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ORIGINAL RESEARCH PAPER

FLY ASH WASTE FOR OBTAINING BUILDING MATERIALS WITH IMPROVED DURABILITY

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Abstract: The fly ash wastes (materials rich in silica, aluminum, and iron) could be advanced valorized by using as pozzolanic materials in the formulation of mortar and concrete. The partial hydrolysis of its, during alkali activation process, gel formation, and polycondensation produce the compulsory properties. The study had as objective to determine the optimal conditions, and the relationships between the fly ash modifying parameters, particle size and morphology, and behavior in chemical agents of the mortar obtained from different wastes. The alkali activation process involved varying the liquid/solid ratio (quantities of liquid phase) and the concentration of the NaOH solution (8 - 12 M). The samples' morphologies, particle size distribution, Blaine surface values, and crystallography were significant changes as a result of the activation, as demonstrated by XRD and SEM analysis. The durability values were substantially improved comparatively with building materials on the base of cement. As a result, treated fly ash is suitable as a potential building material, saving disposal-related issues. Using treated fly ash is environmentally friendly method conserving a large amount of cement, used in the production of building materials and reducing the CO_2 emissions.

Keywords: *alkali activated materials, capitalization, durability, fly ash*

INTRODUCTION

Cement has been used extensively in the last years due to the rapid growth of the industrial and residential construction [1], and production is predicted to rise in the next years [2]. The current technology for obtaining cement requires processing enormous amounts of mineral resources at high temperatures (the temperature is produced by burning fossil or alternative fuels). This fact situates the cement industry in higher carbon dioxide emission polluter: 0.58 t of CO_2 are released for every t of cement [3]. The greenhouse gases emissions are expected to decrease to 0.48 t CO_2 per ton of Portland cement until 2030 as a result of technological discoveries [2]. Using alternative materials as cement feedstock replacements is one tactic in this regard. Recent research has focused on obtained of potential replacements materials for cement binders [4, 5], with the objective of resolving environmental and economic issues by reducing CO_2 emissions through reduced energy use during production [6].

The alkali activated materials are binding materials made from metakaolin or other solid wastes with a similar composition [7], and they have great promise as building materials. A treatment with an alkali concentration solution is used during the activation process to dissolution of the amorphous material and improve it with silica and aluminum oxide.

Massive volumes of solid waste are produced by industrial expansion, which damages extended soil surfaces through disposal or unintentional dispersion [8], harming agriculture. Moreover, air pollution and ground water pollution are produced, all of which are damaging to human health. By-products from the manufacturing of many different products can be used, which lowers disposal and neutralization costs, decreases environmental pollution, and promotes industrial growth based on sustainability principles [9].

Alkali-activation of aluminosilicates produces novel binders with characteristics resembling those of cement. Aluminosilicates can be made from a variety of natural materials or by-products of industry, including various ashes (from power plants, incineration municipal waste, rice husk), slag, red mud, etc. [9, 10]. According to the literature, calcium, aluminum, and silicon-rich materials can be activated to form calcium-silicate hydrates (C-S-H), silicon and aluminum-rich materials can be converted into silico-aluminate hydrates, calcium, aluminum oxides, and silica-rich materials can be prepared as a hybrid alkaline binder [11, 12]. There is a large addressable market for the fly ash convenient valorization at the same time as environmental protection in both the research and business groups.

Significant amounts of FA resulted during the production of energy from solid fuels have negative effects on the environment and human health [13]. The fly ash capitalization could be able to help avoid this problem. Fly ashes may serve as the raw materials for new binders, and this method is a advanced way to recycle them, simultaneously creating materials with great mechanical strength and good durability [14]. Fly ashes are a significant industrial waste that can be a source of new raw materials for use in a variety of industries, including the geopolymers, the cement substitutes, the removal of heavy metals from wastewater, ceramics, catalysts, adsorbents, land stabilizers, zeolites, etc. [15 – 17]. Depending on the coal supply and burning conditions, fly ash has different chemical and physical characteristics [18]. The ash qualities affect the capitalization field [18], so further investigations are necessary for used at large scale. Fly ashes are three-dimensional alumino-silicate networks made of a mixture of silica, alumina, and iron

oxides. Due to their behavior being relatively similar to that of regular portland cement, their alkali-activation methods are frequently utilized for its capitalization [14]. The activation regime, which involves the precursors hydrolyzing at temperatures up to 100 °C by direct activation or by hydrothermal activation at temperatures over 500 °C, followed by gel formation and polycondensation, is the key to the generation of materials with binding properties [16].

