

TECHNICAL AND ECONOMIC JUSTIFICATION OF THE TECHNOLOGICAL SCHEME OF SORPTION MATERIALS PRODUCTION FROM THE COAL FLY ASH

Yelatontsev D.O.

Dniprovsk State Technical University

Abstract. Despite the wide range of industrial applications for ash and slag waste, the actual utilization rate of ash disposed at Ukrainian TPPs is close to zero. Dry ash from electrostatic precipitators is used in the production of construction materials to a very limited extent. An analysis of the possibility of producing commercial materials from ash and slag using hydrochemical methods shows that these methods are mainly used in laboratory practice. Taking into account the content of silica in TPP fly ash, which is more than 50% by weight, it is of practical interest to use it to produce zeolite-like materials that have pronounced adsorption properties and can be used in water and gas purification processes. The known processes for obtaining sorption materials based on fly ash involve alkaline treatment of raw materials and hydrothermal synthesis at temperatures of about 100 °C. At the current stage of development of this technology, the main problem is to increase the synthesis capacity to ensure the profitability of production on an industrial scale. In recent years, in many fly ash-producing countries, the most widespread synthesis has been the one involving the high-temperature fusion of fly ash with sodium hydroxide, but this process is practically unfeasible from a technical and economic point of view, as it requires the use of huge furnaces. The methods of ultrasonic processing and hydrodynamic cavitation can be a possible alternative to high-temperature synthesis, and the conditions provide significant economic advantages for potential production. This paper systematically considers the problems of large-scale synthesis of zeolites from fly ash of thermal power plants and discusses the factors that determine the efficiency of hydrothermal synthesis processes in terms of quality and specific yield of product zeolite. Critical analysis of typical technological processes for the synthesis of zeolites based on TPP's fly ash from showed that hydrothermal synthesis requires the minimum energy consumption and forms very small amount of by-products that require disposal. Unlike fusion synthesis (about 500 °C), the hydrothermal process is possible at much lower temperatures. Also, hydrothermal synthesis enables replacing pure water with less expensive recycled water to save resources. Recommendations are given that may be useful in the development of appropriate production of zeolite materials based on fly ash.

Keywords: fly ash, scaling, technological parameters, technical and economic indicators, waste utilization.

1. Introduction

The discovery that coal ash contains the elements necessary for the synthesis of zeolites (Si and Al), has prompted extensive research to create ways to utilize ash, thereby solving the global problem of coal ash utilization. Fly ash is formed at thermal power plants (TPP) and is the most common by-product of coal combustion [1]. This ash has the potential to leach toxic heavy elements into the groundwater system [2] and poses a threat to human health if inhaled [3].

Many studies have been conducted on the use of fly ash in various fields, such as agriculture, construction, wastewater treatment, and the synthesis of geopolymers and zeolites [4]. However, these applications have not solved the problem of fly ash utilization on an industrial scale. There is a need to further investigate the feasibility of expanding the scale of fly ash processing [5, 6] to realize the synthesis of zeolites from it on a commercial scale.

Coal fly ash is mainly composed of silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3), and calcium oxide (CaO), as well as some unburned carbon [7]. The chemical properties of ash depend on the type of coal being burned, as well as on the processing and storage conditions. This causes high variability in the composition of coal ash obtained from different coal grades processed at the same power plant.

The main and accompanying elements in coal ash are represented in the form of oxides and trace elements, such as As, B, Ba, Be, Cd, Co, Cr, Cu, Ge, Hg, Li, Mo, Ni,

Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, and Zn [8]. The main phases of coal ash are amorphous glass, mullite, and quartz [9]. In addition, the combustion rate and temperature of the coal combustion process affect the morphology of ash particles [10]. Fly ash is mainly composed of spherical particles, such as solid and hollow spheres (cenospheres), with some irregular inclusions of unburned carbon.

Coal ash containing more than 70% of the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ with a low lime content (5%) is classified as Class "F" ash. If the content of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ is from 50 to 70% and the lime content is from 10 and 35%, the ash is classified as class "C" [9, 10]. Class "C" ash can be produced from lignite and bituminous coal, and class "F" ash from bituminous and anthracite coal.

