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Chapter 3

Synthesis of Zeolite from Fly Ash and their Use as Soil Amendment

Maria Harja, Sorin Mihai Cimpeanu, Marcel Dirja and Daniel Bucur

Additional information is available at the end of the chapter
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Abstract

The amendments may be natural or synthetic and by their origin organic or inorganic. Among amendments, the inorganic ones are recommended, such as gypsum, lime, zeolites and altered rocks, including sand, ceramic, perlite, ash, slag, zeolite, pyrites, dolomite, calcined clay, etc. Fly ash-based zeolites can be used as amendments to improve the use of the soil for agricultural purposes. Generally, there are different methods for the synthesis of new materials using solid waste – fly ashes. Methods are known to be composed of a single stage or two stages. The first method – the conventional – is direct hydrothermal conversion of the mixture of ash and alkaline solution (NaOH or KOH), but only 50% of ashes can be converted into zeolite. The second method consists in mixing the ash with KOH and fusion at elevated temperature. The method leads to an advanced conversion – the type of zeolite depending on treatment conditions. Other studies recommend the conversion of ash using microwave ovens or ultrasound bath; in this case, the conversion time is reduced to 1–2 hours. From these methods, the direct method was proposed to be used in synthesizing zeolites for agriculture, with a part in controlling release of fertilizers and as a soil amendment. The synthesized materials were characterized with respect to microstructure (electronic microscopy SEM) and chemical and mineralogical composition (EDAX, X-ray diffraction). By analyzing the obtained data, one may observe the destruction of the ash network and crystallization of the zeolitic phase, especially in the case of treatment by diffusion. The XRD analysis confirms the presence of zeolite in materials obtained. Good results were also obtained in the case of using ultrasound treatment for zeolite synthesis; also, the time of treatment significantly decreased in this case.

Keywords: amendment, fly ash, heavy metals, characterization, synthesis, soil, zeolite
1. Introduction

Soil is the most important component of the surface crust along with water and air of which it is composed of the environment. The mineral composition of soils is very diverse, usually including minerals from the silicate group, oxides, and hydroxides, and minerals ordered mainly on the grain size criteria [1]. The usual minerals are quartz, feldspar, mica and calcite, mullite, kaolinite, montmorillonite, illite, vermiculite, and chlorite. Organic and mineral constituents of soils are represented by organic complexes of metal ions (Cu$^{2+}$, Fe$^{3+}$, Mn$^{2+}$) and associations between clay and organic humic and nonhumic substances.

In the last decade, there has been a decrease in the areas with agricultural uses due to decreased fertility, compaction, acidification, heavy metal pollution, etc. To achieve higher agricultural production, measures must be taken to improve the physical, chemical, and biological properties of soils. Due to the acidity in the soil, nitrification and nitrogen-fixing soil bacteria do not develop; therefore, the content of nitrogen is low [2].

For improving soil characteristics, the research on soil quality being oriented toward finding measures to improve the structure, air, and water regime, restoring the content of organic matter, improving activity of soil microorganisms, knowing the transformation to which applied chemicals are exposed, critical limits of the pollution, reducing the content of heavy metal ions, and evaluating the risks to human health and domestic animals and wildlife.

A soil amendment describes any substances added to a soil to improve or modify its qualities and the conditions including physical, chemical, and biological conditions. An amended soil is a conditioned and a fertilized one. Choosing the amendment depends on what we seek to improve, the degree of soil degradation, its composition, the climate, etc. A suitable amendment to a situation may not be useful in other conditions [3].

The main objective of the amendments is to improve the use of the soil for agricultural purposes. The amendments may be natural or synthetic and by their origin organic or inorganic. Among amendments the inorganic ones are recommended, such as gypsum, lime, zeolites, altered rocks, ceramic, perlite, ash, slag, zeolite, pyrites, dolomite, calcined clay, etc. They contain a variable amount of nutrients, which can affect the pH.

Among inorganic substances used, the study focuses on thermal power station ash and its use in the synthesis of zeolites.

Among industrial wastes, ash plays a leading role because of the large volume and the consequences, due to a growing accumulation. Annually about 600 million tons of ash are produced, 75–80% of which is the one resulted from thermal plants, being considered the fifth as a source of prime mover [4].

