shape either solid or hollow. However, fly ash produced from circulating fluidized-bed combustion (CFBC), a clean coal technology known for its low NOx emission, is commonly with irregular shapes, mainly due to the relatively low combustion temperature (800 – 950 ℃) [8].

Micromorphology observation reveals that the fly ash particles are predominantly spherical in shape and consist of solid spheres, cenospheres, irregular-shaped debris and porous unburnt carbon (see Fig. 5).

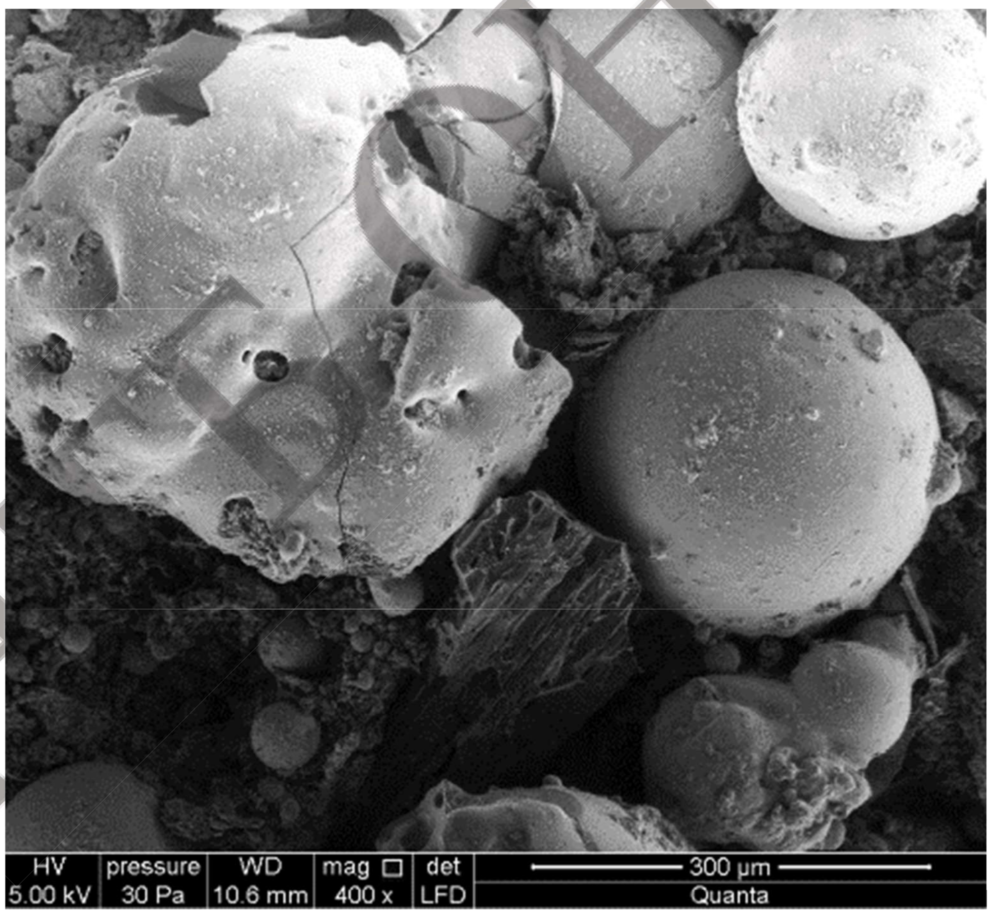

Fig. 5. Micromorphology fly ash

In FBC ash, spherical particles are rarely observed and most of the particles exhibit irregular shapes, primarily because most minerals in the coal do not undergo melting but soften only, under the relatively low boiler temperature of 850–900 °C [5]. The irregular fragments consist mainly of unburnt carbon, anhydrate and calcite.

Synthesis of zeolites, as one of the effective uses for coal fly ash, is gaining more attention, due to the compositional similarity between fly ash and zeolites. Converting fly ash into zeolite can not only reduce the waste landfills but also producing high value-added products. Thus, production of zeolites using fly ash not only convert waste into a relatively higher added value product, but also potentially constitutes one important issue of waste management. Ever since the first study conducted by Holler and Wirsching [9], many methods and process have been proposed for zeolite synthesis using fly ash and all those aim at the digestion of Si – Al containing insoluble glass phase and crystalline phases such as mullite and quartz and subsequent crystallization of zeolite [10] (Fig. 6) .

