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OBTAINING ALKALI ACTIVATED INORGANIC MATERIALS BY RECOVERY OF WASTES

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Abstract

Currently, the large amount of waste produced is a significant problem for the environment and for the people who live near the deposits of by-products obtained from technological processes. Limited storage capacity, as well as the uncontrolled disposal of waste or industrial by-products from landfills, are growing concerns for environmental protection. The recovery of waste can be carried out to obtain new inorganic materials, known under several names, including geopolymers, alkaline activated materials. Aluminosilicate sources can come from industrial by-products such as silica fume, slag, fly ash, etc. In the formulation of this material, the type, ratios and concentrations of the compounds in the mixture are very important to the properties of the new inorganic materials. Prior to synthesis, a compressive analysis of the source materials must be performed to identify the minerals present and their amount relative to the total mass. The aim of this study is the formulation and characterization of new alkaline activated materials with the replacement of cement and establishing the influence of the properties of raw materials over final products.

***Key words**: aluminosilicate sources, inorganic materials, recovery, waste.*

INTRODUCTION

As is well known, Portland cement (OPC) is the most used construction material worldwide due to advantages such as low cost, excellent performance and adaptability. A major impediment to its use would be the process of obtaining it which requires high energy consumption and releases large amounts of CO_2 into the atmosphere thus causing severe environmental pollution. It is estimated that for each ton of cement produced, about 9.5 J of energy is consumed and 0.8 tons of CO_2 are released. Therefore, there is an urgent need to implement alternative green materials with low carbon emissions to replace ordinary Portland cement in the coming years (Alventosa & White, 2021; Cretescu et al., 2018).

The new inorganic materials that are also the subject of the present study are found in specialized literature under various names such as geopolymers, alkaline activated materials. Geopolymers are an alternative material to cement-based materials that have been significantly improved in numerous projects around the world. In this field, research has been intensified to obtain materials with low energy consumption and friendly to the environment (Aziz et al., 2021; Li et al., 2022). The new materials are synthesized following the geopolymerization reaction between an aluminosilicate material and an alkaline activator alone or composed of the KOH/NaOH solution and the potassium/sodium silicate solution resulting in a three-dimensional and amorphous structure at low temperatures (Prasanphan et al., 2019; Duxson et al., 2007; Arnoult et al., 2018).

The geopolymerization reaction is a complex process consisting of three main stages: dissolution, hydrolysis and polycondensation (De Silva et al., 2007). Numerous factors such as the types of aluminosilicate materials, their chemical compositions and the types and amounts of activators influence the activation mechanism (Mohamed et al., 2021; Nath & Kumar, 2019). From the studies carried out so far, it can be observed that for obtaining geopolymeric materials the most frequently used aluminosilicate by-products are those with a high content of alumina (Al_2O_3) and silica (SiO_2). Si and Al-rich wastes such as power plant fly ash, blast furnace slag are vital wastes in the production of geopolymer material.

Fly ash is grouped into two major classes (class F and class C) which are differentiated by the total amount of SiO_2, Al_2O_3, Fe_2O_3 depending on the type of coal burned, cooling conditions and combustion processes. Class C fly ash contains more than 10% calcium oxide, while Class F fly ash has a maximum calcium oxide content of 10% (Alterary & Marei, 2021).

Fly ash and granulated blast furnace slag are not the only wastes that can be activated alkaline thus obtaining materials with promising characteristics, but they are among the by-products that are obtained in large quantities and thus need to be stored. The recovery of larger amounts of waste provides opportunities for recycling and the opportunity for the development of a sustainable and ecological infrastructure (Mohamed et al., 2024).

Fly ash is rich in SiO_2 and Al_2O_3, while in the case of granulated blast furnace slag the predominant oxides are those of calcium and silicon. Following the alkaline activation of ash and slag waste, we obtain the aluminosilicate gel that gives the newly obtained material high mechanical and chemical resistance (Yong-Sing et al., 2021). The new inorganic materials are obtained following a relatively simple process, a major advantage is represented using industrial waste as a raw material in obtaining them, the materials are made at ambient temperature, thus the alkaline materials are obtained with reduced CO_2 emissions (Caftanachi et al., 2023; Toobpeng et al., 2024).