According to Moutaoukil et al. [19], curing fly ash class C for an hour had no detrimental effects on the mechanical strength. Kanaan *et al*. [20] demonstrated that the alkaline solution concentrations, the curing circumstances, and the chemical compositions of the raw materials influence the alkali-activated binders' ability to harden. Natural pozzolan and NaOH (8 - 14 moles·L^{-1}) were used to create a microstructure with a high mechanical and chemical strength.

For a higher compressive strength, Naghizadeh *et al*. [21] suggested treating fly ash alkaline with sodium hydroxide and sodium silicate at room temperature. The majority of recent studies have concentrated on examining how the composition of the raw materials, alkali kinds and compositions, temperatures, solid-liquid ratios, etc., affect the mechanical strength of alkali-activated materials made from fly ash.

Our goals were to replace some of the high energy-consuming cement from the concrete/mortar preparation, while maintaining the required resistance parameters, for eliminate this potential pollutant (due primarily to the large amounts that resulted) in a manner that was somewhat environmentally friendly. The results of earlier studies suggested that the most crucial variables affecting the size and shape of the treated materials are molar concentration of the alkaline solution, the liquid-fly ash ratio, type of activators and temperature [14].

In this work, fly ash was alkaline activated with sodium hydroxide using a low-cost process in an effort to convert the waste into a different type of cementation material. The materials' particle size distribution and durability characteristics were connected. The findings might also apply to the ashes made from coals with lignin sourced from other regions.

MATERIALS AND METHODS

Materials synthesis

The fly ash (FA) for this study was from the power plant located in Iasi, Romania (FA1 and FA2) and FA type C from import. NaOH (Merck) was used as activator. The sample were noted: sample 1 - FA1, sample 2 - FA2 and sample 3 - FA type C). The sample preparation consisted of mixing the raw materials (fly ash, slag, sand and rheological additives) with liquid phase (NaOH solutions between 8 - 12 M, sodium silicate and water), the stirring for 15 minutes. The solid/liquid ratios were selected as the least amount of alkali and silicate solution required for workability.

The samples (3 for each experiment) were matured for 24 h at ambient temperature and keep in standard specified conditions.

The chemical resistance was tested for HCl, H_2SO_4 and KOH solutions. The samples were weighed and surface was examined by microscopy with resolution of 400 x. The samples were immersed in solution with imposed concentration. The level and concentration of liquid phase were verified, and after 7 and 14 days the samples were taken out of

solutions, washed to remove reagents and dried in air at constant mass. The mass lost was determined and surfaces were examined before and after immersion.
For comparison was used a mortar prepared with cement.

Methods of characterization

The chemical, morphological and physical properties of the fly ash and slag were investigated by Scanning Electron Microscopy - SEM, Energy dispersive X-ray spectroscopy (EDAX) and X-ray diffraction analysis - XRD. The particles size distribution was determined by using a Shimadzu SALD 7001 laser diffraction analyzer.

RESULTS AND DISCUSSIONS

Material characterization

EDAX analysis was used to determine the fly ash's chemical composition, and the results showed that the material contain Si, Al, Na, Fe, and Ca [22]. The chemical composition of the samples underwent significant changes as a result of the alkali treatments used.
Given that aluminum is relatively readily converted to aluminate in highly alkaline conditions, dealumination of the initial fly ash (an increase in the Si/Al ratio) may be the explanation of the improved mechanical properties of new synthesized materials.
The fly ash from the thermal power plant in Iasi Municipality can be seen in the SEM picture in Figure 1 to contain numerous spherical particles with dimensions ranging from 1 to 10 micrometers that are embedded in a pseudo-matrix of extremely irregular, firmly shattered cages with thin walls [22, 23].

