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MICROPILOT SCALE TESTING OF ADVANCED INORGANIC MATERIALS OBTAINED FROM WASTES

BY

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Abstract. Traditional building materials have a major contribution to carbon emissions, consumption of natural resources, all these affecting environmental. To avoid the disadvantages that come from the cement industry, one strategy could be to use alternative materials as substitutes for cement-based materials. In plus these materials can be obtaining from by products, secondary sources of silicates and aluminates. In the present study, a characterization of the materials obtained following the activation of some aluminosilicate wastes with an alkaline mixture consisting of KOH and Na_2SiO_3 in different mass ratios will be carried out. KOH solutions had molarities between 5-10 M. The tests that were carried out are: workability of the fresh material, density of the hardened material, mechanical properties, capillarity absorption and resistance in the acid, alkaline and salts environments. The results allow the best conditions to be established in order to manufacture suitable materials with the proper characteristics.

Keywords: alkaline activation, by-products, mechanical properties, chemical attack resistance.

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1. Introduction

Global industrialization has an impact on the environment because it uses natural resources and produces a lot of industrial waste. The demand for building materials has grown in tandem with the growth of the civil and industrial construction industries. The Portland cement production has a significant impact on carbon emissions, and natural resource use, which affects environmental sustainability (McLellan *et al*., 2011; Vrabie *et al*., 2023).

The high development of construction industries in recent years has led to the use of large amounts of cement (Salamanova *et al*., 2021), and production is expected to remain around 4100 Mt/year or even increase in the coming years (*European statistic*). Current technology in cement production involves large quantities of mineral resources and their processing at high temperatures, usually generated by burning fossil fuels. Due to the improvement of technologies, by 2030 CO_2 emissions are expected to decrease to 0.48 t CO_2 per ton of cement (Samantasinghar and Singh, 2020). One strategy could be the use of alternative materials as substitutes for cement-based materials. In recent decades, the alkali-activated materials have been widely studied due to their environmental benefits (Klimenko *et al.,* 2021). The quantity of CO_2 released in the traditional building materials is between 316-340 kg/m^3 and in the case of alkaline activated materials it is between 110-200 kg/m^3. As a percentage, we can say that there is a potential to reduce greenhouse gas emissions between 25-45%, even going up to 70%.

The newly developed materials are alkali-activated semi-crystalline aluminosilicates formed as a result of the reaction of aluminosilicates in alkaline media (Davidovits, 1989). The chemical composition of these materials is similar to zeolites, but the microstructure is amorphous (Xu and Van Deventer, 2000, Puertas *et al.,* 2000). The alkaline activation process represents an efficient method of transforming by-product aluminosilicate materials into high efficiency materials that can thus be used in building industry. Natural aluminosilicates as well as industrial by-products are used for the synthesis of inorganic materials: metakaolin, fly ash, slag, silica fume, etc. (Kumar and Kumar, 2011).

The main advantages of these alkaline activated materials are the use of industrial waste as raw materials, the produced materials are made at ambient temperature, they do not require high temperatures to obtain, thus the alkaline activated materials are obtained with low CO_2 emissions, the production process is relatively simple.

2. Experimental details

2.1. Materials and methods

For alkaline activation in this paper were used: fly ash class F, blast furnace slag, silica flour and un-densified silica fume. Blast furnace slag was supplied by Nanovision Chemicals of Greece. HSH Chemie Romania supplied the undensified silica fume. The quartz sand was supplied from S.C. Bega Minerale Industriale SA in different grain sizes.

The alkaline activator used is a mixture composed of sodium silicate solution and potassium hydroxide solution in different mass ratios. Potassium hydroxide solution (5-10 M) was prepared using potassium hydroxide (KOH) flakes of 98% purity and distilled water. Sodium silicate solution was purchased from PQ Corporation in the Netherlands. All materials were used without preliminary purification or mechanical preparation.

2.2. Samples preparation

The preparation of the material consists in: initially the powdery part is mixed (additives together with the source material and sand), followed by the preparation of the liquid part (initially the KOH solution is prepared, it is left to cool at room temperature to be mixed with the sodium silicate). This procedure (Cotofan *et al.*, 2022) is valid for the three bicomponent materials Sample 1-AIM1, Sample 2-AIM2, Sample 3-AIM3. The samples were prepared at micro-pilot scale.