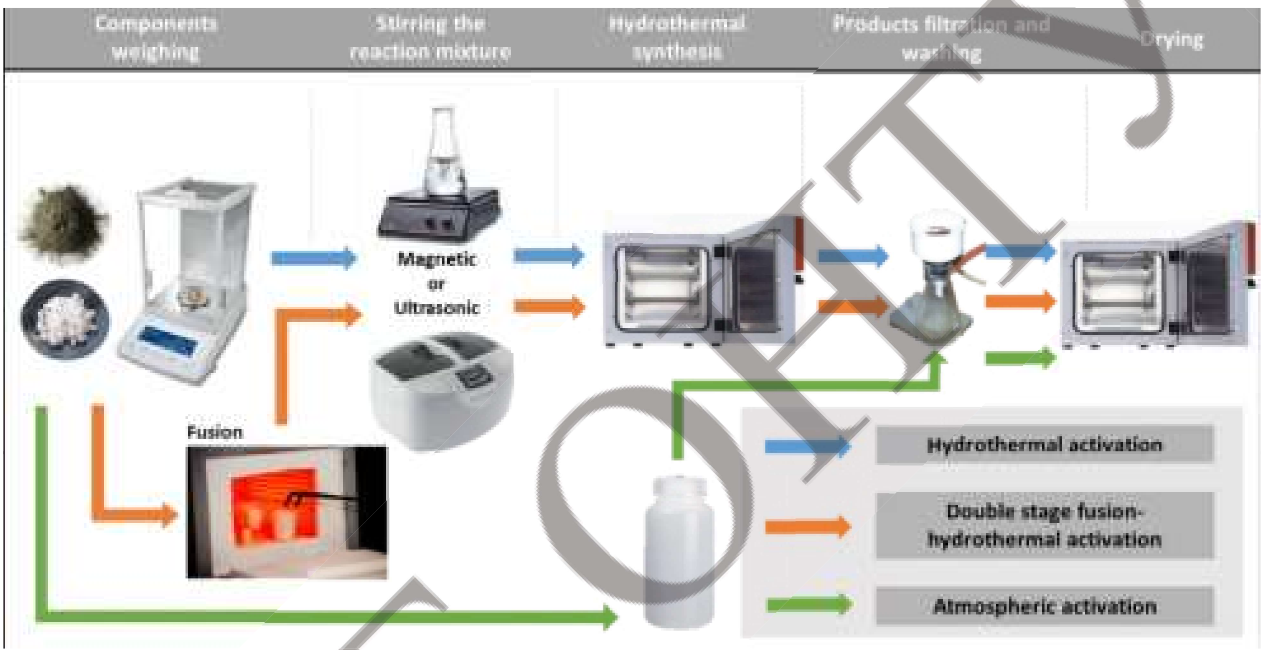

Fig. 6. - Synthesis of fly ash zeolites by hydrothermal activation, double-stage fusion–hydrothermal activation and atmospheric crystallization [12]

Simple hydrothermal process was most commonly used for direct synthesis of zeolites, where fly ash mixed with in alkaline solutions such as sodium hydroxide with different concentration at temperature from 80 to 200 ℃ for up to 96 hrs. However, this method usually leads to a low conversion (<75%) leaving a significant amount of fly ash residual in the products.In comparison, a two-step synthesis method proposed by Shigemoto et al. [13], where an alkali fusion stage is introduced prior to the hydrothermal treatment, demonstrated significant improvement on zeolitization process and high crystalline zeolite products were produce.

Microwave-assisted Synthesis. Microwave assisted method utilises microwave in the hydrothermal process. The microwave assists the zeolite synthesis at earlier stage due to the stimulated dissolution of SiO_2 and Al_2O_3 from fly ash and reduce its reaction time. However, it will retard the formation of zeolite in the middle to later stage. Therefore, by utilising microwave in the earlier hydrothermal process can effectively shorten the reaction time of zeolite synthesis from fly ash [14]. In the study done by Querol, application of microwave to the conventional synthesis can lead to the significant reduction of reaction time from 24 hours to 30 min.

III. OBJECT, SUBJECT, AND METHODS OF RESEARCH

The object of research The object of research is fly ash from hard coal combustion in one of the Polish power plants

The subject of research is the methods of the synthesis was carried out using various NaOH fly ash mass ratio and the effect of NaOH concentration in the activating solution on composition of synthesized sample was tested.

