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METHODS FOR OBTAINING OF NEW ADD-VALUE MATERIALS BY FLY-ASH MODIFICATION

BY

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Abstract. Modified fly ash materials are currently on an upward trend internationally. The recovery of waste such as ash resulting in obtaining new products has an economic advantage but also has a significant impact on the environment because of reducing pollution due to storage. At present, there are many methods to synthesize new materials from wastes, the best known being fly ash. For the synthesis of novel materials, the most well-known methods will be used. It is known that the methods are formed of a single or two stages. The direct hydrothermal conversion of a mixture of ash and alkaline solution (NaOH, KOH) is the first and most common approach, however only 50% of the ash can be transformed in this instance. The second method involves combining the ash with KOH and fusing the mixture at high temperatures. This procedure results in a sophisticated conversion. According to literature studies, the conversion of ash can be done by using microwave ovens or ultrasonic baths, the conversion time in this case being reduced to 1 - 2 hours. The direct technique was proposed to be utilized to create novel materials by synthesis based on these processes, with numerous applications in industries such as building and agriculture.

Keywords: fly ash, synthesis, direct hydrothermal conversion, alkaline solution, microwave ovens, ultrasonic baths.

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1. Introduction

Modified ash products are becoming more popular around the world. The recovery of waste, such as fly ash, that contributes to the manufacture of new products has a financial benefit as well as a significant environmental benefit due to the reduction of pollution caused by storage. The novel materials created by using fly ash have a wide range of applications in building and agriculture (Harja *et al.*, 2022a).

The building industry depend on procuring new materials as cement alternatives, as well as the reuse of waste, all of which have a substantial environmental impact by preserving non-renewable resources, reducing waste released into the environment, and lowering pollutant emissions (Vasile *et al*., 2021). Research initiatives are being established to improve existing technologies as well as to develop new, modern, and efficient waste recovery systems.

Because worldwide cement production has increased at an accelerated rate in recent decades, resulting to an increase in cement plant energy consumption and negative environmental effects that have been linked to cement producers, all study in this field has been done (Harja *et al*., 2022a; Vasile *et al*., 2021).

Fly ash is also used in agriculture since it includes nearly all micro and macro-elements, with the exception of organic carbon and nitrogen (Ahmaruzzaman *et al*., 2010). Ash can also include trace levels of heavy metals, which can pollute groundwater and be absorbed by plants. This material is used as a filler to rehabilitate acidic soils that have a pH of less than 6.5. The primary goal of the fly ash shift is to promote soil utilization for agricultural objectives. Soils contain a wide range of minerals, including silicates, oxides, and hydroxides (Ailincai *et al*., 2014). Minerals such as quartz, feldspar, mica, calcite, mullite, kaolinite, and others are common.

Due to declining fertility, compaction, acidity, heavy metal contamination, and other factors, agricultural land has decreased in recent decades (Savic *et al*., 2014). To reduce heavy metals in polluted soils, a variety of techniques can be applied, including solidification, cementation, phytoremediation, and soil flushing. Fixation of heavy metals in contaminated soils using amendments (a product that is put into the soil to enhance qualities and conditions, including physical, chemical, and biological conditions) is one of them (Ciocinta *et al*., 2012; Chmielewská, 2015; Zaharia *et al*., 2022). The addiction of heavy metals in the soil has been done mostly with various amendments, such as zeolites, phosphates, cements, lime, and carbonates, or in recent years with synthetic amendments such as zeolites (Ciocinta *et al*., 2013; Fansuri *et al*., 2008), geopolymers and phosphates (Cao *et al*., 2003; Li *et al*., 2022; Liu *et al*., 2018).

The fixation treatment is based on the decrease of the mobility as well as the availability of the metal because of the application of the amendments. Thus, the adverse effects of heavy metals on the environment are reduced (Guo *et al*., 2006). The mechanism of removal of these heavy metals is based on operations such as adsorption, precipitation, cation exchange and complexation.