Numerous studies have been conducted to investigate the leaching of coal ash into the groundwater system surrounding ash dumps [11–21]. In particular, it has been reported that ash placed in the dumps is capable of releasing trace elements into the environment over time. All trace elements (As, Zn, Pb, Ni, Mo, Cr and Cu) were leached into the soil to varying degrees (4.4–27.4%).

In addition, the potential health hazards of coal ash for the population living in the vicinity and workers exposed to the ash have been reported. The leaching of toxic compounds from fly ash into human lungs by inhalation of fly ash dust has been reported, and diseases such as lung cancer, asthma and many others are associated with fly ash inhalation [22].

The purpose of this work is to review the known technologies for the synthesis of zeolites based on fly ash from the TPP and to substantiate the main technical and economic indicators of the technology of hydrothermal synthesis of zeolites on an industrial scale.

2. Chemistry of the synthesis of zeolites from coal ash

Zeolites are crystalline aluminosilicates that have cavities and pores at the molecular level. They occur as natural minerals and are also known to be synthetically produced in laboratories for use as sorbents, catalysts, and ion exchange materials [23].

The first synthesis of zeolites from coal ash was carried out in 1985 [24]. Today, a number of methods are known for the synthesis of various types of zeolites from coal ash [25–34], most of which involve the dissolution of the Al-Si phases of the ash with alkaline reagents (such as NaOH and KOH) followed by the precipitation of zeolite material. One of the most well-known methods of converting fly ash into zeolite is melting with sodium hydroxide and a two-stage process [28]. The latter process produces more "pure" zeolites, however, it is relatively more expensive. Schematic diagrams of the one- and two-stage processes are shown in Fig. 1 and Fig. 2.

In [25] they developed a process in which coal ash is fused with sodium hydroxide at high temperatures before hydrothermal treatment. The ratio of ash:NaOH = 1.0:1.2 was optimal at a melting point of 550°C, which ensured the transformation of ash particles into sodium salts (silicate and aluminate), which formed Na-X zeolite structures after hydrothermal treatment. The scheme of this process is illustrated in Fig. 3.

From the critical analysis of typical technological processes for the synthesis of zeolites based on fly ash from the TPP (Fig. 1–3), it was concluded that hydrothermal synthesis is optimal in terms of energy consumption and the formation of by-products that require disposal. Unlike fusion synthesis, the hydrothermal process is possible at much lower temperatures. In addition, in hydrothermal synthesis, it is possible to replace pure (distilled) water with less expensive process or recycled water to further save resources. There are also cases of using acid mine drainage (AMD) for the hydrothermal synthesis of zeolites from coal ash [40, 41].

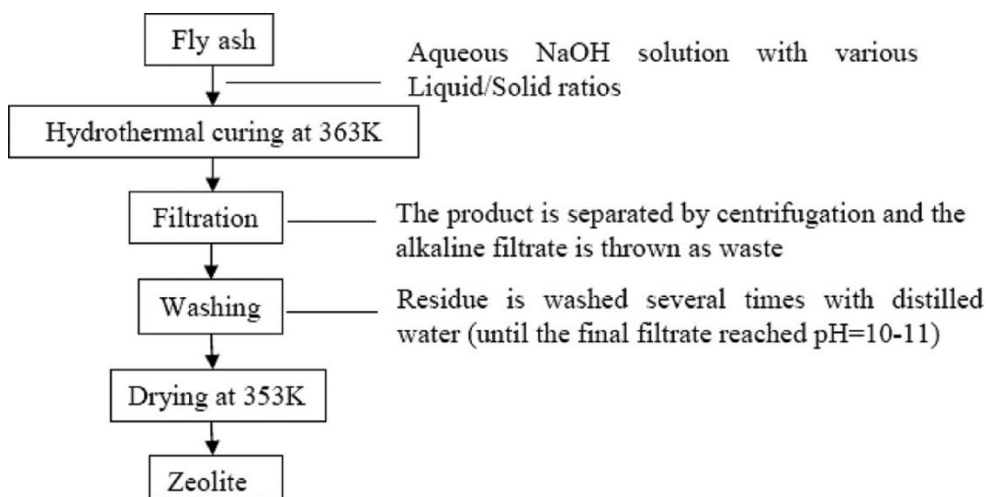


Figure 1 – Flow chart of a typical alkaline-hydrothermal synthesis of zeolites [35]