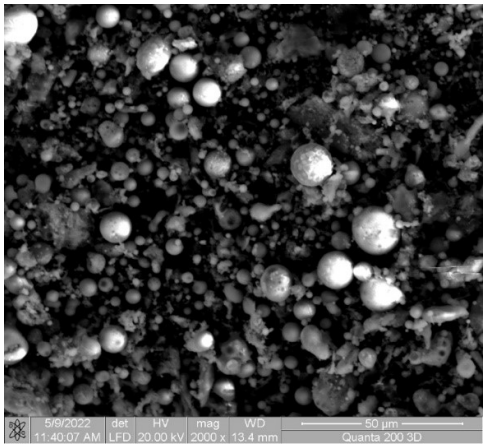


Figure 1. *SEM image of the raw fly ash*

According to SEM photos of the samples, the morphology of the samples on the ash base is radically altering in terms of particle sizes, shapes, and surface roughness (Figure 2). As a result of the alkali solution dissolving the original uneven matrix or serving as feedstock for the subsequent recrystallization operations, it almost completely disappears.

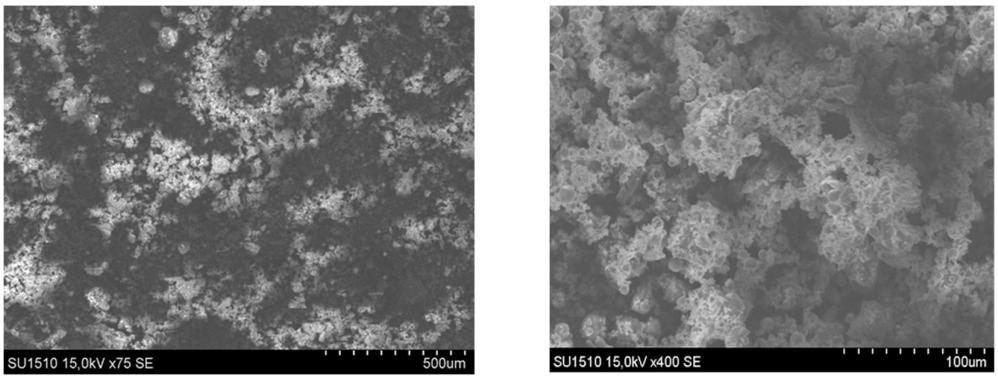


Figure 2. *SEM micrograph of the fly ash samples processed by alkali treatments*

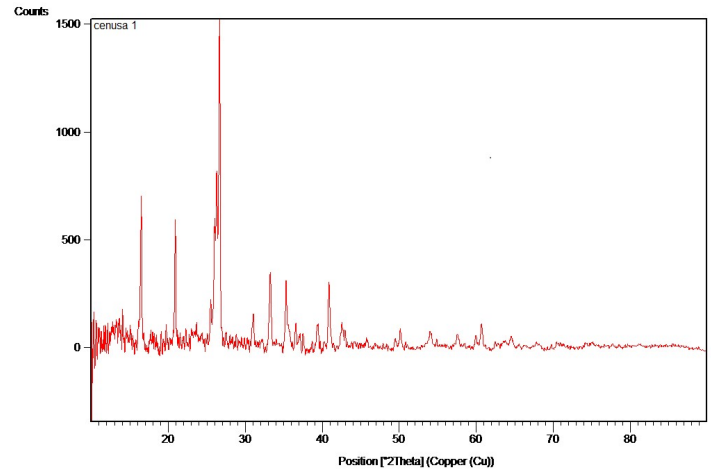
Some of the initial spheres maintain almost unchanged the outer surface aspect, whereas others show a significant increase in the depth and quantity of asperities.
Higher treatment temperatures appear to partly dissolve the initial spheres from the ash, either by roughening their surface or developing flake-like smaller particles almost detached from the surface.
The smooth, spherical particles from the initial ash became quite rough in all of the images, this fact indicating that they are composed of smaller particles with sheet-like and polyhedral shapes that are closely associated.
The elemental chemical composition and the Si/Al ratio have a particularly important role in determining the valorization directions of the ash. The elemental chemical composition determined by EDAX analyses is presented in Table 1.

