We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

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

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

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^{2+}, 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.

Materials	Heavy metals	References
Fly ash	Cd, Pb, Cu, Zn, Cr	[22, 23]
Lime	Cd, Cu, Ni, Pb, Zn, Cr	[18, 19]
Phosphate salt	Pb, Zn, Cd, Cu	[3, 16]
Hydroxyapatite	Zn, Pb, Cu, Cd	[15]
Slag	Cd, Pb, Zn, Cr	[24]
Ettringite	Cd, Cu, Pb, Zn, Cr	[25]

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)$_2$, CaCO$_3$, CaMgCO$_3$, CaHPO$_3$, Ca(H$_2$PO$_3$)$_2$, K$_2$HPO$_4$, H$_3$PO$_4$, and (NH$_4$)HPO$_4$ 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(H$_2$PO$_4$)$_2$ could replace CaHPO$_4$ due to lower cost and higher solubility in the field study. The combination of Ca(H$_2$PO$_4$)$_2$ and CaCO$_3$ 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.

Materials	Abbreviations	Chemical form
NaP1	NaP1	Na$_6$Al$_6$Si$_{10}$O$_{32}$·12H$_2$O
Sodalite	S	Na$_6$(H$_2$O)$_8$Si$_6$Al$_6$O$_{24}$
Analcime	A	NaAlSi$_2$O$_6$·H$_2$O
Faujasit	Fau	Na$_2$Al$_2$Si$_{3.3}$O$_{8.8}$·6.7H$_2$O
Tobermorite	T	Ca$_5$(OH)$_2$Si$_6$O$_{16}$·4H$_2$O
Na-X	Na-X	Na$_{88}$(H$_2$O)$_{220}$Si$_{104}$Al$_{88}$O$_{384}$
Na-Y	Na-Y	Si$_{192}$O$_{384}$
Zeolite A	Zeolitul A	NaAlSi$_{1.1}$O$_{4.2}$·2.25H$_2$O
Hydroxy-sodalite	HS	Na$_{1.08}$Al$_2$Si$_{1.68}$O$_{7.44}$·1.8H$_2$O
Zeolite X	X	NaAlSi$_{1.23}$O$_{4.46}$·3.07H$_2$O
Zeolite Y	Y	NaAlSi$_{2.43}$O$_{6.86}$·4.46H$_2$O
Cancrinite	Can	Na$_7$Ca$_{0.9}$(CO$_3$)$_{1.4}$(H$_2$O)$_{2.1}$Si$_6$Al$_6$O$_{24}$
Gismondine	Gis	Ca$_{3.68}$(H$_2$O)$_{17.2}$Si$_{8.8}$Al$_{7.2}$O$_{32}$
Chabazite	Cha	K$_{3.2}$Na$_{0.75}$(H$_2$O)$_{8.4}$Si$_{8.2}$Al$_{3.8}$O$_{24}$
Linde A	Linde A	Na$_{96}$(H$_2$O)$_{216}$Si$_{96}$Al$_{96}$O$_{384}$
Clinotobermorite	CT	Ca$_5$(Si$_6$O$_{17}$)·5H$_2$O
Nephelin	Nep	Na$_3$H$_2$OSi$_3$Al$_3$O$_{12}$
Tobermorite	T	Ca$_5$(OH)$_2$Si$_6$O$_{16}$·4H$_2$0
Phillipsite	Ph	K$_2$Al$_2$Si$_3$O$_{10}$·H$_2$O
K-chabazite	K-Cab	K$_2$Al$_2$SiO$_6$·H$_2$O
Linde F	Linde F	KAlSiO$_4$·1.5H$_2$O
Kalsilite	K	KAlSiO$_4$

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: (—Si—O—Al—O—), poly-sialic – SiO_2/Al_2O_3 = 2; (—Si—O—Al—O—Si—O—), poly-sialic siloxo – SiO_2/Al_2O_3 = 4; and (—Si—O—Al—O—Si—O—Si—O—), poly-sialic disiloxo – SiO_2/Al_2O_3 = 6. The composition of the mixture and the reaction conditions such as SiO_2/Al_2O_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_2O_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.

	1–3 mL/g	
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.
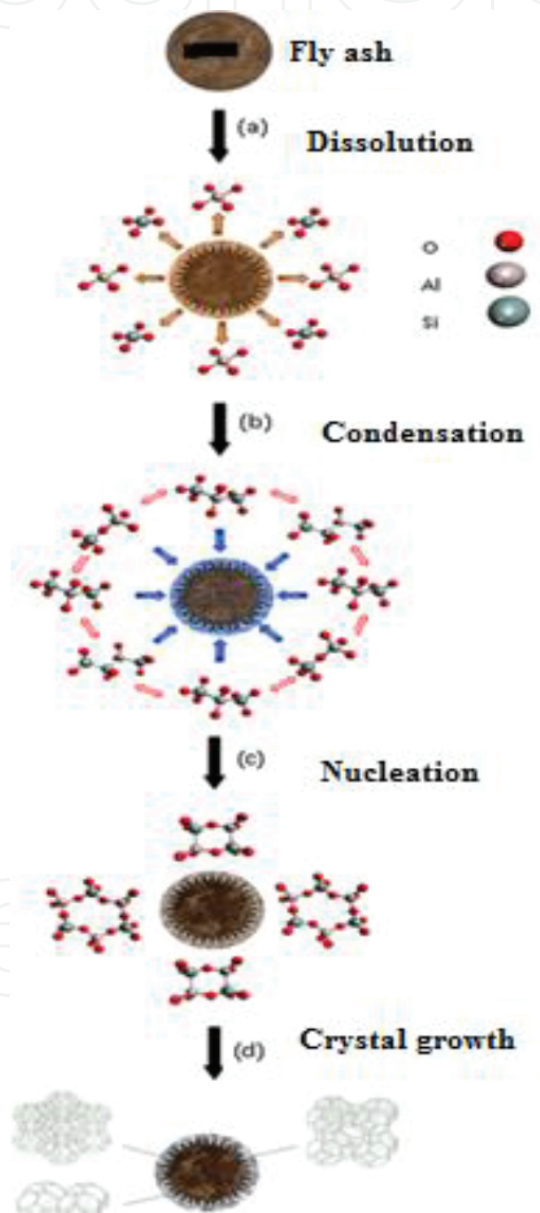
Figure 1. The mechanism of zeolitization of fly ash.