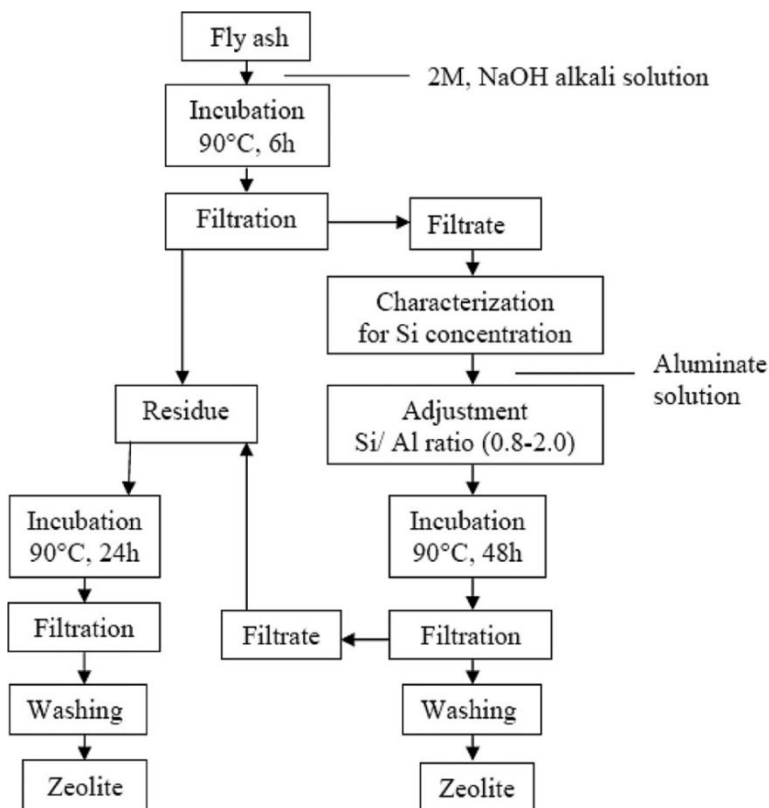


Figure 2 – Flow chart of a two-stage zeolite synthesis [28]

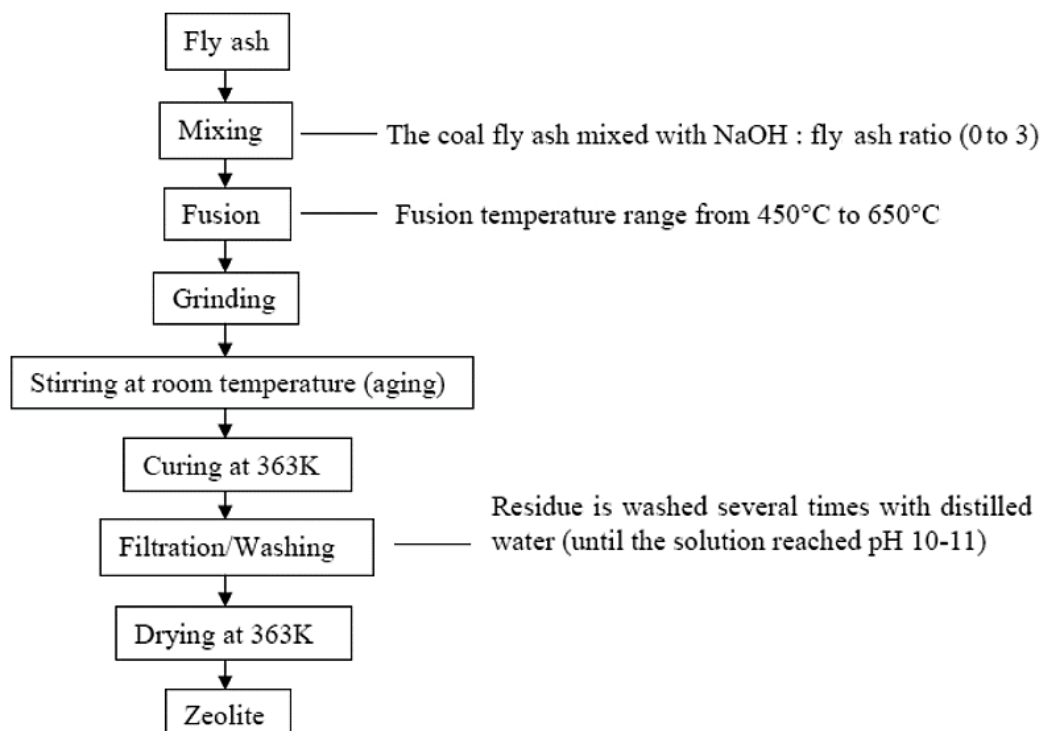


Figure 3 – Flow chart of the synthesis of zeolites by fusion [25]