Table 1. *The chemical composition of fly ash [%]*

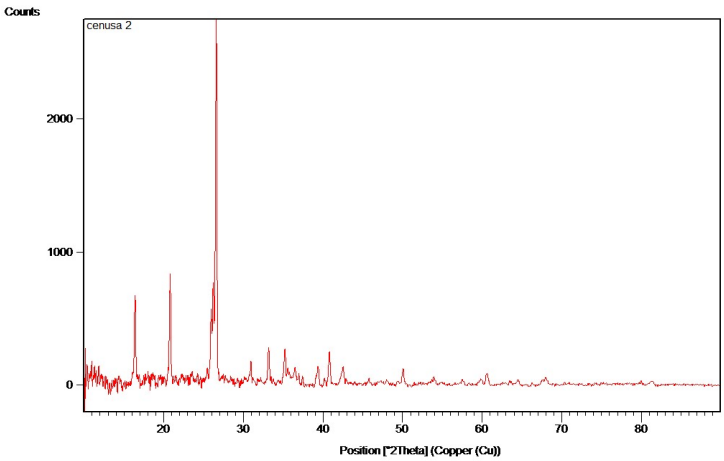
Element	O	C	Na	Mg	Al	Si	K	Ca	Ti	Fe
FA1	35.6	7.72	0.79	0.7	18.09	31.81	1.75	1.05	0.54	2.06
FA3	36.83	2.23	0.85	0.8	17.23	31.24	0.9	7.95	0.02	3.04

The changes noted by EDAX analysis demanded an extensive investigation of the crystalline phases of the alkali-treated solids.
Figure 3 depicts the XRD patterns of a series of samples. The FA1 contains quartz - identified as (101), (110) and (112) plans giving maxima at 2θ values of 26.6, 20.9 and 50.1 θ, respectively; mullite phase ($3Al_2O_32SiO_2$), assigned at 26, 26.2, 33.2, 35.2, 40.8, 42.6 (230) and 60.6°, corresponding to the (120), (210), (220), (111), (121) (331) plans [24], (JCPDS 15–0776) and to hematite (H), known as (104), (110) and (116) plans, giving picks at 33, 35 and 54°, respectively.
The alkali treatments employed for synthesizing the materials have a significant impact on the formation of crystalline phases. Small quantities of aluminum silicate phases were highlighted in the obtained materials: sodalite - identified by the (211) and (310) plans (24.3 and 31θ); chabazite, identified by the (311) and (310) plans (30 and 30.2 θ) [25]. The initial quartz, mullite and hematite remained however the majority crystallographic phases from the products. These findings are in line with the literature [26].
The XRD spectra shown in Figure 3, demonstrates that FA1 contains elements, such as: quartz (Q), mullite (M), hematite (He), and a vitreous phase. The elements existing in the vitreous phase of the ash are estimated by XRD analysis combined with EDAX analysis, indicating the presence of Si, Al, Ca and K. These elements were included in 2 main

crystalline phases: quartz and calcium-alumino silicates, respectively in a phase vitreous which also contains different amounts of K, Na, Ca, Mg and Fe.



FA 1



FA3

Figure 3. *XED difractogram for fly ash. Cards: Ms = 07-0042; I = 26-0911; Q = 85-1780; M = 79-1455; 83-1881; R = 89-0514; He = 33-0664; K = 14-0164*

From Figure 3 it can be seen that the diffraction peak obtained at 25 θ corresponding to quartz is sharp, having the highest intensity. Broad and less intense peaks are obtained at lengths between 30 θ - 70 θ. Peaks at values lower than 15 θ correspond to carbon and are found to be more intense in the case of FA1.

Based on the data presented in Table 1, it is found that the sum of SiO_2 + Al_2O_3 + Fe_2O_3 is greater than 70 %, which makes FA1 can be included in class F, while FA3 is class C ash - the oxide content of calcium being elevated.