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 $T = 20°C$, 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 (SiO_2), mullite ($2SiO_2·3Al_2O_3$), hematite (Fe_2O_3), and magnetite (Fe_3O_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**.
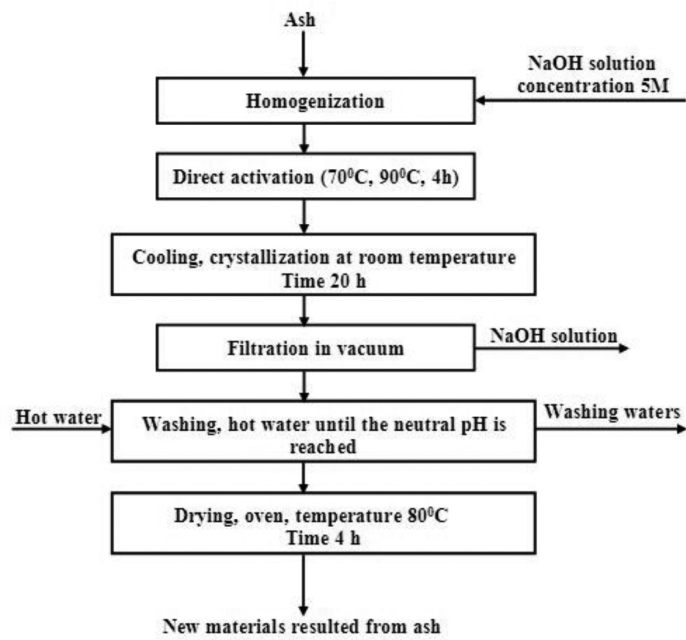
Figure 2. Modification scheme of ash through direct activation.

Zeolite	References
NaP$_1$	[33, 36–38, 45, 58, 59]
NaA, S	[45, 60]
Na-Cha	[33, 61]
Na-X	[41]
NaP1, T, HC, Her, HS	[58]
NaP$_1$, A, P, Nep	[36]
NaP$_{1,}$ HS	[37]
NaP1, HS, T, A	[38]
NaP$_{1,}$ HS, A	[38, 62]
NaP$_{1,}$ F	[63]
Na-A	[40]
Gis, S	[47]
Y	[33]
A	[64]
ZSM-5	[65]
HS, NaA, Linde F	[43]
HS, NaP1, X	[66]
Na-HEU	[42]

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**).

1:5, 90°C, 5M, 4 h, [67]   1:3, 90°C, 5M, 15 h [68]
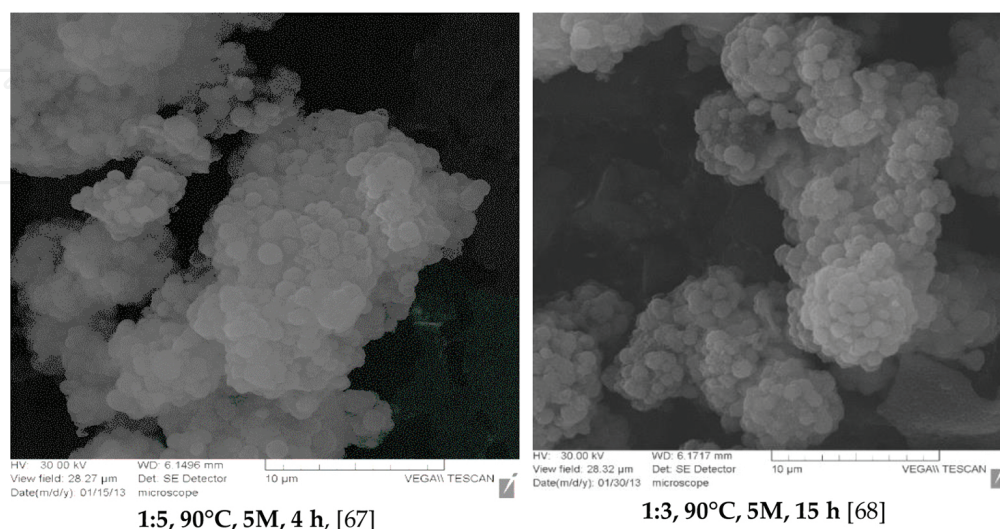
Figure 3. SEM micrographs of zeolites synthesized by direct activation method.

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).