The ash is used in agriculture since it contains nearly all of micro- and macro-elements, except for the organic carbon and nitrogen [5]. Also, the ash can contain moderate amounts of heavy metals, affecting groundwater and may be retained by plants. This material is used as the filling material, the recovery of acid soils, depending on the pH.
Zeolites are crystalline form of alkaline aluminosilicates, with a stable structure. This structure containing cavities has the ability to retain water and negative charge capably to change heavy metals [6]. This negative charge results in the ability of the zeolites to change plant nutrients and eliminate them from the structure. This ability to exchange cations allows nutrients such as nitrogen, calcium, iron, magnesium, potassium, and water to be available in the plant and to be removed at a low speed in time. In this way, the plant can absorb nutrients from the soil whenever it is required. Zeolites improve performance of fertilizers by increasing resistance to wash, immobilization, and gas losses. They increase soil water reserves needed during dry periods and are able to reversibly lose and retain water and to change network’s cations without the change in the structure. They are chemically inert, nontoxic to plants, animals, humans, and the environment and regulate the balance of soil through the immobilization of toxic contaminants.

2. Methods and types of amendments used for reduction of heavy metals

The contamination of soil with heavy metals has been occurring from the last century, but its extent has increased in the last years, due to industrial progresses and amplified user of supplies containing these metals. In the category, heavy metals enter a series of chemical elements, with high toxicity to living organisms. The toxic effect occurs above a certain threshold below which some of them (Co, Cd, Cu, Fe, Ni, Zn, Hg, and Pb) may even be essential components of proteins involved in various metabolic pathways. Thus, if the food would be completely devoid of metals, it would appear nutritional deficiencies.

The heavy metals are found in various concentrations in the soil, water, air, foods of vegetable, or animal origin, depending on the various factors that determine their pollution. Air can be a source of contamination representing a way of handling metals and their deposition on soil and plants (e.g., lead emissions from cars).

Accumulation of heavy metals in soils has implications over human health [7]. The heavy metals from different ecosystems would migrate into groundwater or bioaccumulate in herbs and get into the food chain [8]. In general, heavy metals may affect the soil ecosystem, not only agricultural produce and groundwater quality but also the human health [9].

Heavy metal contamination of the air is the result of numerous anthropogenic activities: combustion of coal, petroleum, nonferrous metal production, production of iron, steel and cement production, installations for waste gas treatment and incineration of waste accumulation, etc. The sources of metals in the soil can be use of fertilizers, pesticides containing metals (fungicides containing mercury, copper, arsenic, zinc, etc.). Of course, depending on the type of soil and geographic location, it can contain high amounts of heavy metals or they can be deficient.

2.1. Methods used for reduction of heavy metals

Many methods such as solidification, cementation, phytoremediation, earth-swap, and soil flushing can be used to reduce the heavy metal from contaminated soils. Among them, fixation
of heavy metal using amendments is a promising technology for removing heavy metals from contaminated soils. The application of soil amendments modified the properties of the contaminating heavy metals that allow their immobilization [10–12].

The fixation of heavy metals in soils had been greatly carried out with different amendments, such as zeolite, phosphates, cements, limes, and carbonates, or in the last years, with synthetic amendments: zeolites [13, 14], geopolymers, and phosphate [15–17]. In recent years, there were a lot of studies regarding amendments including by-products, waste, and low-cost synthetic materials for fixation of heavy metals. Low-cost amendments are required for the enhancement of fixing efficiency.

The fixation treatment is based on the reduction of metal mobility and availability as a result of applying amendments. In this way, the unfavorable effects of heavy metals to environmental receptors are reduced [18]. The mechanism of heavy metals removal is based on adsorption, precipitation, cation exchange, and complexation.

### 2.2. Types of amendments

The fixation efficiency depends on the quantity of the amendments and on the properties of these and soils. The chemical and physical properties are also the influencing factors in the fixation process. The cation mobility is the greatest property that can determine their environmental impact. The heavy metal ions have the individual mobilities and are difficult to find the amendments for reducing the bioavailability.

Among the numerous treatment compounds, some are recommendable for several heavy metals: limes, phosphates, organic matter, industrial by-products, and low-cost zeolites.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Heavy metals</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>Cd, Pb, Cu, Zn, Cr</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>Lime</td>
<td>Cd, Cu, Ni, Pb, Zn, Cr</td>
<td>[18, 19]</td>
</tr>
<tr>
<td>Phosphate salt</td>
<td>Pb, Zn, Cd, Cu</td>
<td>[3, 16]</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>Zn, Pb, Cu, Cd</td>
<td>[15]</td>
</tr>
<tr>
<td>Slag</td>
<td>Cd, Pb, Zn, Cr</td>
<td>[24]</td>
</tr>
<tr>
<td>Ettringite</td>
<td>Cd, Cu, Pb, Zn, Cr</td>
<td>[25]</td>
</tr>
</tbody>
</table>

Table 1. Types of inorganic amendments for metal immobilization [18].