The results for particles size distribution are presented in Figure 4.

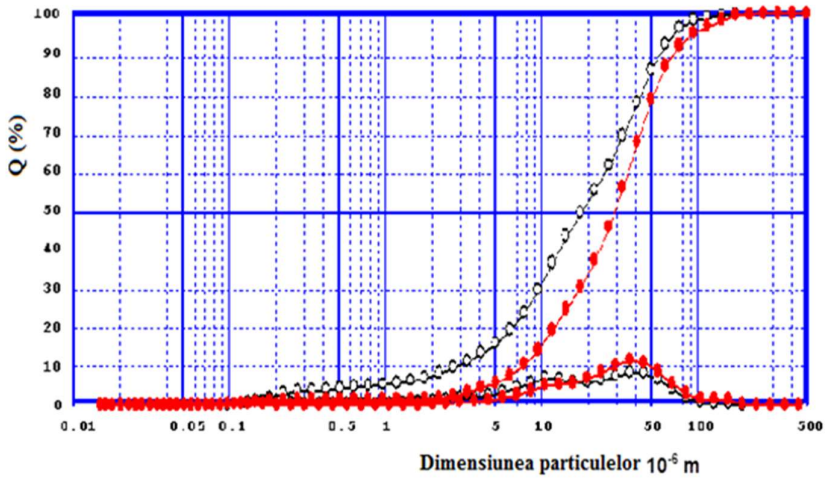
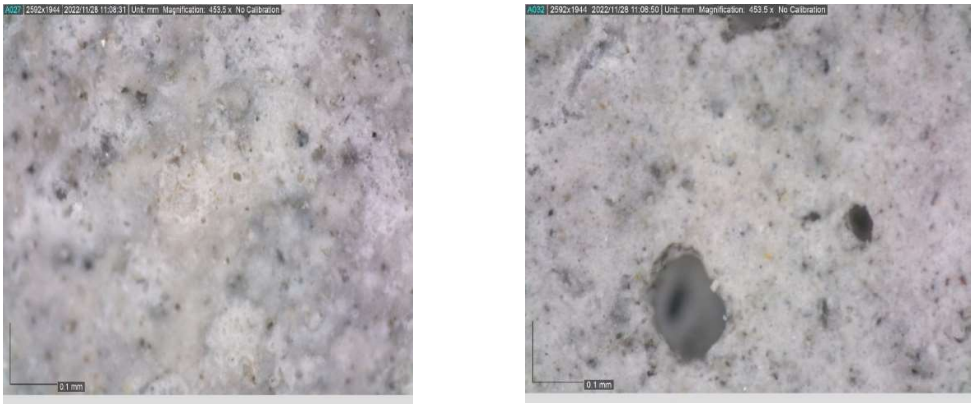


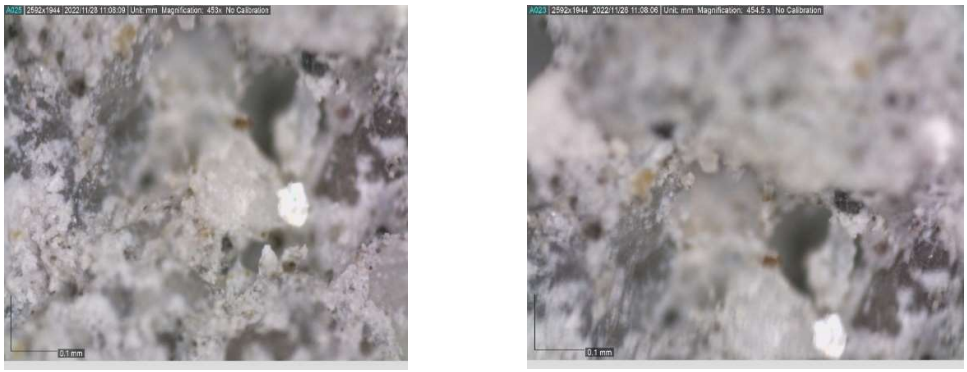
Figure 4. *Particle size distribution of FA1 (black) and FA2 (red)*

The distribution curve shape is asymmetric and wide, and the elementary particles that may be detected have sizes that are less than 0.1 micrometers. For the examined samples, a typical median diameter of 0.026 m and a modal diameter of 0.018 m can be established.