The synthesis of zeolites from coal ash using NaOH, Na₂CO₃, and KOH was studied in [29]. It was found that the mechanism of the alkaline hydrothermal reaction consists of three stages, namely, dissolution, condensation, and crystallization. The dissolution stage begins in the temperature range of 298–393 K, and the number of OH⁻ groups and Na⁺ ions in the alkali solution determines the overall reaction rate of zeolite synthesis.

The concentration of NaOH affects not only the degree of conversion of raw materials but also the type of zeolite formed. A study [36] notes that the different type of product formed is explained by an increase in supersaturation, which is achieved by increasing the proportion of soluble substances with an increase in the NaOH concentration. This phenomenon can be described by the Ostwald sequential transformation rule: the higher the supersaturation, the better the conditions for the formation of metastable phases. An example is zeolite “X”, which subsequently recrystallizes and is replaced by a more stable hydroxysodalite.

Other factors affecting the formation of zeolite from coal ash are the SiO₂/Al₂O₃ ratio in the feedstock, cationic impurities, water content, synthesis time and temperature, and mixing intensity. Work [31] shows the effect of the SiO₂/Al₂O₃ ratio on the efficiency of zeolite synthesis. Two types of zeolites (Na-P1 zeolite and hydroxysodalite) were formed from silica-rich and silica-poor ashes, respectively. The SiO₂/Al₂O₃ ratio was adjusted using Al₂O₃ powders and SiO₂ aerosol. According to [37], the optimal SiO₂/Al₂O₃ ratio depends on the content of these oxides in the aluminosilicate glass phase of coal ash, rather than on their bulk composition, since this phase is activated first.

A study [38] showed how the choice of cations can determine the reaction of zeolite crystal formation. Na^+ ions promoted the formation of "P" zeolite, while K^+ ions promoted the formation of shabazite. This is due to the fact that Na^+ ions stabilize the zeolite framework, while K^+ ions act as inhibitors of crystallization and contribute to its slowing down [39].

An increase in the water content in the feedstock leads to an increase in the rate of dissolution of the crystalline and amorphous phases of ash [40]. This led to the study of the possibility of using alternative sources of water (tap water, distilled water, AMD) to replace purified water in the synthesis of zeolites from fly ash. In [41], it was noted that AMD provides the formation of hydroxysodalite, a product of low quality. However, it was found that neutral mine water provides the quality of Na-P1 and "X" zeolites comparable to the model synthesis. Zeolites "X" and ZK-5 were successfully synthesized using seawater at lower temperatures (25°C), and hydroxysodalite was also formed, but zeolite A could not be obtained.

Due to the metastable behavior of zeolite "X", its formation is always competitive with hydroxysodalite, and zeolite "X" is preferentially formed at lower temperatures [42]. It is also known that at higher temperatures, zeolites with a larger particle size are formed. It has been found that the dissolution of aluminum is faster than that of silicon, and both elements must be in a dissolved state to promote crystal growth, with silicon dissolution increasing with increasing temperature. Thus, at higher temperatures, the Si/Al ratio will favor the formation of an "X" type zeolite rather than an "A" type. At high content of vitreous substances, the synthesis time is reduced, while high content of quartz and mullite causes a longer reaction time.

Non-homogeneous mixtures can be formed due to inadequate mixing of the viscous gel that forms before the crystal growth stage [43]. These heterogeneous mixtures form a gel of variable composition that produces random phases. The effect of stirring on the crystallization process has not yet been studied sufficiently, but it is known that effective stirring should perform the following functions:

- Dissolution of the reactants;
- Initial gelation;
- Maintaining the homogeneity of the gel;
- Promoting the destruction of gel structures;
- Maintaining a uniform temperature throughout the reactor;
- Transfer of reagents to growing crystals;
- Retention of zeolite crystals in suspension after the reaction is completed.

A significant change in viscosity during synthesis is also an important factor to consider: the solution can turn into a very viscous gel.