Material	References
Na-X, Na-A	[70]
Na-X	[49]
Na-A	[21, 49]
Na-Y	[47]
Na-X, Na-A, Na-P	[46, 67]
Fau	[47]
Zeolite 13X	[69]
ZFA	[48]
X, A, P, HS	[41]

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_2O_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.


[41]   [71]
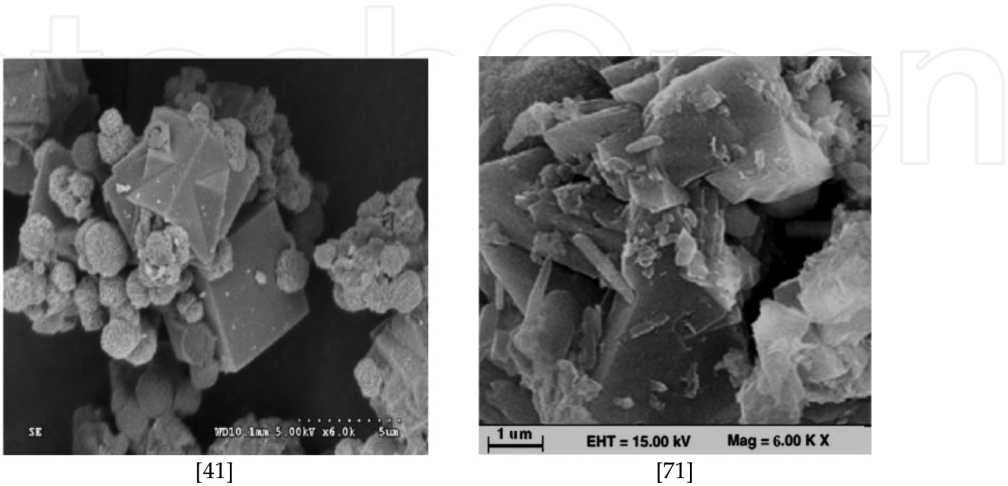
Figure 4. SEM images of materials obtained by fusion.

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 [45].

3.3. Ultrasound method

Ultrasounds (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.

1 - [53]   2 - [77]
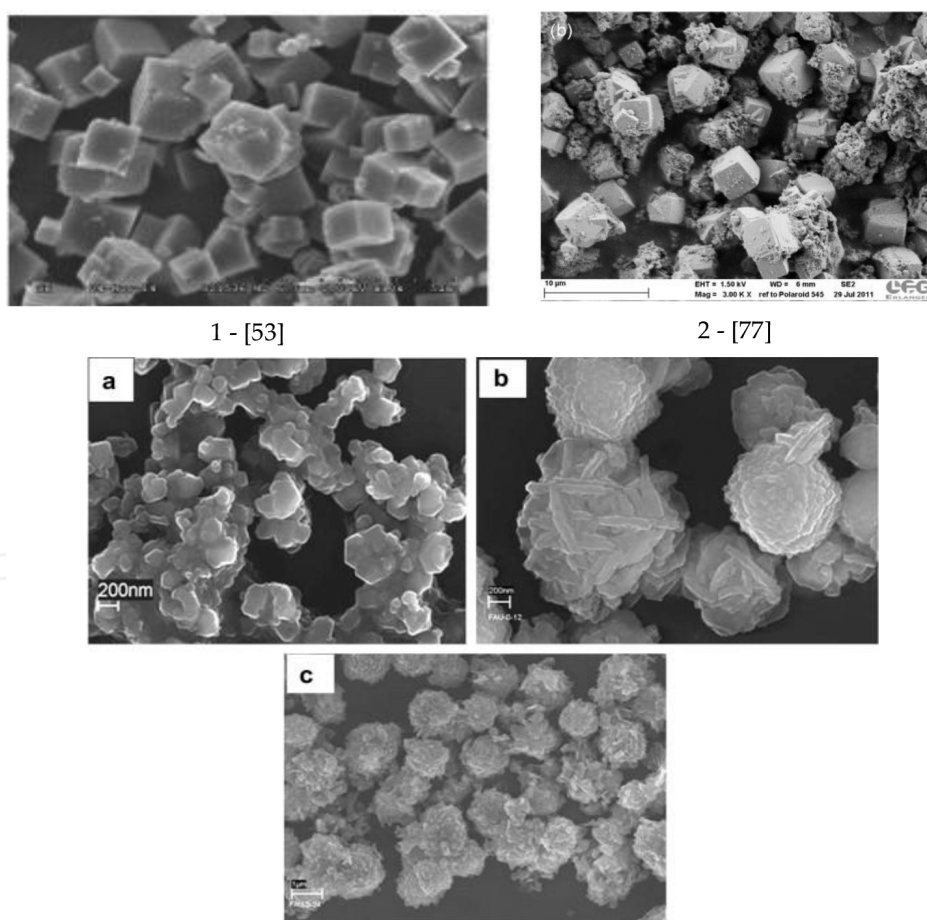
Figure 5. SEM images obtained using ultrasound equipment. 3 - NaP zeolite synthesized by: (a) the sonochemical method at room temperature, 3 hours, (b) the sonochemical method followed by hydrothermal treatment for 12 hours at 100°C (c) sonochemical method followed by hydrothermal treatment for 24 hours 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**).

Materials	References
4A	[51, 77, 79]
NaP	[78, 80]
MCM-22	[21]
X	[56]
Na-X	[81]

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].