Methods of research: The morphology and chemical composition in the micro-area of the main mineral components of the tested materials was determined using a scanning microscope (SEM). The FEI Quanta 250 FEG scanning microscope was used, equipped with a chemical composition analysis system based on radiation energy dispersion X-ray - EDS by EDAX .

IV. RESULTS

4.1. The cycle of continuous improvement of energy services results

In the studied fly ash the dominant chemical components were SiO_2 and Al2O_3, while the main phase components were mullite, quartz and hematite, and a significant share of amorphous substance (glass and unburnt organic substance) (tab.2).

Table 2 Elemental analysis of coal fly ash in wt%

Component	Bituminous (%)
SiO_2	49,73
Al_2O_3	29,57
Fe_2O_3	7,15
CaO	4,65
MgO	3,19
Na_2O	1,39
K_2O	2,86
LOI	7

*Loss on ignition

Fly ash is a material that is heterogeneous in terms of its phase and chemical composition. The presence of oxide minerals - Al_2O_3, Fe_2O_3, MgO, CaO was established in the mineral composition of bottom ash; silicates and aluminosilicates - with island, ring, chain, layered and spatial structure. In terms of phase composition, the ashes are also agglomerates of various nature. The microscopic image of the surface morphology and samples of ash particles is presented in Fig. 7.

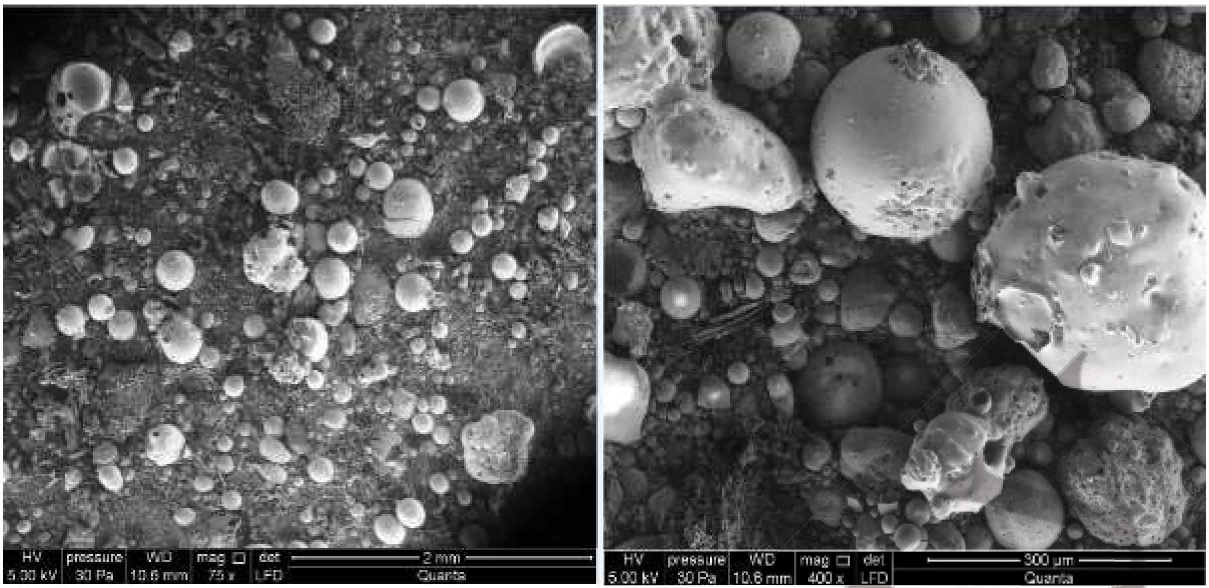

Fig. 7. Microphotograph of fly ash

The process was carried out under the following permanent conditions temperature: 80°C, time – 24 hours, water solution of NaOH (L)/fly ash (g) ratio – 1,4:1,0; 1,8:1,0. After hydrothermal synthesis, the presence of unreacted fly ash phases was found in the products, as well as new phases, the quality and quantity of which depend on the NaOH to fly ash mass ratio used for synthesis (Fig. 8).