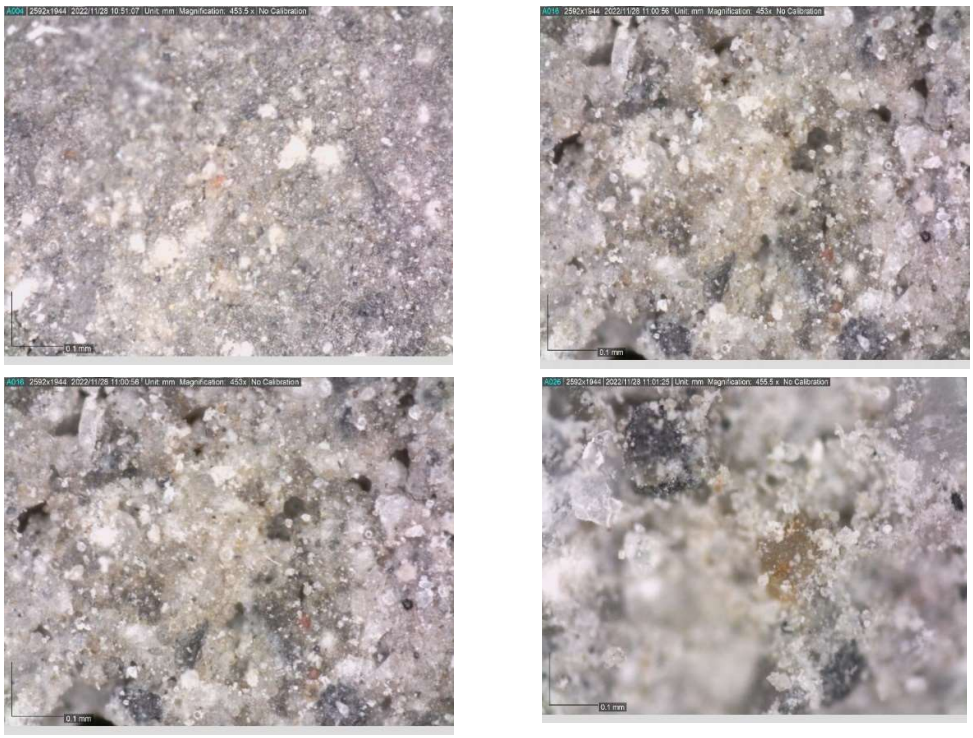
Chemical resistance of obtained materials

The samples were immersed into the solutions and kept in the laboratory during 7 and 14 days at a temperature of (20 ± 2) °C. After that, the samples were washed and dried at constant mass. After drying the samples were weighed and the loss of mass, Δm, was determined. Figure 5 presents the images of samples before and after immersion in different solutions.