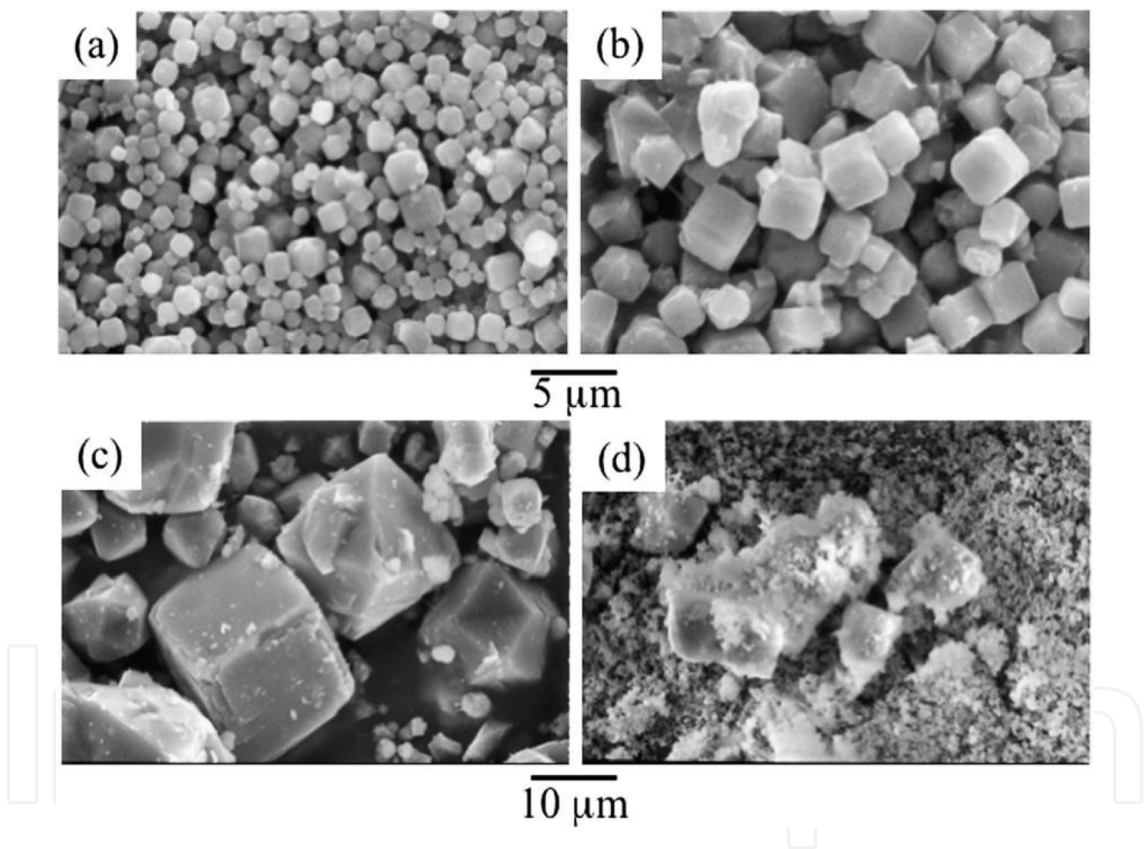| Materials	References
ZSM-11	[84]
Sodalite	[68, 85]
FAU	[86]
NaA	[83, 87]
4A, Na-P1	[88]

Table 7. New materials obtained by the ultrasound method.

Figure 6. SEM images of the materials obtained by the microwave method at different molar ratios of SiO_2/Al_2O_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.
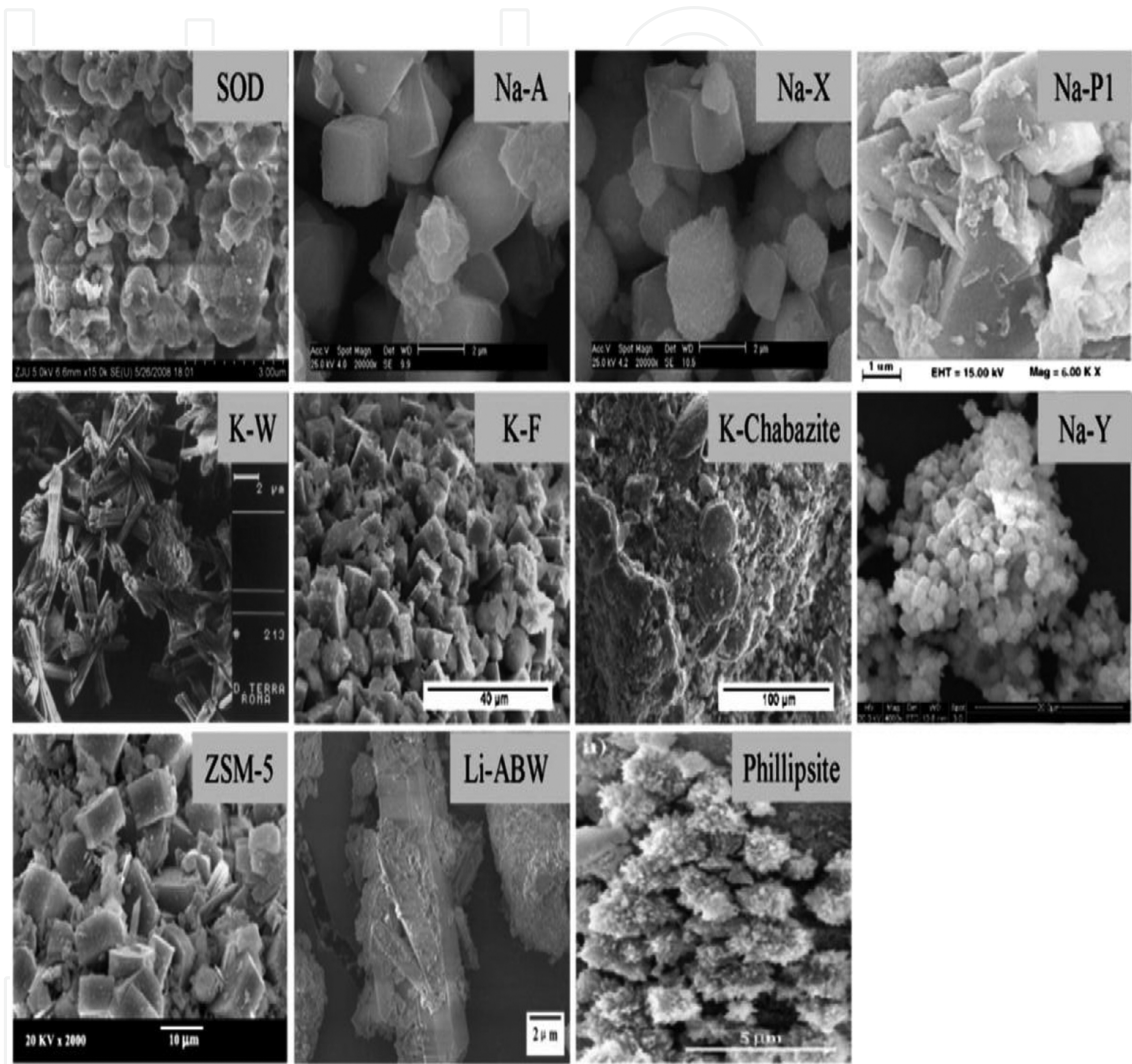