Firstly, additives used for heavy metal immobilization can be classified into inorganic, organic, and both inorganic-organic materials. According to the nature of different materials, there are three resources including natural materials, artificial synthetics, and by/co-products used for fixing process. Natural materials that are available in a large quantity or are waste products from industrial or agricultural sources may have potential as low-cost sorbents. Due to their low cost, after utilization they can be disposed of without expensive regeneration. In addition,
inorganic or organic amendments are used to improve soils’ substrate characteristics. The types of inorganic amendments are presented in Table 1.

The materials including CaO, Ca(OH)₂, CaCO₃, CaMgCO₃, CaHPO₄, Ca(H₂PO₄)₂, K₂HPO₄, H₂PO₄, and (NH₄)HPO₄ are the typical amendments used for the immobilization of heavy metals. On the other hand, zeolites decrease the metal concentration in soil solution, the metal mobility, and leachability and transform heavy metal cations from soluble into insoluble cations [16, 19, 20]. Wang et al. [21] reported that Ca(H₂PO₄)₂ could replace CaHPO₄ due to lower cost and higher solubility in the field study. The combination of Ca(H₂PO₄)₂ and CaCO₃ significantly reduces the extractable metal concentration and successfully immobilize heavy metals on the site. Quicklime (CaO) was a more effective additive because it is readily soluble and available for reactions, and its addition to a soil material results in larger pH increases.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Abbreviations</th>
<th>Chemical form</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaP₁</td>
<td>NaP₁</td>
<td>Na₄Al₅Si₄O₁₆·12H₂O</td>
</tr>
<tr>
<td>Sodalite</td>
<td>S</td>
<td>Na₄(H₂O)₈Si₄AlO₁₄</td>
</tr>
<tr>
<td>Analcime</td>
<td>A</td>
<td>Na₄Si₃O₆·H₂O</td>
</tr>
<tr>
<td>Faujasite</td>
<td>Fau</td>
<td>Na₂Al₅Si₃O₉·6.7H₂O</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>T</td>
<td>Ca₁₀(OH)₃Si₃O₉·4H₂O</td>
</tr>
<tr>
<td>Na-X</td>
<td>Na-X</td>
<td>Na₁₀(H₂O)₈Si₄Al₄O₃₄</td>
</tr>
<tr>
<td>Na-Y</td>
<td>Na-Y</td>
<td>Si₁₀O₃₄</td>
</tr>
<tr>
<td>Zeolite A</td>
<td>Zeolitul A</td>
<td>NaAl₄Si₄O₃·2.25H₂O</td>
</tr>
<tr>
<td>Zeolite X</td>
<td>X</td>
<td>NaAl₄Si₄O₃·1.8H₂O</td>
</tr>
<tr>
<td>Zeolite Y</td>
<td>Y</td>
<td>NaAl₄Si₄O₃·4.4H₂O</td>
</tr>
<tr>
<td>Cancrinite</td>
<td>Can</td>
<td>NaCa₃(SiAl)₆O₁₆·SiAlO₃₄</td>
</tr>
<tr>
<td>Gismondine</td>
<td>Gis</td>
<td>Ca₆Na₂(OH)₁₂·Si₄Al₂O₁₂</td>
</tr>
<tr>
<td>Chabazite</td>
<td>Cha</td>
<td>K₂₂Na₁₀(OH)₆Si₄Al₂O₁₄</td>
</tr>
<tr>
<td>Linde A</td>
<td>Linde A</td>
<td>Na₁₀(H₂O)₈Si₄Al₄O₃₄</td>
</tr>
<tr>
<td>Clinotobermorite</td>
<td>CT</td>
<td>Ca₃(SiAl)₆·5H₂O</td>
</tr>
<tr>
<td>Nephein</td>
<td>Nep</td>
<td>Na₂H₂O₈Si₄Al₂O₁₄</td>
</tr>
<tr>
<td>Tobermorite</td>
<td>T</td>
<td>Ca₆(OH)₆Si₃O₉·4H₂O</td>
</tr>
<tr>
<td>Phillipite</td>
<td>Ph</td>
<td>K₂Al₂Si₄O₁₀·2H₂O</td>
</tr>
<tr>
<td>K-chabazite</td>
<td>K-Cab</td>
<td>K₂Al₂Si₄O₁₀·2H₂O</td>
</tr>
<tr>
<td>Linde F</td>
<td>Linde F</td>
<td>KAlSi₄O₁·1.5H₂O</td>
</tr>
<tr>
<td>Kalsilite</td>
<td>K</td>
<td>KA₃SiO₄</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of zeolite obtained from fly ash [31, 32].
Zeolites are crystalline aluminosilicate form alkali [26, 27]. They have a stable structure with three-dimensional five silica tetrahedra in a unique symmetrical arrangement [28]. This structure containing cavities has the ability to retain water and negative charge inside the opening cation binds to change [29]. This negative charge results in the ability of zeolites to change plant nutrients and eliminate them from the structure [29].