The intensity of stirring during the aging stage was investigated in [44]. It was shown that stirring during hydrothermal synthesis can have a detrimental effect on the stability and purity of the zeolite. It was believed that during the aging stage, shear could promote zeolite formation as it facilitates the dissolution of coal ash in the alkaline solution. The four-blade impeller was found to be optimal for the synthesis of zeolite used during the aging stage. However, it should be noted that as the scale of zeolite synthesis in the hydrothermal reactor increases, some form of mixing will also

need to be implemented, given the need to maintain a homogeneous mixture [45]. The synthetic gel used in the hydrothermal synthesis stage is significantly different from the solution during aging.

Considerable research has been conducted on the use of class F ash for zeolite synthesis, which was first proposed in [45, 46]. These studies focused on the use of alternative methods such as ultrasound or melting to reduce the time and temperature of hydrothermal synthesis [47–49]. In addition, studies have also shown that ultrasonic methods can be used to form zeolites “A” and “X” (zeolite “X” with a new hierarchical morphology). According to [50], the three main steps involved in the mechanism of formation of zeolites from coal ash are as follows:

1. Transition of Si^{4+} and Al^{3+} ions from coal ash into solution;
2. Condensation of silicate and aluminate ions in an alkali solution with the formation of an aluminosilicate gel;
3. Crystallization of aluminosilicate gel crystals to form zeolites.

The above process can be visualized in Fig. 4.

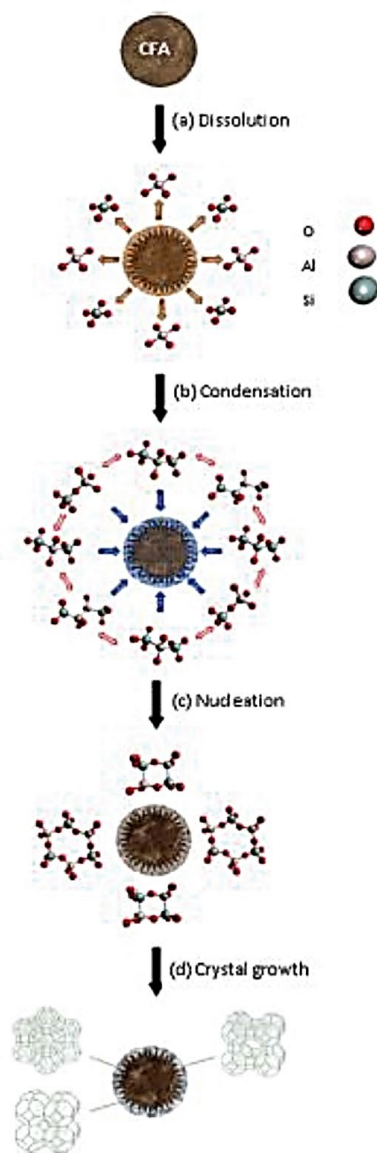


Figure 4 – Schematic representation of the formation of zeolites from fly ash [51]

When using microwave-assisted synthesis [52], the activation time required for the hydrothermal transformation is radically reduced from 2448 to 30 min. Continuous microwave irradiation slows down the formation of zeolite in crystalline form by inhibiting the zeolite in the intermediate gel. Early microwave irradiation was found to enhance zeolite formation. Heating at the middle stage, however, significantly inhibits zeolite formation. Therefore, it was advisable to heat with microwave radiation at an early stage and then to carry out conventional heating.

Ultrasound is promising when using cavitation to create high temperatures and pressures or "hot spots" under conditions close to atmospheric conditions [53]. The main form of cavitation is acoustic cavitation generated by sound waves, in which ultrasound generates and destroys cavities in microseconds. These hot spots can reach temperatures of over 5000 K and cooling rates of over 10^7 °C/s. In a recent study [49], a 90-minute high-temperature melting was replaced by a 10-minute high-intensity ultrasonic irradiation. It was shown that 24% of the silicon was extracted from the fly ash, compared to 32% in standard melting, which also reduced the crystallization time of zeolite "A".

Hydrodynamic cavitation is the creation of cavitation when a fluid stream passes under controlled conditions through obstacles such as vent tubes and diaphragms. It is generated when the pressure in the throat drops below the vapor pressure of the liquid, causing the liquid to form a series of cavities. When the pressure is restored after mechanical constriction, these cavities collapse [53–55]. Hydrodynamic cavitation is used on the scale of pilot plants [56]. It has been shown that cavitation mixing methods used in a jet circuit reactor provided intensive mixing.