The aim of this study is the formulation and characterization of new alkaline activated materials obtained from waste by replacing cement. The objective in this work was to obtain an industrial waste-based material with similar mechanical properties to cement-based materials, so that they can be used as construction materials with various applications. At the same time, by reusing this waste produced in large quantities, we contribute to protecting the environment. The recovery of waste leads to the reduction of environmental pollution as well as to the reduction of the costs of their elimination and neutralization.

The large volumes of waste resulting from various industries harm the soil through uncontrolled disposal or unintentional dispersal, as well as air and groundwater pollution, with negative effects on human health (Harja et al., 2023).

MATERIALS AND METHODS

The various wastes: fly ash type F, furnace slag and undensified silica fume were used in this study to obtain the new materials. The slag was purchased from Nanovision Chemicals in Greece. HSH Chemie Romania supplied silica fume undensified. The quartz sand in the composition of the material was provided by S.C. Bega Minerale Industriale SA, with different grain sizes.

The alkaline activator is represented by the mixture of potassium hydroxide solution and sodium silicate solution in different mass ratios. KOH solution with molarities between 7-10 M was prepared from KOH flakes of 98% purity and distilled water. The sodium silicate solution was supplied by PQ Corporation of the Netherlands, having a specific gravity of 1.39 and a modulus ratio (Ms) of 3.3. The raw materials used did not require preliminary purification and mechanical preparation. The chemical composition of the source materials used is shown in the Table 1.

Table 1. Chemical composition of the source materials used in the formulation (%)

Chemical component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Fly ash	51.31	15.01	6.23	5.11	1.06	1.19
Slag	8.81	2.97	21.51	79.15	2.85	-
Silica Fume	93.05	-	-	0.11	-	0.32

Although slag is a vital source of Si and Al, particles must be smaller than 45 μm if used in construction materials.

The use of a percentage of blast furnace slag presents advantages for the material because it is easy to obtain, is chemically resistant and has very good thermal characteristics. Blast furnace slag and class F fly ash are often combined to increase the reactivity of these alkaline binders that possess a low calcium concentration (Vrabie et al., 2023).

Silica Fume contains mainly SiO_2 as can also be seen in Table 1, it has a very high specific surface and acts as a reactive pozzolan, it is used in small quantities compared to the other cementitious materials. Due to the very fine particle size, it greatly improves chemical resistance, minimizes chloride ion penetration, greatly reduces permeability and reduces material segregation.

SAMPLE PREPARATION

The parameters to be followed in formulating the material are: KOH molarity, sodium silicate/potassium hydroxide ratio, water/binder ratio, alkaline solution/binder ratio, sand/binder ratio. The two formulated materials Sample 1-FA and Sample 2-FA/Slag present molarities between 7-10 M, a sodium silicate/KOH ratio between 1 and 3, the water/binder ratio being in the range 0.3-0.5.

The synthesis of the bicomponent inorganic material takes place in two stages: initially, the powdery part in which we have the source material is mixed with sand and additives, followed by the preparation of the alkaline solution (the KOH solution of established molarity was previously prepared and left at room temperature for cooling). The mixing of the potassium hydroxide solution with the sodium silicate solution took place before the material was made.

To achieve the desired workability and to ensure a complete reaction, mixing was maintained at 10 minutes for both formulations. The powdery part must be free of moisture to reduce the influence of water on the total mixture. The fresh material is poured into molds, compacted with the help of a vibrating mass to remove air from the material and ensure its uniformity. After 24 hours the material is removed, labeled and aged at room temperature until testing. The samples (three for each experiment) were tested for the apparent densities and mechanical strengths (compressive and flexural strength), these tests being the most used according to the literature. Figure 1 shows the procedure for obtaining the new inorganic material.

The determination of the apparent density of the alkaline activated material was carried out in accordance with the SR EN 12190:2002 standard - Products and systems for the protection and repair of concrete structures.

Determination of compressive strength of repair mortar. This is calculated for each material sample as the ratio of mass to volume. The volume of the samples was calculated by measuring the dimensions of the prism (40 x 40 x 160 mm), the dimensions were measured using an electronic device. The mass of the sample was determined using an analytical balance with a capacity of 620 g and with a precision of 0.001 g under laboratory conditions. Density was determined at 1, 7, 14, 28 days.