In the products of synthesis, the share of sodium-containing phases increases with the increasing concentration of NaOH in the solution used for the process. Fly ash was examined using scanning electron microscopy (SEM). The fly ash was then subjected to an alkaline treatment with sodium hydroxide (NaOH) to carry out the process of synthesizing a zeolite-like material (Fig. 9).

Zeolites are mainly hydrated aluminosilicates of alkali, alkaline earth elements or, much less often, other cations. Very valuable are their properties (sorption, catalytic, molecular sieve, ion-exchange, etc.) are the result of the specific structure of their aluminosilicate skeleton, which forms the structure of zeolites, in which there are systems of channels and outlet chambers as a result of a series connection of parallel rings of aluminum and silicon tetrahedral.

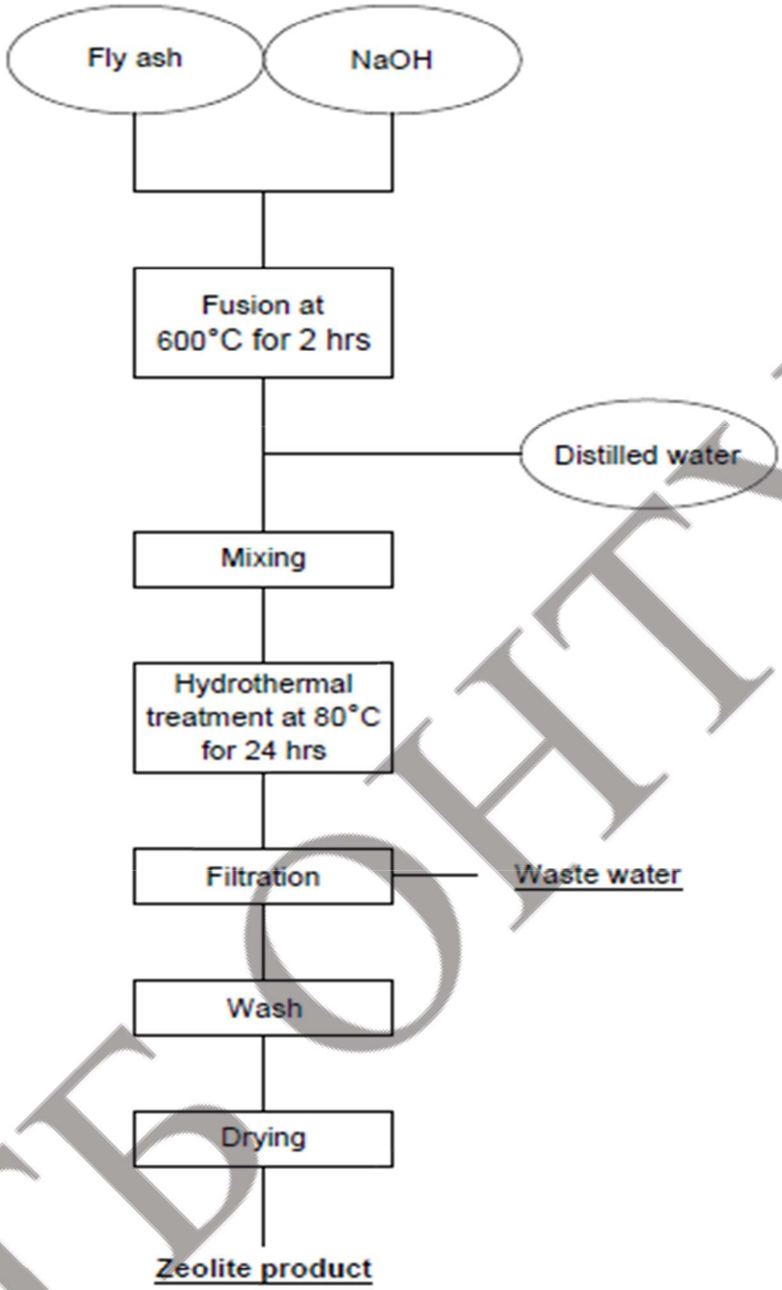

Fig. 8. High temperature fusion - hydrothermal treatment process for the synthesis of zeolites from fly ash