3. Prospects for scaling up the technological process of synthesis of zeolites from fly ash of thermal power plants

In [40], experiments were carried out at a pilot plant using a 10 m³ reactor and the optimal synthesis conditions were established: 2 M NaOH, ash content in the solution - 21 kg/dm³, temperature 150°C and time 24 hours. They also reported a high cation exchange capacity of zeolites in relation to ammonium and heavy metals.

Wdowin et al. [45] developed a technological line for the conversion of coal ash into zeolite. It can be divided into four stages:

- 1) loading;
- 2) synthesis;
- 3) separation of reaction products;
- 4) processing of the resulting material.

The total volume of the reaction tank was 130 dm³ with a working volume of 100 dm³. The zeolite Na-P1 was synthesized under the following conditions: loading 20 kg of fly ash, 12 kg of NaOH, 90 dm³ of H₂O; temperature 80°C; duration 36 hours.

As can be seen from most of the literature, the main type of zeolite obtained from coal ash is the Na-P1 type. It is anticipated that future research should focus on whether type "X" zeolite can be synthesized on an industrial scale. This type of zeolite is widely used as a liquid catalytic cracking catalyst for petroleum refining and as a catalyst for nitrogen oxide removal for stationary sources and automobile exhaust

gases [57]. The hierarchical structure of the pores allows zeolites to perform maximum structural functions in a limited volume, which ensures a high degree of diffusion efficiency.

Hydrodynamic cavitation should be investigated as an alternative to replace the high-temperature melting process for large-scale production. Following the work [58], where it was shown that the jet loop increases the content of amorphous substances in the ash and reduces the amount of quartz and mullite, which promotes the synthesis of zeolites. Thus, this method can be used to synthesize zeolites instead of melting.

Stirring is crucial in the process of zeolite synthesis from coal fly ash, but the difficulty lies in determining the effect of the stirrer design on the hydrothermal treatment efficiency. Although it has been shown that the type of impeller and the stirring speed have a significant impact on the aging stages of zeolite synthesis [44], there is still a need to investigate these effects during the crystallization process. It is assumed that during the hydrothermal process, it is advisable to use stirrers that provide a minimal shear effect. On an industrial scale, stirring is required not only to ensure homogeneity but also to evenly distribute the heat required for crystallization. No thorough studies have yet been conducted to show the effect of stirring during the hydrothermal treatment process.

The above emphasizes the need for in-depth studies of mixing during the hydrothermal synthesis of zeolites. The results of such studies can be used in industrial conditions to ensure high yields of zeolites and ensure their quality.

4. Initial feasibility study for the production of zeolites based on fly ash from thermal power plants

A flow chart detailing the process of producing zeolites based on the TPP fly ash is shown in Fig. 5.