Zeolites are recognized as “intelligent fertilizers” because of the ion exchange capacity (CEC) and high porosity [30]. The ability to exchange cations allows nutrients such as nitrogen, calcium, iron, magnesium, potassium, and water to be available in the plant and be eliminated slowly [26, 29, 30]. In this way, plants can absorb nutrients from the soil when required. Zeolites improve performance by increasing resistance to wash fertilizers, immobilization, and gas leaks. They increase water reserves in soil needed during dry periods and are able to reversibly lose and retain water and change cations’ network without changing the structure. They are chemically inert, nontoxic to plants, animals, humans, and the environment and regulate the balance of soil by immobilization of toxic contaminants to the plant [26].

As a result, the application of the zeolite increases ion-exchange capacity, which allows the retention followed by a controlled release of nutrients, reduces the consumption of fertilizer and water necessary to complete the potassium, increases the availability of the use of phosphorous adsorbed toxic contaminants, acts as a buffering agent pH and alkalinity, reduces the effects, improves the aeration, allows the activity of microorganisms, establishes the alkali metal balances, and is cheap. It can have nutritional value that helps germination, root development, and plant growth and grain [28–30].

Zeolites with chemical composition presented in Table 2 are used, due to the special properties such as adsorption, ion exchange, molecular sieve, hydration, dehydration, bulk density, porosity, and structure [27, 28], to interact with other minerals from the soil, resulting in improved soil structure [26].

3. The methods to obtain zeolites from fly ash

One possibility to recover the ash is the conversion in zeolites. The zeolites prepared by alkali activation of fly ash are aluminum-silicates and include three classes of inorganic polymers, depending on the ratio of silica/alumina: (\text{Si—O—Al—O—}), poly-sialic – \text{SiO}_2/\text{Al}_2\text{O}_3 = 2; (\text{Si—O—Al—O—Si—O—}), poly-sialic siloxo – \text{SiO}_2/\text{Al}_2\text{O}_3 = 4; and (\text{Si—O—Al—O—Si—O—Si—O—}), poly-sialic disiloxo – \text{SiO}_2/\text{Al}_2\text{O}_3 = 6. The composition of the mixture and the reaction conditions such as \text{SiO}_2/\text{Al}_2\text{O}_3 ratio, hydroxide concentration, activation temperature, curing time, ratio of the solid/liquid, and pH significantly affect the formation and properties of zeolites. Limits of variation in these parameters are broad enough: ratio \text{SiO}_2/\text{Al}_2\text{O}_3 2–6, activation temperature 80–150°C, concentration of (Na or K) hydroxide 1–5 M, curing time of 4–48 hours, and the ratio of the solid/liquid 1/1–1/4 [33, 34].