Fly ash from power plants is the main industrial waste resulting from burning coal; due to its composition and properties it is one of the most useful secondary raw materials. Combustion of coal in thermal power plants generates large amounts of inorganic residues, such as: ash, fly ash, flue gas desulphurizes and slag (Ahmaruzzaman, 2010; Harja *et al.*, 2022b).

The resulting amounts of slag and ash represent about 18-40% of the amount of fuel burned, depending on the physical properties, chemical and mineralogical composition, combustion systems, etc. (Buema *et al*., 2020).

Currently, along with other energy sources, the combustion of fuels in thermal power plants occupies an important place in the production of electricity and heat. As an energy source, coal is widely used worldwide in thermal power plants.

2. Methods of modifying fly ash

Due to the significant amount generated worldwide, fly ash is the most suitable for obtaining new materials, but other wastes can also be used (Buema *et al*., 2021; Mignoni *et al*., 2007; Rahman *et al*., 2009).

The modified fly ash materials are obtained by alkali activation of fly ash, they are aluminium-silicates and include three classes of inorganic polymers depending on the ratio of Si / Al (Criado *et al*. 2007; Kruszewski *et al*., 2021).

The following are the most crucial parameters in the activation process:

- Ration solid/liquid;
- activation time;
- temperature;
- concentration of alkaline solutions.

The limits of variation of these parameters are: the activation temperature (80 - 150°C), the maturation time (4 - 48 h), the hydroxide concentration (1 - 5 M), the solid-liquid ratio (1 / 1 -1 / 4) (Criado *et al*. 2007; Kruszewski *et al*., 2021).

Two methods are known for the synthesis of new materials using fly ash. Following research, Holler and Wirsching proposed several methods for obtaining new materials from fly ash such as:

- direct activation method (hydrothermal method);
- fusion method followed by direct activation method;
- ultrasound method;
- microwave method followed by the direct activation method.

Fig. 1 shows the ideal structure of a new ash-based material according to literature (Singh, 2018).

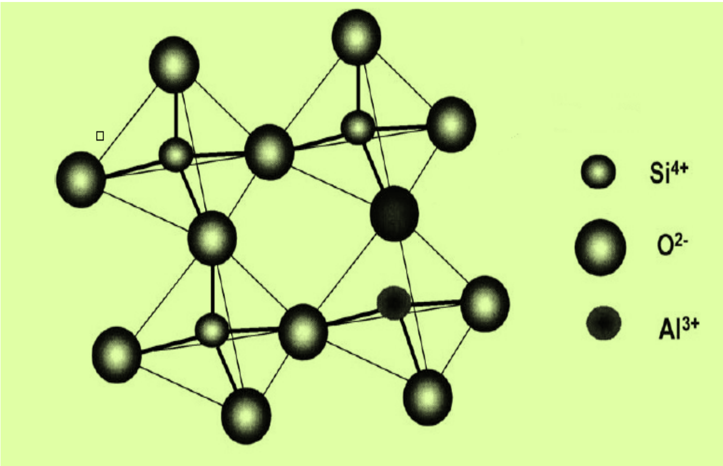


Fig. 1 – The ideal structure of ash-based material (Singh, 2018).

2.1. Direct activation method (hydrothermal method)

Ash modification by direct activation has been a research topic for over 20 years. It has been determined that the ash consisting mainly of quartz (SiO_2), hematite (Fe_2O_3), mullite ($2SiO_2$ $3Al_2O_3$) and magnetite (Fe_3O_4) can be modified by the method of direct activation.

The direct activation method contains a single step and aims to use the whole part of the silica content contained in the ash to produce new materials, without any separation.

Fly ash is commonly activated in autoclaves at temperatures ranging from 80 to 200°C, with various activating agents (KOH or NaOH), contact time of 3 - 96 hours, solution concentration of 0.5 to 5 M, and the ratio L / s of 1 to 20 mL/g. Based on data published in literature several researchers have studied the possibility of obtaining new ash-based materials, varying the working conditions (Singh, 2018). Depending on the experimental conditions and the chemical composition of the fly ash used, different materials are obtained. The principle of the method is based on the direct activation of the ash, in a closed system with alkaline solutions (NaOH, KOH, LiOH).