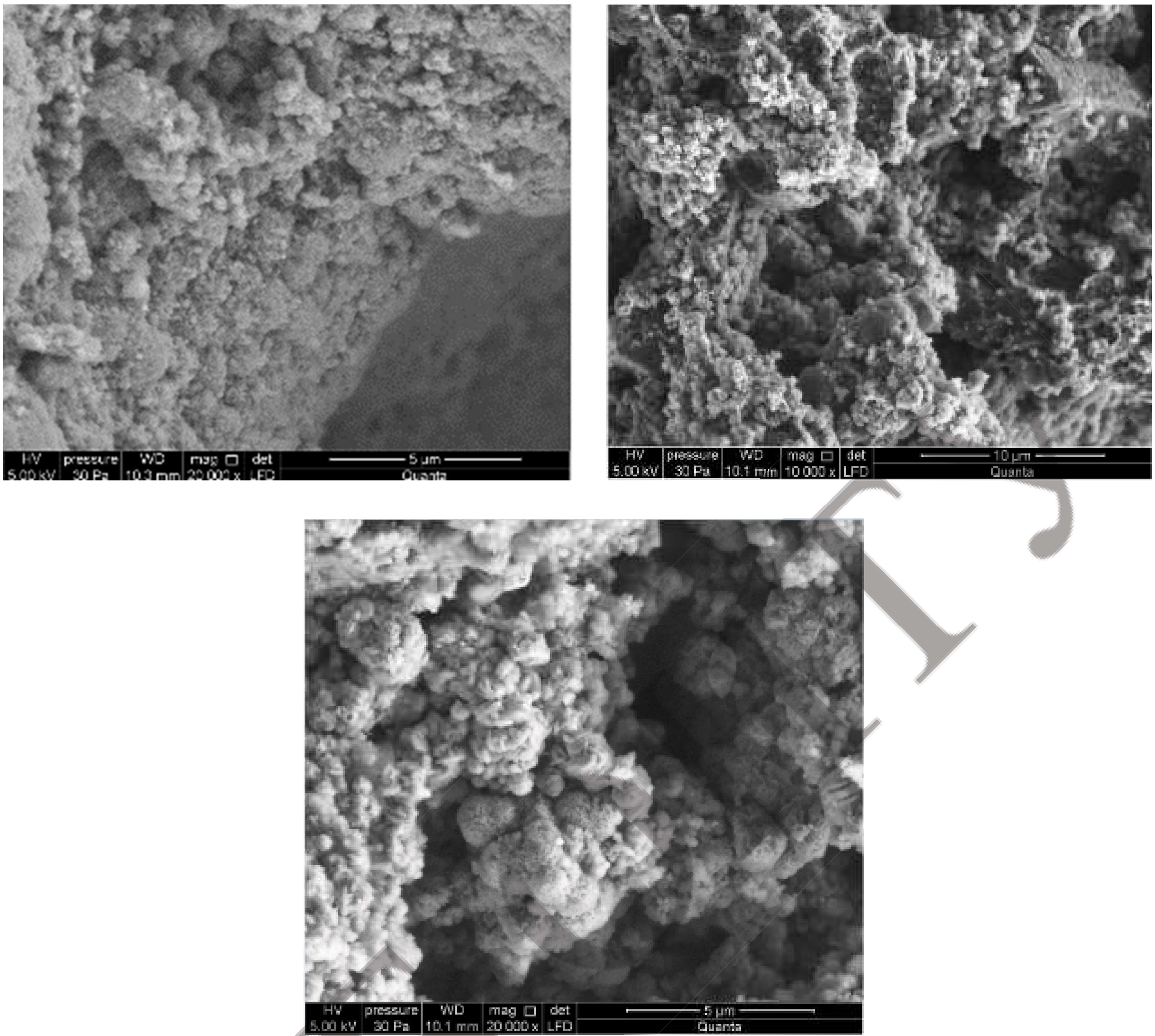

Fig. 9. Zeolite material

These rings form the so-called secondary structural divisions, which are the most common criterion for their division into various structural types.

V. CONCLUSIONS

The generation of coal fly ash is anticipated to increase for many more years, as a result of the world's increasing reliance on coal-fired power generation. Understanding the generation, characterizations and hazards provides both a background and a basis for the alternative uses of fly ash. This review has attempted to investigate the production of fly ash at the global level and covers a wide range of applications to understand the status of fly ash utilization and thus develop alternative recycling technologies. The knowledge of the various ways to use fly ash, such as in soil amelioration, the construction industry, the ceramic industry and zeolite synthesis, is essential for better management of fly ash and the reduction of environmental pollution.

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