Generally, there are two main methods for the synthesis of new materials using solid waste – fly ashes. Methods are known to be composed of a single stage or two stages.
<table>
<thead>
<tr>
<th>1–3 mL/g</th>
</tr>
</thead>
</table>
| 1.0 M NaOH | 90°C | Zeolite A  
| | 200°C | NaP1, Her (8 activation hours)  
| 2.0–3.0 M NaOH | 150°C | NaP1, Fau  
| | 200°C | NaP1, Her  
| 5.0 M NaOH | 150–200°C | NaP1, Her  
| | 200°C | Her, A, HS, HC  
| 2.0 M KOH | 150–200°C | KM  
| 5.0 M KOH | 150°C | KM, Cha, Linde F  
| 3–6 mL/g |  
| 0.5 M NaOH | 150°C | NaP1 (48, 72 activation hours)  
| 1.0 M NaOH | 120°C | NaP1, A (6 activation hours)  
| 1.0–3.0 M NaOH | 100°C | S, Gis (24, 48, 120, 288 ore)  
| 10–18 mL/g |  
| 0.5 M NaOH | 150°C | NaP1, HS, A (48, 96 activation hours)  
| | | NaP1, T (72 activation hours)  
| 0.5–2.0 M NaOH | 95°C, 120°C | NaP1 (24 activation hours)  
| 0.5–2.0 M NaOH | 150°C | NaP1, HS, T (9, 24, 48 activation hours)  
| 0.5–2.0 M NaOH | 150°C | NaP1, HS, T, A (24, 72 activation hours)  
| 2.0 M NaOH | 100°C | 4A  
| 0.5–3.0 M NaOH | 90–175°C | NaP1  
| | 175–225°C | A, HS, T, Nep  
| 2.0–3.0 M | 90°C | Zeolite A  
| | 150°C | NaP1, Fau  
| | 200°C | NaP1, Her  
| 3.0–5.0 M NaOH | 150–200°C | HS, HC, Tob  
| 0.5–1.0 M KOH | 150–200°C | KM, T  
| 3.0 M KOH | <150°C | Linde F, T  
| 5.0 M KOH | <150°C | Linde F, T  

Table 3. Zeolites from fly ash as a function of hydroxide (NaOH/KOH) concentration, temperature and L/s ratio.

In 1985, Holler and Wirsching synthesized, for the first time, zeolites from fly ash by direct activation method [35]. As a result of studies carried out by Holler and Wirsching, several researchers have proposed various methods to obtain new materials based on fly ash in articles and patents:
• direct activation method (hydrothermal method): [36–44];
• fusion method followed by direct activation method: [45–49];
• ultrasound method: [13, 50, 51];
• microwave followed by direct activation method.

Table 3 presents the main types of new materials, which can be obtained as a function of zeolitization conditions.

Figure 1. The mechanism of zeolitization of fly ash.

The first method – the conventional one, it is direct hydrothermal conversion of the mixture of ash and alkaline solution. Only 50% of ashes can be converted into P-zeolite or hydroxy
sodalite. The second method consists in mixing the ash with alkaline reagents and fusion at elevated temperature (typically 550°C) to convert the ash into a soluble potassium silicate and potassium aluminate, followed by dissolution in an alkaline solution. Fusion method is performed with KOH and NaOH. The method leads to an advanced conversion, the type of zeolite depending on treatment conditions. The third method consists in the extraction of silicon from ashes in the first stage, after that solution was added in a well-established proportion, which leads to a very pure zeolite. Also, experimental studies recommend the conversion of ash using microwave ovens; in this case, the conversion time is reduced from 24–48 hours to 30 minutes. To use this method, extensive research is required because not every type of ash can be changed. Even if the direct method was considered, it is disappointing regarding the zeolite purity and simplicity, and synthesis in a single step was proposed to be used in synthesizing zeolites for agriculture, with a part in controlling release of fertilizers and as a soil amendment.

The main limitation of the synthesis process of zeolites is the temperature (125–200°C) to dissolve Si and Al from the ash particles. If the temperature is reduced, then the yield of the synthesis is considerably reduced, and it is necessary to have a greater reaction time. However, KM, herschelite, K-chabazite, and Linde F can be obtained in the range of 125–200°C.

Fly ash mainly consists of amorphous and subordinate crystalline phases such as quartz, mullite, and hematite. The amorphous material represents the most reactive phase during the zeolitization process. If there is a big content of vitreous phase, the activation time is reduced, and the alkaline hydroxide solution is less concentrated.

After treatment, the samples were allowed to cool for 20 hours at room temperature \( T = 20^\circ C \), filtered, washed, and dried.

Murayama et al. [52] and Bukhari et al. [53] showed that the conversion mechanism implicates the steps: dissolution, crystallization, and/or condensation (Figure 1).

Either method is used; the most important parameters in the modifying process are activation time; concentration of the solutions used for modification; temperature; and ratio of ash-solution.

3.1. Direct activation method (hydrothermal method)

The experimental results demonstrated that the fly ash consists predominantly of quartz (\( \text{SiO}_2 \)), mullite (\( 2\text{SiO}_2\cdot3\text{Al}_2\text{O}_3 \)), hematite (\( \text{Fe}_2\text{O}_3 \)), and magnetite (\( \text{Fe}_3\text{O}_4 \)) can be modified by direct activation method. The method consists in conversion of fly ash into zeolite by treatment of these with alkaline solution, such as NaOH or KOH for extraction of the components (aluminum and silica), and heat treatment for growth of zeolite crystals.