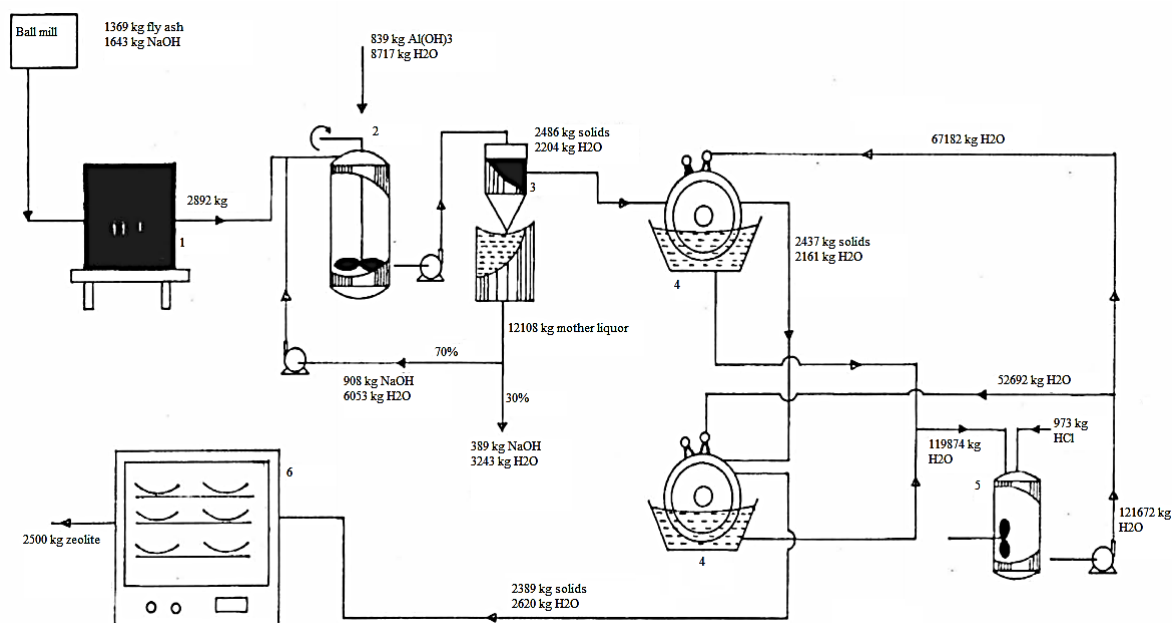


Figure 5 – Schematic diagram of the technological process of synthesis of zeolites from fly ash of thermal power plants by the hydrothermal method [59]

The analysis was performed for a planned zeolite production capacity of 2500 kg/day (minimum economically feasible capacity). The main equipment requirements are summarized in Table 1, along with the specific design capacity and cost estimates. Taking into account the cost of chemicals, electricity, and labor requirements, as well as maintenance costs, the annual operation and maintenance costs are estimated at around UAH 50 million (Table 2).

Taking into account the annual production volume and the profit margin of about 2.3 UAH/kg, the annual profit is about UAH 52 million (Tables 3, and 4). Based on this, the payback period looks quite attractive and is about 40 months.

Table 1 – Capital costs

Cost item	Cost, thousand UAH/year
Ball mill (2 pcs., working volume 3 m ³ , power 1.4 t)	940
Muffle furnace (3 pcs., capacity 2 t/day)	21.15
Mixer-crystallizer (4 pcs., working volume 35 m ³)	517
Filter press (4 pcs., capacity 4 m ³ /h)	564
Stove (2 units, capacity 1.5 t/day)	940
Collectors for neutralization and product storage	1645
Installation equipment (pumps, pipelines, mixers, etc.)	2726
In total	7353.15

Table 2 – Operating costs

Cost item	Cost, million UAH/year
Chemical reagents	
NaOH	21.29
Al(OH) ₃	10.29
HCl	5.79
Fly ash	0.57
Energy consumption	7.44
Workforce	4.08
Planned repairs (3% of capital costs)	0.22
In total	49.68

Table 3 – Cost of production of zeolites from TPP fly ash

Cost item	Cost, million UAH
Annual operating costs	49.68
Depreciation of equipment	2.7
Depreciation of land areas	0.9
Interest on total capital investment	0.49
Total annual costs	53.77
Cost of production, hryvnias/kg	2.7

Table 4 – Analysis of profitability of production

Item	Value
Consumption of reagents, kg/day	
fly ash	4107
NaOH	4926
Al(OH) ₃	2517
HCl	2920
Capital investments, UAH million	7.353
Annual production capacity of zeolites, t/year	2500
Specific profit, UAH/kg	2.3
Annual income, UAH million/year	51.81
Payback period, months	40

The characteristics of zeolite-based on TPP fly ash and its commercial analogue are practically the same (Table 5).

Table 5 – Comparative characteristics of zeolites obtained from TPP fly ash and a commercial analog [59]

Characteristic	The zeolite is obtained from the fly ash of the TPP	The zeolite of "A" grade
Color	Creamy	White
Average particle size, μm	2–3	2–3
CaO, g/g	160–170	160–180
Density, g/cm^3	2.03	2.00
Moisture content, %	19–20	19–20
pH	9.5–10.5	10–11
Crystallinity, %	96–99	80–85
Si, %	33±0.5	33.0±0.5
Al, %	27±0.5	27.5±0.5
Na ₂ O, %	16±0.5	16.5±0.5
Si/Al molar ratio	1.1–1.2	0.9–1.0
Specific surface area, m^2/g	600–700	500–700

5. Conclusions

This review highlights the current state of the art and prospects for scaling up the synthesis of zeolite from coal ash. Modern research demonstrates the possibility of avoiding the energy-intensive pre-synthesis step by using acoustic cavitation provided by ultrasonic devices, but the scalability of this method for large-scale production remains a subject of debate.