In the case of the mono-component material (in which the mixing is done with water) Sample 4-AIM4 the procedure is simple, here only the first stage (mixing the powdery part) is required. Alkaline activated materials are obtained after a 10 min. mixing. After mixing, the necessary tests are carried out on the fresh material (consistency of the material), then it is poured into molds to check the strength of the hardened material (density, compressive strength, flexural strength, water absorption, resistance to chemical attack). The samples (3 for each experiment) were cured for 24 hours at ambient temperature, and keep in standard specified conditions.

After demolding the material samples with dimensions of 40x40x160 mm, their density is calculated by weighing using a precision balance with a capacity of 620 g and an accuracy of 0.001 g. The dimensions of the samples are measured with an accuracy of 0.1 mm using appropriate instruments according to the standard SR EN 12190: 2002.

The density was determined at 7 days, 14 and 28 days, at the same time were determined and mechanical and chemical resistance. They are also subjected to flexural and compressive tests, being the most used tests according to the specialized literature.

Figure 1 shows the procedure for obtaining of the inorganic materials (AIM) by alkaline activation.

Fig. 1 – Alkaline activated material synthesis.

3. Results and discussion

The workability of the obtained materials

The workability (consistency) of the thixotropic material is measured by the spreading of a sample when it is placed on a flow table, the spreading being carried out by a defined number of shocks, this test was carried out in accordance with the SR EN 13395-1:2003 standard – Determination of workability. Part 1: Flow test of thixotropic mortars.

To determine the consistency of the newly formulated material, 4 samples of alkaline activated material were tested. The results obtained are presented in Table 1.

Table 1
Material workability values (mm)

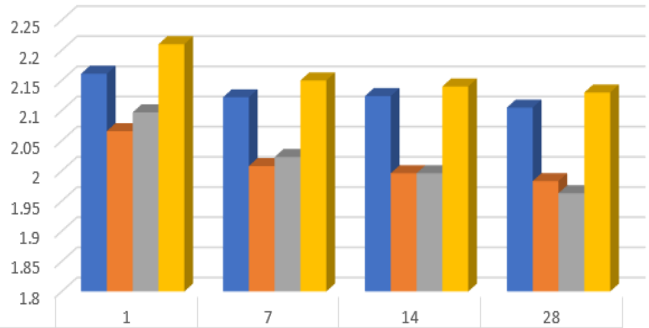
Sample	Spread (mm)	Average of measurements (mm)
Sample 1-AIM1	145/149	147
Sample 2-AIM2	133/130	131.5
Sample 3-AIM3	139/141	140
Sample 4-AIM4	140/135	137.5

The maximum flow was obtained for the AIM1, it decreases in the case of the sample AIM2, fact explained by addition of blast furnace slag (approximately 30% of the binder) and by increase molarity of the solution KOH, Fig. 2.

Fig. 2 – Sample 1 (a); Sample 2 (b).

The AIM density

Density influencing the mechanical properties of AIMs. It was calculated for each material sample as the ratio of mass (m) to volume (v). The graphic representation of the densities for the four samples is shown in Fig. 3.



	1	7	14	28
Sample 1-AIM1	2.161	2.122	2.124	2.105
Sample 2-AIM2	2.066	2.008	1.996	1.983
Sample 3-AIM3	2.097	2.023	1.996	1.963
Sample 4-AIM4	2.21	2.15	2.14	2.13

Fig. 3 – Alkaline activated material density.

The samples with the highest densities recorded at 28 days are AIM1 and AIM4, both samples having some percentage of slag incorporated.

The compressive strength and flexural strength

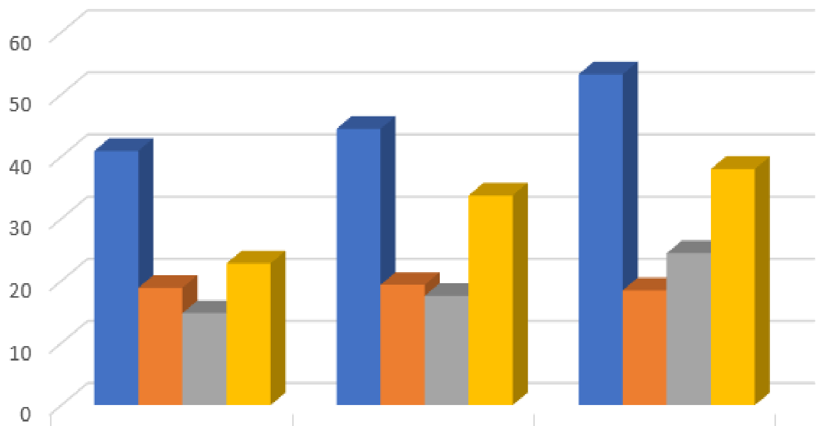
Compressive strength is influenced by several factors such as the type and fineness of aluminosilicate sources, calcium content, type and dosage of alkaline activator, alkaline solution/binder ratio, curing time, etc.