The main disadvantage of the process is the character of the product and the relatively low transformation efficiency of the ash into a new material. Si and Al dissolve in ash in the presence of OH^- anions and tetrahedral forms SiO_4^{4-} and AlO_4^{5-}.

Fig. 2 depicts a scheme for the direct activation approach of producing new materials.

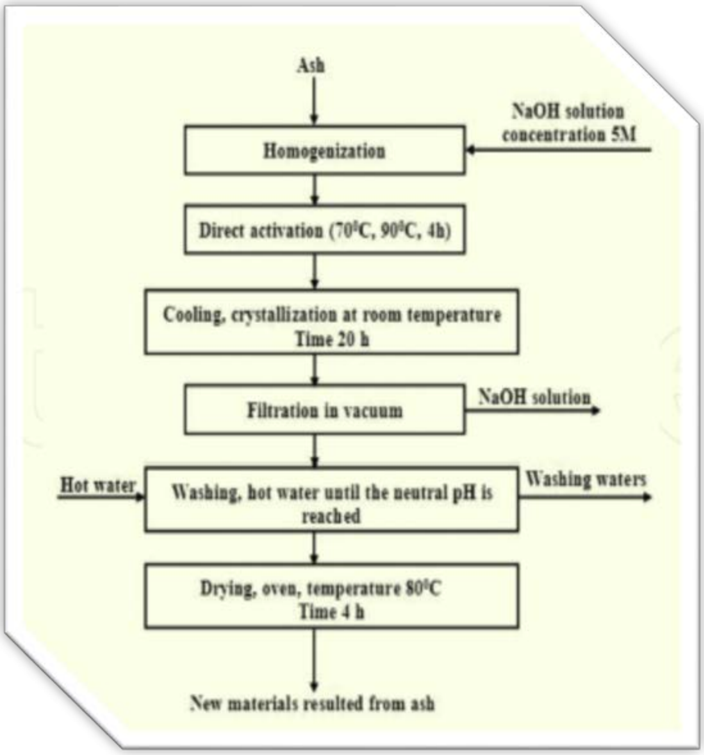
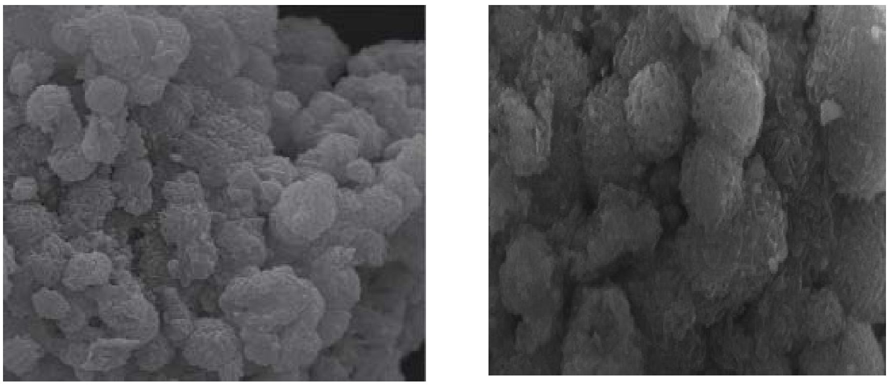


Fig. 2 – Modification scheme of ash through direct activation.

The synthesis of new ash-based materials is therefore an equilibrium reaction between the alkaline solution and the solid phase. Fig. 3 shows SEM images for two materials obtained by the direct activation method.



(Izidoro *et al.*, 2012) (Shoumkova and Stoyanova, 2013)

Fig. 3 – SEM images for new materials obtained by the direct activation method.

From the figure above it can be seen that the morphology of the ash undergoes significant changes when it is homogenized with alkaline solution.

The direct activation method has been improved by using treatments involving an alkaline fusion step, followed by hydrothermal treatment.