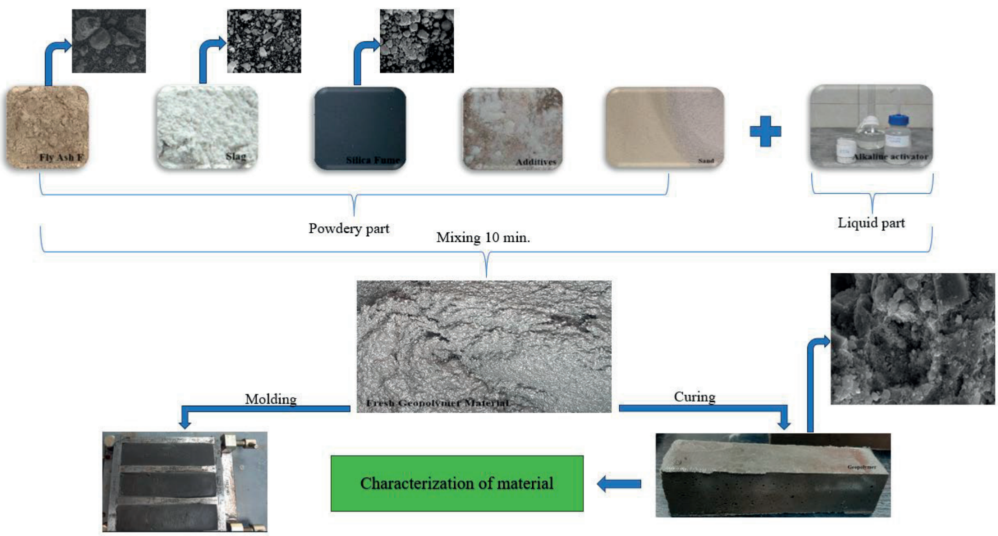

Figure 1. Synthesis of the new inorganic material

RESULTS AND DISCUSSIONS

Density of alkaline activated materials

The density of the cured material influences the mechanical properties of the newly formulated alkali-activated materials.

The graphic representation of the densities for the two material samples is shown in Figure 2.

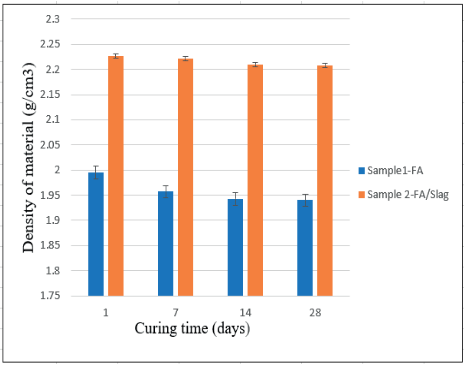

Figure 2. The density of the obtained material

The highest density of the hardened material at 28 days was recorded for Sample 2-FA/Slag, with a value of 2.208 g/cm^3, Sample 2 contains 30% slag from the total binder.

Compressive strength

The main design criterion of this new alkaline activated material was to determine the compressive strength as well as the flexural strength. A 15/250kN hydraulic press was used for this test.

In the formulation of this material, the aluminosilicate sources, type, ratios and concentrations of the compounds in the mixture are very important to the properties of the new inorganic material. Prior to synthesis, a microanalysis of the source material was performed to identify the minerals present and their amount relative to the total mass.

The alkaline solution concentration influences the release of Si^{4+} and Al^{3+} from the source material during the activation process. High concentration alkaline solution is generally beneficial for achieving high compressive strength but there is an optimum range. The compressive strengths were determined on cube samples of 40 x 40 x 40 mm. Determining the compressive strength of a construction material is an important characteristic that verifies its quality (Caftanachi et al., 2023).

The compressive strength of a construction material is determined according to the SR EN 12190: 2002 standard. The tests were performed at 7, 14 and 28 days, obtaining the results represented in Figure 3.