The compressive strengths were determined on 40x40mm cubic specimens, obtained following tests in which the flexural strength was determined. The compressive strength of a material is an important characteristic that checks its quality. This is determined according to the SR EN 12190: 2002 standard.

The flexural strength is determined on prismatic specimens with dimensions of 40x40x160 mm according to the SR EN 1015-11:2020 standard. The tests were carried out at different curing time Fig. 4 and Fig. 5.

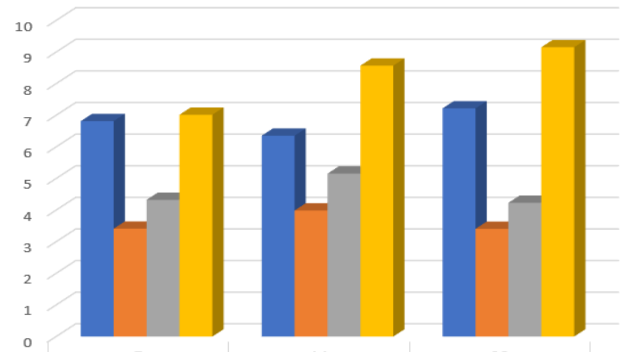
The 53.25 MPa (highest value of compressive strength at 28 days) was recorded for AIM1, which also has the highest molarity of the KOH solution, according to these results can be conclude that the high concentration of alkaline solution is generally beneficial in order to obtain a high resistance to compression, in accord with literature (Bhutta *et al.*, 2017). High alkalinity leads to the dissolution of aluminosilicates and also increases the rate of material structure forming reactions.

The improvement of mechanical resistances can also be achieved by adding a certain percentage of blast furnace slag. By reducing porosity of the binder mixture increases compressive strength value.



	7	14	28
Sample 1-AIM1	40.937	44.4755	53.2535
Sample 2-AIM2	18.893	19.359	18.48
Sample 3-AIM3	14.8035	17.587	24.46
Sample 4-AIM4	22.81	33.7665	38.0055

Fig. 4 − The value of compressive strength for synthesized AIM.



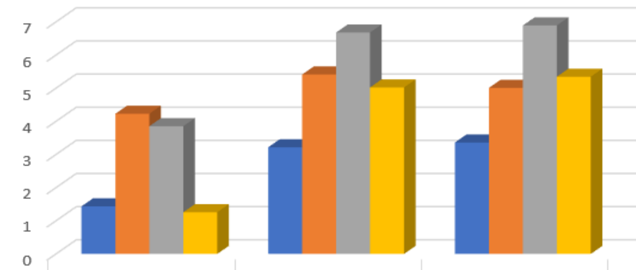
	7	14	28
Sample 1-AIM1	6.815	6.353	7.219
Sample 2-AIM2	3.413	3.987	3.407
Sample 3-AIM3	4.325	5.154	4.231
Sample 4-AIM4	7.017	8.569	9.152

Fig. 5 – The flexural strength of synthesized AIM.

Water absorption of AIM

Water absorption is an important characteristic for construction material, it indicates the permeability of the materials and therefore the degree of reactivity. Depending on the degree of geopolymerization, a more or less porous material will result.

The absorption test was performed for the four material formulations and an evolution of the capillary absorption is shown in Fig. 6.



	10 min	90 min	1440 min
Sample 1-AIM1	1.435	3.218	3.363
Sample 2-AIM2	4.229	5.413	5.01
Sample 3-AIM3	3.854	6.68	6.892
Sample 4-AIM4	1.258	5.023	5.345

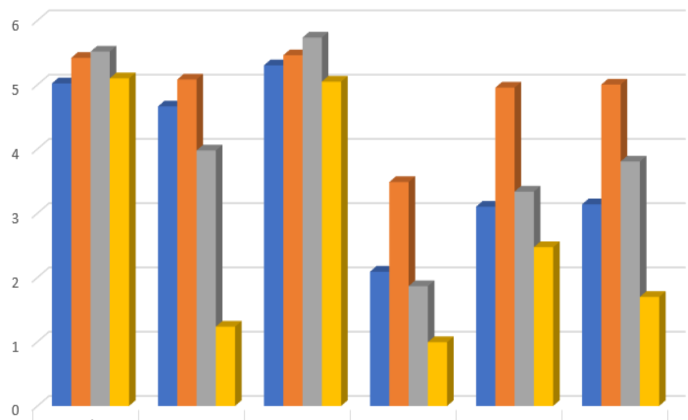
Fig. 6 – The capillary absorption of the alkaline activated material.