2.2. Fusion method followed by direct activation method

Shigemoto *et al*. proposed the fusion method in 1993. The ash is combined with solid NaOH and heated to a high temperature before being converted directly. This method includes an alkaline fusion phase prior to the direct activation method, which could increase the alteration process greatly (Demir and Derun, 2019; Mishra *et al*., 2006).

Several authors have reported on the modification of fly ash using the fusion approach followed by direct activation (Izidoro *et al*., 2013; Mishra *et al*., 2006). This method is known as an indirect method because it consists of two steps:

- fusion stage (temperature between 450 - 600℃, contact time 1 - 3 hours)
- direct activation stage (temperature between 60 - 100℃, contact time 4 - 96 hours)

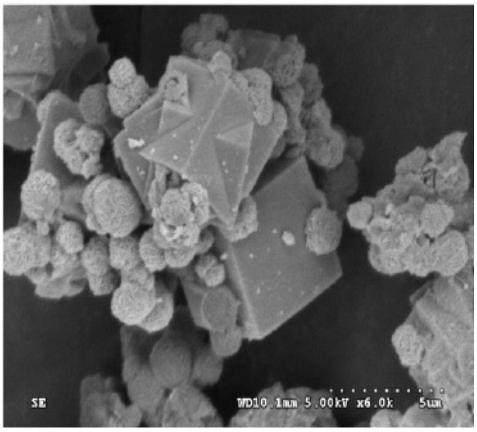
After the fusing step, the materials were given time to age (room temperature, contact time about 20 hours).

The crystallinity of materials synthesized from ash using this process is higher than materials produced using the traditional hydrothermal method. The crystallinity of materials synthesized from ash using this process is higher than materials produced using the traditional hydrothermal method.

Using the fusion technique followed by direct activation, a larger amount of alkaline extract ash silicates and alumina can be achieved. The basic material's SiO_2 to Al_2O_3 ratio has a significant impact on the development of novel materials. Direct activation can also be used to create new Na-A and Na-X materials, however the fusion process followed by direct activation has a higher degree of alteration. This approach has the disadvantage of requiring the separation of solid leftovers after a high concentration of silicon and aluminum has been dissolved in an alkaline solution.

The possibility of generating a desired type of zeolite with high purity and regular particles grows with the disposal of the wastes, but it leaves a new solid waste with a very low production yield (Demir and Derun, 2019).

Fig. 4 shows a few instances of novel materials created by the fusion process and direct activation.



(Zhang *et al*., 2011)

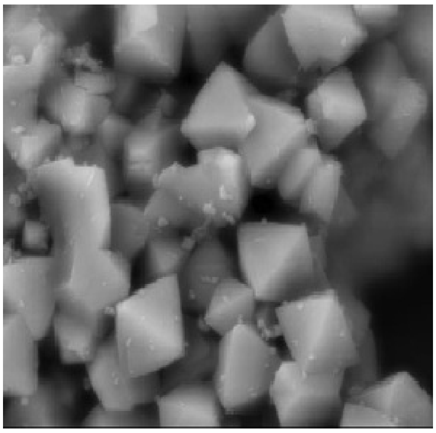

(Izidoro *et al*., 2013)

Fig. 4 – SEM images for materials obtained by the fusion method.

2.3. Ultrasound method

Ultrasound is mechanical energy that propagates in all directions in the form of beams (Schmachtl *et al*., 2000).

It's an indirect strategy that entails looking into the degree of interaction between ultrasonic wave transmission qualities and the precursor species of new materials when they're being synthesized.

Special attention is required to obtain new materials based on flying ash, which have various advantages, the most prominent of which is the shortened reaction time and crystallization temperature (Harja *et al*., 2022a, 2022b; Park *et al*., 2001; Andac *et al*., 2005; Harja *et al*., 2013; Curteanu *et al*., 2014; Harja *et al*., 2012).

The use of ultrasound has been shown to increase the compressive strength and increase the thermal stability of the material (Feng *et al*., 2004).