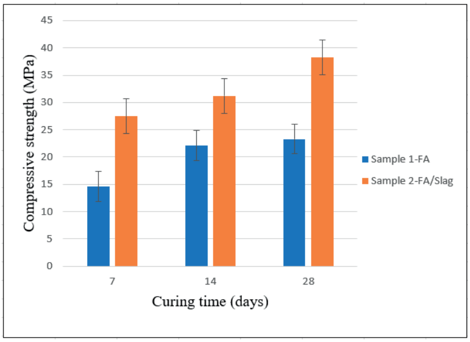

Figure 3. Compressive strength of alkali activated materials

The Sample 1-FA having a low concentration of KOH (7M) records low values in compressive at 28 days, only 23.26 MPa. By adding slag, the compressive strength at 28 days increases at 38.25 MPa.

Flexural strength

Alkali activated material based on fly ash has low flexural strength. A classic method is to incorporate fibers into the material matrix, as this hybridization can improve bond strength and flexural strength. In this way, the resistance to flexural and splitting can be improved. Fibers for the reinforcement of alkaline fly ash-based materials can be polyvinyl alcohol (PVA) fibers (Nematollahi et al., 2015; Sun & Wu, 2008), cotton fibers (Alomayri et al., 2014a; 2014b).

The principle of the test method aims to determine the flexural strength of prismatic specimens with the dimensions of 40 x 40 x 160 mm according to the SR EN 1015-11:2020 standard.

The tests were carried out at 7, 14 and 28 days, obtaining the following results and they were represented in Figure 4.

From the data presented, the following can be concluded: the Sample 1 had 5.04 MPa in flexural respectively, while Sample 2-FA/Slag had a flexural strength over 6.5 MPa.

The low concentration of the potassium hydroxide solution leads to a weak chemical reaction.

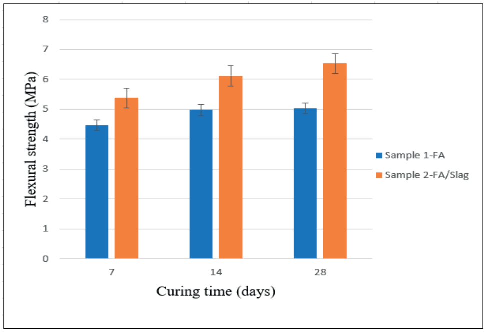

Figure 4. Results for flexural strength

The 10 M molarity of the KOH solution results in a flexural strength of the newly formulated material (Sample 2-FA/Slag) of 6.53 MPa at 28 days. It is observed that the sample presents an optimum alkaline solution concentration, obtaining higher values of flexural and compressive strength. A higher concentration of KOH leads to higher mechanical strengths of material since silicon and aluminum in the source material are dissolved much faster. A 10M concentration of KOH leads to a fast reaction and implicitly to obtaining a denser aluminosilicate gel.

Another parameter that is reflected in the mechanical resistances of the new material is the addition of slag to the amount of binder. The formulation with an addition of 30% slag registers high values in both compressive and flexural strength.

CONCLUSIONS

The main properties of alkali activated materials are related to the precursor type. The Si/Al ratio has a positive influence over mechanical properties of alkali activated materials because increase the amount of silica and the Si-O-Si bonds are stronger than the bonds formed by Si-O-Al or Al-O-Al bonds.

The compressive strength of alkali-activated fly ash material depends on the raw material source, alkali solutions, Si/Al ratios, chemical composition, curing conditions and additives.

When granulated blast furnace slag and fly ash are used together to obtain a composite system, rapid chemical reactions occur and develop reaction products that contribute to significant changes in setting time, development of material microstructure, improvement of mechanical properties as well as durability of the combined system.

Although fly ash was originally used as a partial replacement for Portland cement to increase durability, reduce costs and lower carbon footprint, alkaline activated material technology using all fly ash or a fly ash/slag mixture as a binder offers an even lower carbon footprint and energy consumption, along with the beneficial use of a larger volume of industrial by-product that is otherwise likely to end up in a landfill with negative effects on the environment.

The obtained new alkaline activated material is economical, environmentally friendly, mechanically durable as seen in its high value of compressive strength: 23.5-38.5 MPa at 28 days, while the flexural strength is in the range of 5.05-6.5 MPa at 28 days, both values above requirements.

Following these obtained results can conclude that this activated alkaline material can be used without problems in the construction materials industry, research remains open to study more industrial by-products for the purpose of incorporation into new materials.

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