The resistance to chemical attack

Permeability has an important impact in the durability of AIM, as higher permeability characteristics allow the penetration of aggressive ions, which accelerate the degradation process. The resistance to severe environments decreases with the increase in the permeability of the material, due to the penetration of substances to the materials. Compressive strength, tensile strength and porosity are all affected when an alkali activated material is exposed to severe environments.

Resistance to chemical attack aims to determine the changes that occur on the surface of the tested materials and ultimately determine the mass loss (Harja *et al.*, 2023). The samples were immersed in the solutions and kept in the laboratory for 7, 14 and 30 days at a temperature of (20 ± 2)°C. Between each test, the samples are removed from the reagents, washed to remove it, and dried for 48 hours to remove absorbed water. After complete drying at ambient temperature, the samples were weighed on the analytical balance and the mass loss, Δm, was determined.

In Fig. 7 shows the mass losses in reagents at 30 days (%) for the four developed materials.



	HCl	H2SO4	HNO3	MgSO4	Na2SO4	KOH
Sample 1-AIM1	5.021	4.662	5.302	2.09	3.101	3.138
Sample 2-AIM2	5.417	5.081	5.458	3.485	4.954	5.002
Sample 3-AIM3	5.515	3.976	5.734	1.864	3.336	3.804
Sample 4-AIM4	5.099	1.234	5.047	0.993	2.471	1.697

Fig. 7 – Mass losses in reagents of activated alkaline material.

From the presented data it can be observed:

- the highest mass losses in the case of all samples were obtained in the immersion in acidic solutions, but the mass losses are recorded around the value of 5%, which means a good resistance in acidic environments;
- for all materials, excellent resistances are obtained in basic and sulfate solutions, these having small mass losses, but the smallest mass losses occurring in the case of the one component sample;
- in conclusion, it was demonstrated that inorganic materials obtained by alkaline activation can be successfully used in aggressive environments.

3. Conclusions

According to the experimental study carried out, fly ash together with additions of blast furnace slag and silica fume can be successfully used as a substitute for classic building materials.

The components used for AIM formulation have a very important influence over AIM properties.

The alkaline activation is directly influenced by raw materials (pouzolanic activity and oxidic composition), particle size distribution, the type and concentration of the activator the ratios of liquid/solid, etc. The content of each component to the whole is critical in successfully developing the mechanical and chemical strengths of the material.

The new developed materials have the advantages by using industrial wastes as raw materials, low activation temperature, as result in low CO_2 emissions, the production process is relatively simple, etc.

Experimental results demonstrated that AIM1 has the best resistance to chemical agents. Mass losses are a maximum of 5.3% in nitric acid solutions and a maximum of 3.13 % in potassium hydroxide solutions. This sample also shows high mechanical strengths, recording a value of 53.25 MPa in compression and 7.2 MPa in flexural respectively at 28 days. The density of the material is closely related to the resistances, reaching the value of 2.1 g/cm^3 at 28 days. According to the capillary absorption results, it also has the lowest water absorption at a maximum of 3.4% at 1440 minutes.

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TESTARE LA SCALA MICROPILOT A MATERIALELOR ANORGANICE AVANSATE OBŢINUTE DIN DEŞEURURI

(Rezumat)

Materialele de construcţie tradiţionale au o contribuţie majoră la emisiile de carbon, consumul de resurse naturale, toate acestea afectând mediul. Pentru a evita dezavantajele care vin din industria cimentului, o strategie ar putea fi utilizarea materialelor alternative ca înlocuitori pentru materialele pe bază de ciment. În plus, aceste materiale pot fi obţinute din produse secundare, surse secundare de silicaţi şi aluminaţi. În studiul de faţă se va realiza o caracterizare a materialelor obţinute în urma activării unor deşeuri de aluminosilicat cu amestecuri alcaline constând din KOH şi Na_2SiO_3 în diferite rapoarte de masă. Soluţiile de KOH au avut molarităţi între 5-10 M. Încercările care au fost efectuate sunt: lucrabilitatea materialului proaspăt, densitatea materialului întărit, rezistenţa la compresiune, rezistenţa la încovoiere, absorbţia de apă şi rezistenţa la atac chimic. Rezultatele obţinute la scara micropilot permit stabilirea condiţiilor optime pentru obţinerea materialelor cu proprietăţi impuse.