For obtaining one pre-established type of zeolite, it can be possible to insert with aluminum or silica compounds. By the direct activation method, materials were obtained as zeolite X [45, 54, 55], zeolite A, analcime, chabazite, or hydroxy-sodalite as a function of temperature, pressure, Si/Al ratio, alkaline solution, reaction time, pH, etc. [37, 56, 57].

Scheme for the preparation of new materials by direct activation method is shown in Figure 2.
Figure 2. Modification scheme of ash through direct activation.

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaP₁</td>
<td>[33, 36–38, 45, 58, 59]</td>
</tr>
<tr>
<td>NaA, S</td>
<td>[45, 60]</td>
</tr>
<tr>
<td>Na-Cha</td>
<td>[33, 61]</td>
</tr>
<tr>
<td>Na-X</td>
<td>[41]</td>
</tr>
<tr>
<td>NaP₁, T, HC, Her, HS</td>
<td>[58]</td>
</tr>
<tr>
<td>NaP₂, A, P, Nep</td>
<td>[36]</td>
</tr>
<tr>
<td>NaP₃, HS</td>
<td>[37]</td>
</tr>
<tr>
<td>NaP₁, HS, T, A</td>
<td>[38]</td>
</tr>
<tr>
<td>NaP₁, HS, A</td>
<td>[38, 62]</td>
</tr>
<tr>
<td>NaP₁, F</td>
<td>[63]</td>
</tr>
<tr>
<td>Na-A</td>
<td>[40]</td>
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<tr>
<td>Gi, S</td>
<td>[47]</td>
</tr>
<tr>
<td>Y</td>
<td>[33]</td>
</tr>
<tr>
<td>A</td>
<td>[64]</td>
</tr>
<tr>
<td>ZSM-5</td>
<td>[65]</td>
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<tr>
<td>HS, NaA, Linde F</td>
<td>[43]</td>
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<tr>
<td>HS, NaP₁, X</td>
<td>[66]</td>
</tr>
<tr>
<td>Na-HEU</td>
<td>[42]</td>
</tr>
</tbody>
</table>

Table 4. Zeolites obtained by direct activation method.
Direct activation method comprises one step in seeking to use the content of silica in ash to produce a new material. Treatment takes place in an autoclave at temperatures between 80 and 200°C with agents brought to KOH and NaOH for 3–96 hours contact solution concentration: 0.5–5 M and the ratio L/s 1–3 mL/g and 10–18 mL/g (Table 4).

![SEM micrographs of zeolites synthesized by direct activation method.](image)

The main disadvantage of the direct conversion method is relatively low-conversion degree. Several studies have focused on the relationship between composition of the raw materials and the synthesis conditions. However, conditions are not clearly established, and the combination of crystalline phases obtained is often unpredictable.

In Figure 3, the particles’ morphology of zeolites synthesized by direct activation method is shown.

From Figure 3, it can be seen that ash morphology changes significantly, increasing mainly newly formed crystals on the surface of the particles. Following zeolitization, surface area increases significantly.

3.2. Fusion method followed by direct activation method

To obtain ash zeolites, the fusion step was proposed before the hydrothermal treatment. The ash mixed with solid NaOH is heated at high temperature, after which it is subjected to direct conversion. The alkaline fusion step before direct activation significantly improves zeolitization [45, 69].

Ash changing using the fusion method followed by direct activation has been reported by several authors [49, 69].

This method is known as the indirect method, as it consists of two phases:

- the fusion phase (450–600°C temperature, contact time 1–3 hours)
the direct activation phase (temperature 60–100°C for 4–96 hours contact)

After the conclusion of the fusion phase, the materials were allowed time to age (room temperature, contact time of approximately 20 hours).

<table>
<thead>
<tr>
<th>Material</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-X, Na-A</td>
<td>[70]</td>
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<tr>
<td>Na-X</td>
<td>[49]</td>
</tr>
<tr>
<td>Na-A</td>
<td>[21, 49]</td>
</tr>
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<td>Na-Y</td>
<td>[47]</td>
</tr>
<tr>
<td>Na-X, Na-A, Na-P</td>
<td>[46, 67]</td>
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<tr>
<td>Fau</td>
<td>[47]</td>
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<tr>
<td>Zeolite 13X</td>
<td>[69]</td>
</tr>
<tr>
<td>ZFA</td>
<td>[48]</td>
</tr>
<tr>
<td>X, A, P, HS</td>
<td>[41]</td>
</tr>
</tbody>
</table>

Table 5. New materials obtained by the fusion method followed by direct activation.