Hydrodynamic cavitation provided by a jet circuit system may be a second alternative, but there is a need for systematic research to substantiate the potential of a jet circuit system for the extraction of excess silicon and aluminum from coal ash.

The critical importance of intensive mixing and appropriate impeller type during hydrothermal synthesis is emphasized, with an emphasis on the requirement of

minimum shear during crystallization in large hydrothermal reactors. It is expected that the recommendations will provide a clear understanding of the design of appropriate scale-up operations for the synthesis of zeolite from fly ash from thermal power plants.

A preliminary calculation showed that it would be economically feasible to produce about 2500 t/year of grade "A" zeolite, with annual operation and maintenance costs of about UAH 50 million. The estimated cost of zeolite production will be UAH 2.7 per kg, which is significantly less than the cost of importing commercial grade "A" zeolite. The expected payback period is about 40 months.

Thus, the technology of producing zeolites based on fly ash from the TPP is quite versatile, environmentally friendly, cost-effective and competitive.

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About the author

Yelatontsev Dmytro Oleksandrovych, Candidate of Technical Sciences (Ph.D.), Associate Professor, Associate Professor of the Department of Chemical and Biological Technologies, Dnipro State Technical University under the Ministry of Education and Science of Ukraine (DSTU, MSE of Ukraine), Kamianske, Ukraine, sauron11652@gmail.com.

ТЕХНІКО-ЕКОНОМІЧНЕ ОБҐРУНТУВАННЯ ТЕХНОЛОГІЧНОЇ СХЕМИ ВИРОБНИЦТВА СОРБЦІЙНИХ МАТЕРІАЛІВ ІЗ ЗОЛИ ВІНОСУ ТЕС

Єлатонцев Д.О.

Анотація. Незважаючи на досить широкий спектр промислового застосування золошлакових відходів, фактичні показники утилізації золи, що розміщується на золовідвалах українських ТЕС, близькі до нуля. Суха зола, що відбирається від електрофільтрів, знаходить своє застосування у виробництві будівельних матеріалів у дуже обмежених обсягах. Аналіз можливості отримання комерційних матеріалів із золошлаків гідрохімічними методами свідчить про реалізацію цих методів переважно в лабораторній практиці. З урахуванням вмісту в золі виносу ТЕС діоксиду кремнію, в кількості понад 50% мас., представляє практичний інтерес можливість використання його для отримання цеоліт-подібних матеріалів, що мають виражені адсорбційні властивості і можуть бути застосовані у процесах водоочищення та газоочищення. Відомі процеси отримання сорбційних матеріалів на основі золи виносу передбачають лужну обробку сировини та гідротермальний синтез при температурах порядку 100 °С. На сучасному етапі розвитку даної технології основною проблемою є збільшення потужності синтезу для забезпечення рентабельності виробництва в індустріальних масштабах. В останні роки в багатьох країнах-виробниках золи найбільшого поширення набув синтез, що включає високотемпературне сплавлення летючої золи з гідроксидом натрію, проте цей процес є практично нездійсненним з техніко-економічної точки зору, оскільки потребує використання печей величезного розміру. Можливою альтернативою високотемпературному синтезу можуть стати методи ультразвукової обробки та гідродинамічної кавітації, а умови забезпечення істотних економічних переваг потенційного виробництва. В даній роботі системно розглядаються проблеми великомасштабного синтезу цеолітів із золи виносу ТЕС, обговорюються фактори, які визначають ефективність процесів гідротермального синтезу з позицій якості та питомого виходу продукційного цеоліту. Критичний аналіз типових технологічних процесів синтезу цеолітів на основі золи-винусу ТЕС показав, що гідротермальний синтез вимагає мінімальних витрат енергії і утворює дуже малу кількість побічних продуктів, які потребують утилізації. На відміну від синтезу плавленням (близько 500 °С), гідротермальний процес можливий при значно нижчих температурах. Крім того, гідротермальний синтез дозволяє замінити чисту воду на дешевшу оборотну воду для економії ресурсів. Надаються рекомендації, які можуть бути корисними при розробці відповідних виробництв цеолітових матеріалів на основі золи виносу ТЕС.

Ключові слова: зола виносу, масштабування, технологічні параметри, техніко-економічні показники, утилізація відходів.