Figure 7. SEM images of zeolites synthesized from ashes [62, 67, 71, 74, 90, 91].

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_2O_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_2O_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.

Author details

Maria Harja[1], Sorin Mihai Cimpeanu[2], Marcel Dirja[3] and Daniel Bucur[4*]

*Address all correspondence to: dbucur@uaiasi.ro

1 "Gheorghe Asachi" Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Iasi, Romania

2 University of Agronomical Sciences and Veterinary Medicine, Bucharest, Romania

3 University of Agricultural Sciences and Veterinary Medicine, Cluj Napoca, Romania

4 University of Agricultural Sciences and Veterinary Medicine, Iasi, Romania

References

[1]   Ailincai C., Jitareanu G., Ailincai D., Zbant M. Evolution of main soil physical and chemical characteristics as influenced by tillage systems and fertilizers. Lucrari Stiintifice. Seria Agronomie, 2014;47:121–128.

[2]   Savic R., Ondrasek G., Josimov-Dundjersk J. Heavy metals in agricultural landscapes as hazards to human and ecosystem health – a case study on zinc and cadmium in drainage channel sediments. Journal of the Science of Food and Agriculture, 2014;95(3): 466–470.

[3]   Pearson M.S., Maenpaa K., Pierzynski G.M., Lydy M.J. Effects of soil amendments on the bioavailability of lead, zinc, and cadmium to earthworms. Journal of Environmental Quality, 2000;29:1611–1617.

[4]   Bucur R.D., Cimpeanu C., Barbuta M., Ciobanu G., Paraschiv G., Harja M. A compre-hensive characterization of ash from Romania thermal power plant. Journal of Food, Agriculture & Environment, 2014;12(2):943–949.

[5]   Ahmaruzzaman M. A review on the utilization of fly ash. Progress Energy Combustion Science, 2010:36(3):327–363.

[6]   Ciocinta R.C., Harja M., Bucur D., Rusu L., Barbuta M., Munteanu C. Improving soil quality by adding modified ash. Environmental and Engineering Management Journal, 2012;11(2):297–305.

[7]   Majid A., Argue S. Remediation of heavy metal contaminated solid wastes using agglomeration techniques. Minerals Engineering, 2001;14(11):1513–1525.

[8]   Lin C.F., Lo S.S., Lin H.Y., Lee Y.C. Stabilization of cadmium contaminated soils using synthesized zeolite. Journal of Hazardous Materials, 1998:60:217–226.

[9]   Adriano D.C. Trace Elements in Terrestrial Environments; Biogeochemistry, Bioavail-ability and Risks of Metals, 2nd edn, Springer, New York, 2001; 866 pp.

[10] Ciocinta R.C., Cîmpeanu S.M., Bucur R.D., Harja M., Barbuta M., Gurita A.A. Potential applications in agriculture of new materials synthesized from ash. Scientific Papers. Series E. Land Reclamation, 2012;101–104.

[11] Chmielewská E. Abundantly available natural or bioinspired materials for aqueous pollutants removal. Current Green Chemistry, 2015;2(4):371–378.

[12] Diels L., van der Lelie N., Bastiaens L. New developments in treatment of heavy metal contaminated soils. Reviews in Environmental Science Bio/Technology, 2002;1:75–82.

[13] Ciocinta R.C., Harja M., Bucur D., Buema G. Optimization of the conditions for conversion of ash into zeolite materials. Journal of Food, Agriculture & Environment, 2013;11(1):1108–1012.

[14] Fansuri H., Pritchard D., Zhang D. Manufacture of low grade zeolites from fly ash for fertilizer application. 2008; Research Report 91.