Previous studies have also shown that the ash-synthesized materials by this method have a higher crystallinity and cation exchange capacity compared to the materials synthesized by the conventional hydrothermal method. The fusion method followed by direct activation method allows for a higher amount of alkaline extract ash silicates and alumina. The formation of new materials depends heavily on the SiO$_2$/Al$_2$O$_3$ ratio of the base material.

Table 5 presents the main types of new materials, which are obtained.

Figure 4 provides a few examples of new materials obtained by the fusion method followed by the direct activation.

Figure 4. SEM images of materials obtained by fusion.
Obtaining new Na-A and Na-X type materials is also possible by direct activation, but when obtained by the fusion followed by direct activation method, these have higher cation exchange capacity and larger pores. The disadvantage of this method consists in the fact that the method involves the separation of the solid residues after a high content of silicon and aluminum has been dissolved in the alkaline solution. Disposal of the residues increases the possibility of obtaining a desired type of zeolite with high purity and regular particles, while leaving a new solid waste, with a very low production yield [Śś].

3.3. Ultrasound method

Ultrasound (USs) are a form of mechanical energy that propagates in all directions in the form of beams. The ultrasound method has been reported primarily by Schmachtl et al. [72]. The ultrasound method is an indirect method, which is based on the investigation of the degree of interaction of the wave transmission ultrasonic properties with the precursor species of new materials, as they pass through the synthesis mixture. The method has been used in the synthesis of a wide range of nano- and microparticles.

Figure 5. SEM images obtained using ultrasound equipment. 3 - NaP zeolite synthesized by: (a) the sonochemical method at room temperature, 3 hours, (b) the sonochemical method followed by hydrothermal treatment for 12 hours at 100°C (c) sonochemical method followed by hydrothermal treatment for 24 hours at 100°C [78].
Of the various applications of the ultrasound treatment obtaining new ash-based materials requires special attention because it offers several advantages, the most significant being a reduced reaction time and crystallization temperature [21, 50, 51, 67, 73–75].

Feng et al. [76] showed that this method increases the compressive strength and thermal stability of the material. By accelerating the dissolution of the Al-Si, it improves polycondensation and the formation of semicrystalline phases. Ultrasound accelerates the chemical reactions of the components, the method being used to obtain new materials from sources, which contain Al and Si [72].

Ultrasound influences the physicochemical properties of the crystals, which result in following the synthesis. The effects of ultrasound are due to cavitation, a phenomenon may be defined as the occurrence of bubbles, which rise to the surface and then break. This can be explained by the fact that rapid successive expansions and compressions in liquid give rise to excessive stress in some areas.

The molar ratio of reactants, contact time, and temperature is important parameters that determine the type and properties of the new material. The disadvantage of this method is that the application of ultrasound changes the morphology of the crystals (crystal size decreases with power increase – Figure 5).

By applying different temperatures, concentrations of alkaline solution, the solid/liquid ratio, and the contact time, one can obtain materials with specific applications (Table 6).

<table>
<thead>
<tr>
<th>Materials</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A</td>
<td>[51, 77, 79]</td>
</tr>
<tr>
<td>NaP</td>
<td>[78, 80]</td>
</tr>
<tr>
<td>MCM-22</td>
<td>[21]</td>
</tr>
<tr>
<td>X</td>
<td>[56]</td>
</tr>
<tr>
<td>Na-X</td>
<td>[81]</td>
</tr>
</tbody>
</table>

Table 6. New materials obtained by the ultrasound method.

3.4. Microwave method followed by hydrothermal activation

Querol et al. [36] obtained a zeolite using ash with a Si/Al ratio of 1.85 with a 62% amorphous phase, while the crystalline phases included: mullite (13%), magnetite (13%), quartz (7%), anhydrite (0.7%), and anorthite (0.3%). Two alkaline solutions of NaOH and KOH were used to obtain the zeolite crystals. The concentration of the solutions ranged from 1.0 to 5.0 M, and the temperature ranged between 150°C and 225°C, using both the conventional method and the microwave method (microwave oven with the available power of 1000 W). The crystallization time was reduced from conventional conversion of 8–98 hours to 10–30 minutes of microwave-assisted conversion. By changing the above-mentioned parameters, different stages of zeolite were obtained: Na-P1, hydroxy-sodalite, analcime, Linde F, tobermorite and kalsilit. Generally speaking, microwaves play a positive role in obtaining Na-P1. Experimen-
tally, it was found that microwaves applied in the first 15 minutes, followed by 2 hours of synthesis led to the best results in as far as the ion-exchange capacity was concerned [53].