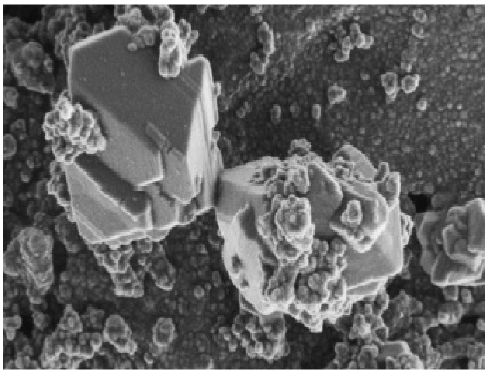
There is an improvement in polycondensation and the development of semicrystalline phases as Al - Si dissolution is accelerated.

The chemical resistance of the components is accelerated by the use of ultrasound, which is utilized to create new materials from basic materials comprising Al and Si (Schmachtl *et al*., 2000).

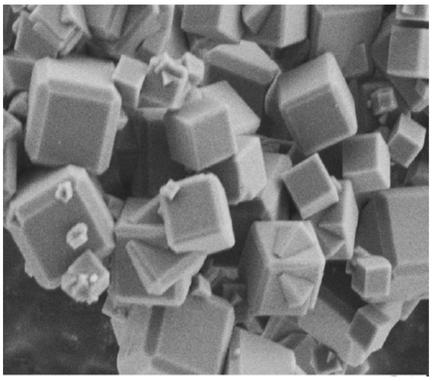
Ultrasound has an effect on the physico-chemical properties of the crystals created during the synthesis. The effects of ultrasound are caused by cavitation, a phenomenon that manifests itself as bubbles rising to the surface and breaking. Temperature, contact time, and the molar ratio of reactants are all critical characteristics that influence the kind and qualities of the new material.

The main disadvantage of using ultrasound is that their application leads to changes in the morphology of the crystals (the size of the crystal decreases with increasing power of ultrasound - in some cases with the advanced destruction of particles – Fig. 5c).

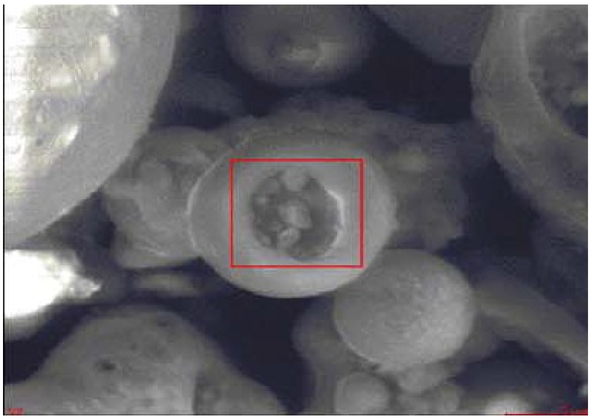
Fig. 5 provides a few examples of new materials obtained by the ultrasound method.



a) Belviso *et al*., 2011



b) Musyoka *et al*., 2012



c) Harja *et al*., 2013

Fig. 5 – SEM images for ultrasound materials.

By applying different temperatures, alkaline solution concentrations, solid/liquid ratio, contact time, materials with specific applications can be obtained, Fig. 6.

New materials with modified fly ash with various synthesis parameters and various types of ash:

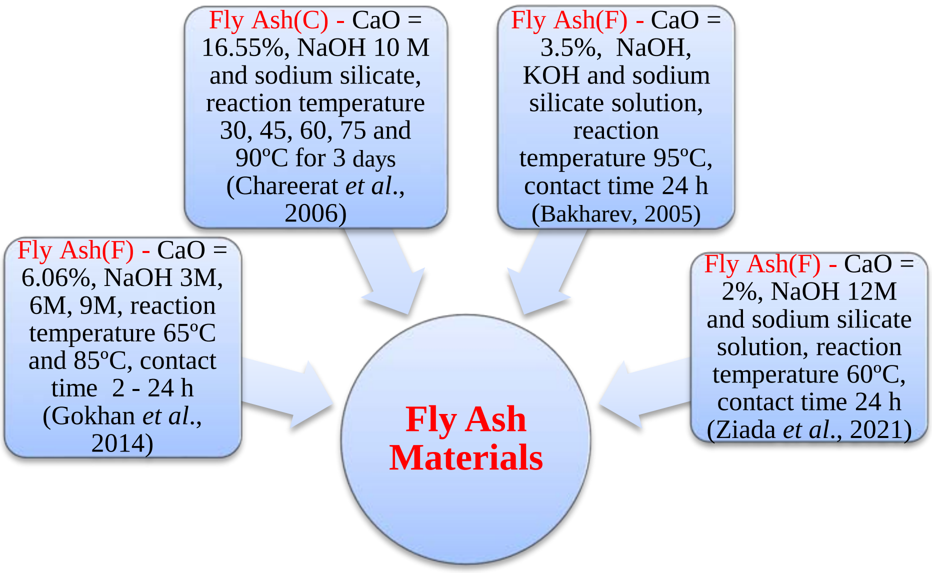


Fig. 6 – Methods and conditions for fly-ash modification.

3. Conclusions

Chemical, physico-chemical, or mechanical treatment can be used to convert wastes into new high-value-added products. Aluminum silicates are the products of alkaline activation of fly ash, and depending on the silica/aluminum ratio, there are three types of inorganic polymers.

The composition of the mixture, as well as reaction conditions such as the SiO_2/Al_2O_3 ratio, alkali solution concentration, activation temperature, curing duration, solid/liquid ratio, and pH, all have an impact on the formation and quality of the materials produced.

The following parameters have wide ranges of variation: ratio SiO_2/Al_2O_3 = 2 – 6, activation temperature of 80 – 150°C, NaOH or KOH solution concentration 1 – 10 M, curing duration 2 – 48 hours, and solid / liquid ratio 1 / 1–1 / 4.

Direct activation (hydrothermal procedure), ultrasonic method, fusion method followed by direct activation method, microwave method followed by hydrothermal activation are the methods utilized for the synthesis of new materials from solid waste - fly ashes, respectively.

The very high temperature required to dissolve Si and Al from ash particles is the fundamental restriction of the synthesis process. When the temperature is low, the synthesis yield is greatly lowered, necessitating a longer reaction time. The general recommended method for obtaining new materials is direct activation, it has advantages both economically and practically.

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MATERIALE PE BAZĂ DE CENUȘĂ MODIFICATĂ CU DIVERSE APLICAȚII

(Rezumat)

Materialele pe bază de cenușă zburătoare modificată se află în prezent pe un trend ascendent la nivel global. Scopul valorificării unor deșeuri precum cenușa este acela de a obține noi produse ce prezintă un avantaj economic precum și un impact important asupra mediului înconjurător ca urmare a reducerii poluării datorată depozitării. În prezent există numeroase metode pentru a sintetiza noile materiale cu utilizarea deșeurilor solide, cel mai cunoscut fiind cenușa zburătoare. Se va urmări în prezentul studiu metode de sinteză a noilor materiale. Se știe că metodele sunt compuse dintr-o singură etapă sau două etape. O primă metodă – cea convențională – este reprezentată de conversia hidrotermală directa a amestecului de cenușă și soluție alcalină (NaOH, KOH) însă în acest caz doar 50% din cenușă poate fi convertită. Cea de-a doua metodă are la bază amestecarea cenușii cu KOH și fuziunea la temperaturi ridicate. Această metodă conduce la o conversie avansată. Conform studiilor efectuate, conversia cenușii se poate realiza și prin utilizarea cuptoarelor cu microunde sau băilor cu ultrasunete, timpul de conversie în acest caz fiind redus la 1-2 ore.

Pornind de la aceste metode a fost propusă metoda directă pentru a fi utilizată în scopul obținerii de noi materiale prin sinteză cu diverse aplicații în domenii precum construcție, agricultură.