[15] Ma L.Q., Tcaina S.J., Logan T.J. In situ lead immobilization by apatite. Environmental Science and Technology, 1993;27:214–220.

[16] Cao X.R., Ma L.Q., Chen M., Singh S.P., Harris W.G. Phosphate-induced metal immobilization in a contaminated site. Environmental Pollution, 2003;122:19–28.

[17] Ciccu R., Ghiani M., Serci A., Fadda S., Peretti R., Zucca A. Heavy metal immobilization in the mining-contaminated soils using various industrial wastes. Minerals Engineering, 2003;16:187–192.

[18] Guo G., Zhou Q., Ma L. Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: a review. Environmental Monitoring and Assessment, 2006;116:513–528.

[19] Bolan N.S., Adriano D.C., Mani A.P., Duraisamy A. Immobilization and phytoavailability of cadmium in variable charge soils. II. Effect of lime compost. Plant and Soil, 2003;251:187–198.

[20] Chen M., Ma L., Singh S., Cao X., Melamed R. Field demonstration of in situ immobilization of soil Pb using P amendments. Advanced Environmental Research, 2003;8:93–102.

[21] Wang S., Terdkiatburana T., Tade M.O. Single and co-adsorption of heavy metals and humic acid on fly ash. Separation and Purification Technology, 2008;58:353–358.

[22] Ciccu R., Ghiani M., Peretti R., Serci A., Zucca A. Heavy metal immobilization using fly ash in soils contaminated by mine activity. In: International Ash Utilization Symposium, May, 2001. Center for Applied Energy Research, University of Kentucky, Paper #6.

[23] Buema G., Cimpeanu S.M., Sutiman D.M., Bucur R.D., Rusu L., Cretescu I., Ciocinta R.C., Harja M. Lead removal from aqueous solution by bottom ash. Journal of Food, Agriculture & Environment, 2013;11(1):1137–1141.

[24] Deja J. Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-activated slag binders. Cement Concrete Research, 2002;32:1971–1979.

[25] Albino V., Cioffi R., Marroccoli M., Santoro L. Potential application of ettringite generating systems for hazardous waste stabilization. Journal of Hazardous Materials, 1996;51:241–252.

[26]   Industrial Minerals.net. Zeolite Soil Conditioner. 2006. July 18.

[27]   Virta R.L. Zeolites. 2002. U.S. Geological Survey Minerals Yearbook.

[28]   Mumpton F.A. La roca magica: uses of natural zeolites in agriculture and industry. Proceedings of the National Academy of Sciences of the United States of America, 1999;96:3463–3470.

[29]   Rota Mining Co. Natural Zeolite as Soil Conditioner. 2006. July 18, 2006.

[30]   Zeolite.ca.NorthAmerica'sZeolite.   2006;   http://www.zeolite.ca/SoilConditioner-AG.htm.

[31]   Treacy M.M.J., Higgins J.B. Collection of Simulated XRD Powder Patterns for Zeolites, 2001.

[32]   Harja M., Suteu D., Ciobanu G., Rusu L. Materials based on ash for environmental protection. I. Obtaining and characterization, Scientific Researches, Agronomy Series, 2007;50:14–22.

[33]   Criado M., Fernandez-Jimenez A., Palomo A. Alkali activation of fly ash: effect of the SiO_2/Na_2O ratio Part I: FTIR study. Microporous and Mesoporous Materials, 2007;106:180–191.

[34]   Izquierdo M., Querol X. Leaching behaviour of elements from coal combustion fly ash: an overview. International Journal of Coal Geology, 2001;94:54–66.

[35]   Höller H., Wirsching U. Zeolites formation from fly ash. Fortschritte der Mineralogie, 1985;63:21–43.

[36]   Querol X., Alastuey A., Lopez-Soler A., Plana F., Andres J.M., Juan R., et al. A fast method for recycling fly ash: microwave-assisted zeolite synthesis. Environmental Science and Technology, 1997;31:2527–2533.

[37]   Inada M., Eguchi Y., Enomoto N., Hojo J. Synthesis of zeolites from coal fly ash with different silica-alumina composition. Fuel, 2005;84:299–304.

[38]   Juan R., Hernandez S., Andres J.M., Ruiz C. Synthesis of granular zeolitic materials with high cation exchange capacity from agglomerated coal fly ash. Fuel, 2007;86:1811–1821.

[39]   Izidoro J.C., Fungaro D., Santos F.S., Wang S. Characteristics of Brazilian coal fly ashes and their synthesized zeolites. Fuel Process Technology, 2012;97:38–44.

[40]   Liu H., Peng S., Shu L., Chen T., Bao T., Frost R. Magnetic zeolite NaA: synthesis, characterization based on metakaolin and its application for the removal of Cu^{2+}, Pb^{2+}. Chemosphere, 2013;91:1539–1546.

[41]   Zhang X., Tang D., Jiang G. Synthesis of zeolite NaA at room temperature: the effect of synthesis parameters on crystal size and its size distribution. Advanced Powder Technology, 2013;24(3):689–696.

[42] Sharma P., Sharma M., Tomar R. Na-HEU zeolite synthesis for the removal of Th(IV) and Eu(III) from aqueous waste by batch process. Journal of the Taiwan Institute of Chemical Engineers, 2013;44:480–488.