<table>
<thead>
<tr>
<th>Materials</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-11</td>
<td>[84]</td>
</tr>
<tr>
<td>Sodalite</td>
<td>[68, 85]</td>
</tr>
<tr>
<td>FAU</td>
<td>[86]</td>
</tr>
<tr>
<td>NaA</td>
<td>[83, 87]</td>
</tr>
<tr>
<td>4A, Na-P1</td>
<td>[88]</td>
</tr>
</tbody>
</table>

**Table 7.** New materials obtained by the ultrasound method.

![SEM images](http://dx.doi.org/10.5772/64126)

**Figure 6.** SEM images of the materials obtained by the microwave method at different molar ratios of SiO$_2$/Al$_2$O$_3$: (a) 0.4, (b) 0.8, (c) 4.0, and (d) 10.0 [83].

Fukui et al. [82] used ash with a Si/Al ratio of 2.39 and NaOH at 100°C using the conventional method and the microwave method and obtained preponderantly filipsite. The particles of filipsite were smaller in the case of microwave treatment. Experimentally it has been demonstrated that microwaves increase the rate of nucleation, but result in a slower growth of the germ. The microwaves used for the first 2 hours, followed by conventional heating, positively influence the mechanism of germ formation and growth.
Tanaka et al. [83] used a 600 W microwave oven and the two-step synthesis method in order to obtain Na-A zeolite. The ashes used in the process had a Si/Al ratio of 2.76, a vitreous phase content of 49.4% and the NaOH solution had a concentration of 2.2 M. The mixture was irradiated in the oven for 60 minutes. The material obtained had an ion-exchange capacity of 4.70 meq/g, lower than the commercial material.

Figure 6. SEM images of the zeolites synthesized by the microwave method are shown in Figure 6.

Kim and Lee [79] obtained Na-4A zeolite with an ion-exchange capacity of 5.5 meq/g. The literature indicates that microwave irradiation for 2 hours dissolves the compounds containing Si and Al and P zeolite and hydroxyl sodalite were obtained (Table 7). SEM images of the zeolites synthesized by the microwave method are shown in Figure 6.

Figure 7 presents the studies in the literature in the field of the materials obtained by modifying the ashes, depending on the morphology of the preponderant zeolite [62, 67, 71, 89, 90, 92]. Figure 7 shows also that the morphology differs from one material to another from well-defined tetrahedral crystals to clusters of crystals.
Analysis of the literature data shows that alkaline attack of power plant ash allows one to obtain new materials, a mixture of zeolites, but the type and degree of zeolitization are influenced by the working conditions.

4. Conclusions

Zeolites from ashes are recognized as “intelligent fertilizer” because they have the ability to exchange cations allowing nutrients such as nitrogen, calcium, iron, magnesium, potassium, and water to be available in the plant and be eliminated slowly. The plants can absorb nutrients from the soil when required. Zeolites increase water reserves in soil needed during dry periods and are able to reversibly lose and retain water and change cations’ network without changing the structure. They are chemically inert, nontoxic to plants, animals, humans, and the environment and regulate the balance of soil by immobilization of toxic contaminants to the plant.

The waste – fly ash can be capitalized by conversion in zeolites. The zeolites prepared by alkali activation of fly ash are aluminum-silicates and include three classes of inorganic polymers, depending on the ratio of silica/alumina. The composition of the mixture, and the reaction conditions such as SiO$_2$/Al$_2$O$_3$ ratio, hydroxide concentration, activation temperature, curing time, ratio of the solid/liquid, and pH significantly affect the formation and properties of zeolites. Limits of variation in these parameters are broad enough: ratio SiO$_2$/Al$_2$O$_3$ 2–6, activation temperature 80–150°C, concentration NaOH or KOH solution 1–5 M, curing time of 4–48 hours and the ratio of the solid/liquid 1/1–1/4.

The methods used for the synthesis of new materials using solid waste – fly ashes are direct activation method (hydrothermal method), fusion method followed by direct activation method, ultrasound method, and microwave followed by direct activation method.

The main limitation of the synthesis process of zeolites is the relatively high temperature to dissolve Si and Al from the ash particles. If the temperature is reduced, then the yield of the synthesis is considerably reduced, and it is necessary to have a greater reaction time. However, KM, herschelite, K-chabazite, and Linde F can be obtained in the range of 125–200°C.

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