[43] Shoumkova A., Stoyanova V. Zeolites formation by hydrothermal alkali activation of coal fly ash from thermal power station "Maritsa 3", Bulgaria. Fuel, 2013;103:533–541.

[44] Visa M. Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment. Powder Technology, 2016:294(6):338–347.

[45] Hollman G.G., Steenbruggen G., Janssen-Jurkovicova M. A two-step process for the synthesis of zeolites from coal fly ash. Fuel, 1996;78:1225–1230.

[46] Rayalu S., Meshram S.U., Hasan M.Z. Highly crystalline Faujasitic zeolites from fly ash. Journal of Hazardous Materials, 2000:B77:123–131.

[47] Rios C., Williams C., Roberts C. A comparative study of two methods for the synthesis of fly ash-based sodium and potassium type zeolites. Fuel, 2009;88:1403–1416.

[48] Javadian H., Ghorbani F., Tayebi H., Asl S.M.H. Study of the adsorption of Cd (II) from aqueous solution using zeolite-based geopolymer, synthesized from coal fly ash; kinetic, isotherm and thermodynamic studies. Arabian Journal of Chemistry, 2015;8:837–849.

[49] Izidoro J., Fungaro D., Abbott J., Wang S. Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems. Fuel, 2013;103:827–834.

[50] Park J., Kim B.C., Park A.S., Park H.C. Conventional versus ultrasonic synthesis of zeolite 4A from kaolinite. Journal of Materials Science Letters, 2001;20:531–533.

[51] Andac O., Tather M., Sirkecioglu A., Ece I., Erdem-Senatalar A. Effects of ultrasound on zeolite A synthesis. Microporous Mesoporous Materials, 2005;79:225–233.

[52] Murayama N., Yamamoto H., Shibata J. Mechanism of zeolite synthesis from coal fly ash by alkali hydrothermal reaction. International Journal of Mineral Processing, 2002;64(1):1–17.

[53] Bukhari S.S., Behin J., Kazemian H., Rohani S. Conversion of coal fly ash to zeolite utilizing microwave and ultrasound energies: a review. Fuel, 2015;140:250–266.

[54] Molina A, Poole C. A comparative study using two methods to produce zeolites from fly ash. Mineral Engineering, 2004;17:167–173.

[55] Moreno N., Querol X., Plana F., Andres J.M., Janssen M., Nugteren H. Pure zeolite synthesis from silica extracted from coal fly ashes. Journal of Chemical Technology and Biotechnology, 2002;77:274–279.

[56] Belviso C., Giannossa L., Javier Huertas F., Lettino A., Mangone A., Fiore S. Synthesis of zeolites at low temperatures in fly ash-kaolinite mixtures. Microporous and Mesoporous Materials, 2015;212(8):35–47.

[57] Querol X., Umana J.C., Plana F., Alastuey A., Lopez-Soler A., Medinaceli A., et al. Synthesis of zeolites from fly ash at pilot plant scale. Examples of potential applications. Fuel, 2001;80:857–865.

[58] Moriyama R., Takeda S., Onozaki M., Katayama Y., Shiota K., Fukuda T., et al. Large-scale synthesis of artificial zeolite from coal fly ash with a small charge of alkaline solution. Fuel, 2005;84:1455–1461.

[59] Moutsatsou A., Karakasia O.K., Koukouzas N., Itskos G.S., Vasilatosc C. Synthesis of zeolitic materials utilizing CFB-derived coal fly ash as a raw material. WanteEng-2nd International Conference on Engineering for Waste Valorisation, 2006. Patras.

[60] Harja M., Buema G., Bulgariu L., Bulgariu D., Sutiman D.M., Ciobanu G. Comparative study for removal of cadmium (II) onto low cost adsorbents. Korean Journal of Chemical Engineering, 2015;32(9):1804–1811.

[61] Wu D., Zhang B., Yan L., Kong H., Wang X. Effect of some additives on synthesis of zeolite from coal fly ash. International Journal of Mineral Processing, 2006;80:266–272.

[62] Chareonpanich M., Namto T., Kongkachuichay P., Limtrakul J. Synthesis of ZSM-5 zeolite from lignite fly ash and rice husk ash. Fuel Processing Technology, 2004;85:1623–1634.

[63] Querol X., Moreno N., Umaña J.C., Alastuey A., Hernandez E., Lopez-Soler A., Plana F. Synthesis of zeolites from coal fly ash: an overview. International Journal of Coal Geology, 2002;50:413–423.

[64] Chareonpanich M., Jullaphan O., Tang C. Bench-scale synthesis of zeolite A from subbituminous coal ashes with high crystalline silica content. Journal of Cleaner Production, 2011;19(1):58–63.

[65] Ali I.O., Hassan A.M., Shaaban S.M., Soliman K.S. Synthesis and characterization of ZSM-5 zeolite from rice husk ash and their adsorption of Pb^{2+} onto unmodified and surfactant-modified zeolite. Separation and Purification Technology, 2011;83:38–44.

[66] Izidoro J.C., Fungaro D., Wang S. Zeolite synthesis from Brazilian coal fly ash for removal of Zn^{2+} and Cd^{2+} from water. Advanced Materials Research, 2012;356–360:1900–1908.

[67] Harja M., Buema G., Sutiman D.M., Cretescu I. Removal of heavy metal ions from aqueous solutions using low-cost sorbents obtained from ash. Chemical Papers, 2013;67(5):497–508.

[68] Noli F., Buema G., Misaelides P., Harja M. New materials synthesized from ash under moderate conditions for removal of toxic and radioactive metals. Journal of Radioanalytical and Nuclear Chemistry, 2015;303(3):2303–2311.

[69] Mishra T., Tiwari S.K. Studies on sorption properties of zeolite derived from Indian fly ash. Journal of Hazardous Materials, 2006;B137:299–303.

[70] Purnomo C.W., Salim C., Hinode H. Synthesis of pure Na-X and Na-A zeolite from bagasse fly ash. Microporous and Mesoporous Materials, 2012;162:6–13.

[71] Kazemian H., Naghdali Z., Ghaffari Kashani T., Farhadi F. Conversion of high silicon fly ash to Na-P1 zeolite: alkaline fusion followed by hydrothermal crystallization. Advanced Powder Technology, 2010;21(3):279–283.

[72] Schmachtl M., Kim T.J., Grill W., Herrmann R., Scharf O., Schwieger W., Schertlen R., Stenzel C. Ultrasonic monitoring of zeolite synthesis in real time. Ultrasonics, 2000;38:809–812.

[73] Curteanu S., Buema G., Piuleac C.G., Sutiman D.M., Harja M. Neuro-evolutionary optimization methodology applied to the synthesis process of ash based adsorbents. Journal of Industrial and Engineering Chemistry, 2014;20(2):597–604.

[74] Harja M., Bucur D., Cimpeanu S.M., Ciocîntă R.C. Conversion of ash on zeolites for soil application. Journal of Food, Agriculture & Environment, 2012;10(2):1056–1059.

[75] Harja M., Buema G., Sutiman D.M., Munteanu C., Bucur D. Low cost adsorbents obtained from ash for copper removal. Korean Journal of Chemical Engineering, 2012;29(12):1735–1744.

[76] Feng D., Tan H., Van Deventer J.S.J. Ultrasound enhanced geopolymerisation. Journal of Materials Science, 2004;39:571–580.

[77] Musyoka N., Petrik L., Hums E., Baser H., Schwieger W. In situ ultrasonic monitoring of zeolite A crystallization from coal fly ash. Catalysis Today, 2012;190(1):38–46.

[78] Pal P., Das J.K., Das N., Bandyopadhyay S. Synthesis of NaP zeolite at room temperature and short crystallization time by sonochemical method. Ultrasonics Sonochemistry, 2013;20(1):314–321.

[79] Kim J.K., Lee H.D. Effects of step change of heating source on synthesis of zeolite 4A from coal fly ash. Journal of Industrial and Engineering Chemistry, 2009;15(5):736–742.

[80] Noli F., Buema G., Misaelides P., Harja M. Retention of radiocesium from aqueous solutions using modified power plant ash. Journal of Radioanalytical and Nuclear Chemistry, 2015, 1–8, doi 10.1007/s10967–015–4611–6

[81] Erten-Kaya Y., Cakicioglu-Ozkan F. Effect of ultrasound on the kinetics of cation exchange in NaX zeolite. Ultrasonics Sonochemistry, 2012;19(3):701–706.

[82] Fukui K, Arai K, Kanayama K, Yoshida H. Phillipsite synthesis from fly ash prepared by hydrothermal treatment with microwave heating. Advanced Powder Technology, 2006;17:369–832.

[83] Tanaka H., Fujii A., Fujimoto S., Tanaka Y. Microwave-assisted two-step process for the synthesis of a single-phase Na-A zeolite from coal fly ash. Advanced Powder Technology, 2008;19(1):83–94.

[84] Jury F.A., Polaert I., Estel L., Pierella L.B. Enhancement of synthesis of ZSM-11 zeolite by microwave irradiation. Microporous and Mesoporous Materials, 2014;198(1):22–28.

[85] Xu X., Bao Y., Song C., Yang W., Liu J., Lin L., Microwave-assisted hydrothermal synthesis of hydroxy-sodalite zeolite membrane. Microporous and Mesoporous Materials, 2004;75(3):173–181.

[86] Cheng Z., Han S., Sun W., Qin Q. Microwave-assisted synthesis of nanosized FAU-type zeolite in water-in-oil microemulsion. Materials Letters, 2013;95(3):193–196.

[87] Ansari M., Aroujalian A., Raisi A., Dabir B., Fathizadeh M. Preparation and characterization of nano-NaX zeolite by microwave assisted hydrothermal method. Advanced Powder Technology, 2014;25(2):722–727.

[88] Inada M., Tsujimoto H., Eguchi Y., Enomoto N., Hojo J. Microwave-assisted zeolite synthesis from coal fly ash in hydrothermal process. Fuel, 2005;84(12–13):1482–1486.

[89] Harja M., Rusu L., Bucur D., Ciocinta R.C. Fly ash-derived zeolites as adsorbents for Ni removal from waste water. Revista Romana de Chimie, 2012;57(6):587–597.

[90] Belviso C., Cavalcante F., Lettino A., Fiore S. Effects of ultrasonic treatment on zeolite synthesized from coal fly ash. Ultrasonics Sonochemistry, 2011;18(2):661–668.

[91] Yao Z.T., Ji X.S., Sarker P.K., Tang J.H., Ge L.Q., Xia M.S., Xi Y.Q. A comprehensive review on the applications of coal fly ash. Earth-Science Reviews, 2015;141:105–121.

[92] Harja M., Advanced capitalization of the fly ash to obtain new materials, 2016, Thesis of Habilitation, 205