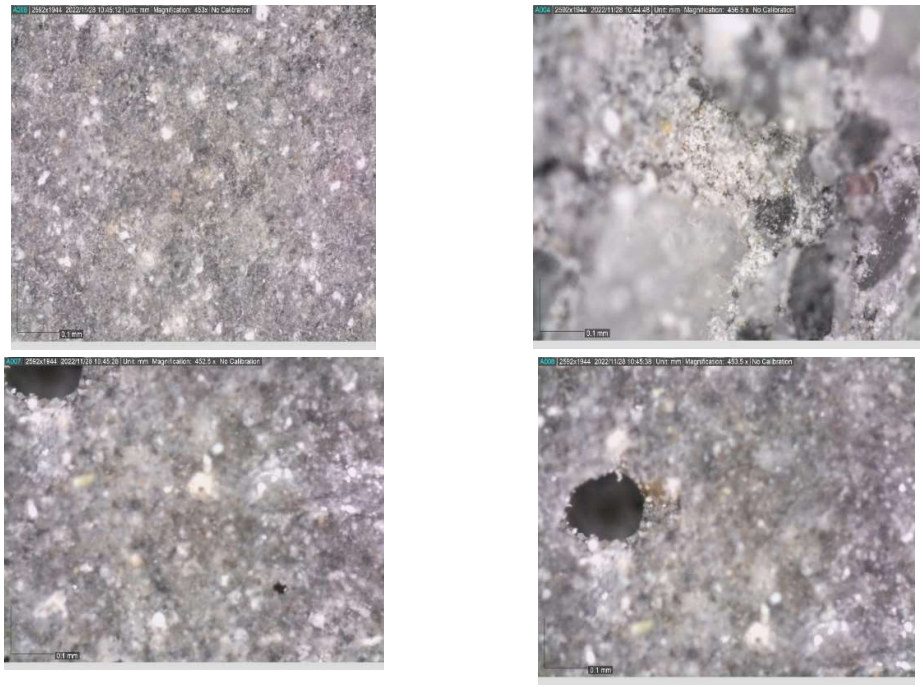




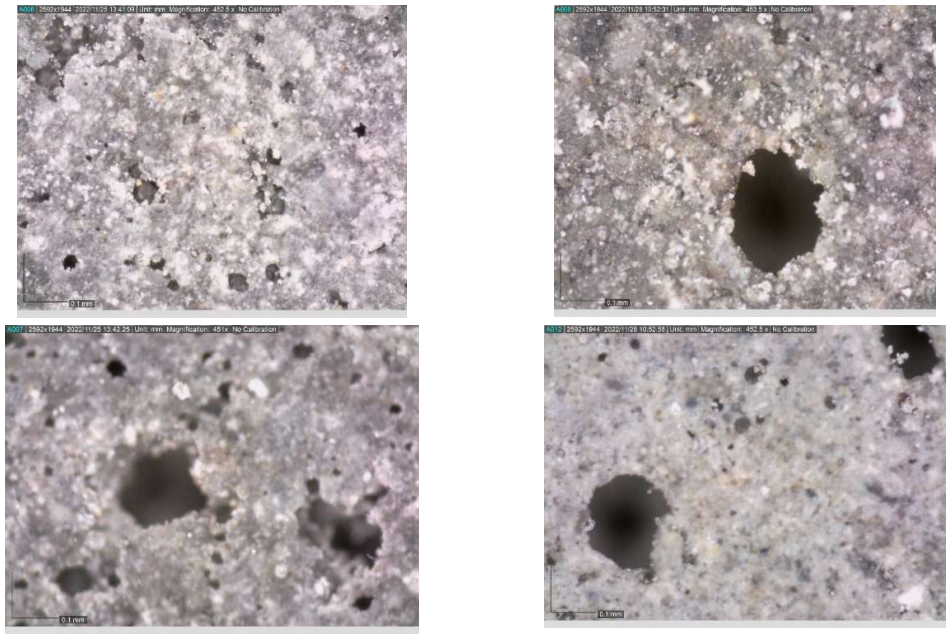
Standard sample before and after chemical exposure



Sample 1



Sample 2



Sample 3

Figure 5. *Images of samples before and after immersion (in order: initial, solutions HCl, H_2SO_4 and KOH)*

Table 2. *Determination of mass loss, [%]*

Concentration of solutions	Time	Standard	Sample 1	Sample 2	Sample 3
HCl, 1%	7 days	2.467	0.0295	1.779	4.513
	14 days	2.668	2.257	3.589	5.369
H_2SO_4, 3%	7 days	8.808	2.016	5.149	5.366
	14 days	8.890	2.347	5.954	5.845
KOH, 30 g·L^{-1}	7 days	8.371	2.162	5.063	5.954
	14 days	8.33	3.639	6.069	6.235

From data given in Table 2, photos presented in Figure 5 and visual observations, the following conclusions resulted:

- All analysed sample have a good resistence in chemical agents, its can be included in E (excelent) class;
- The losses haven't value over 6.1 %;
- The samples are relativelly stable in HCl solutions (excluding sample 3);
- The sample 1 - with FA class F have the best resistente in acidic and bazic media.

CONCLUSIONS

According to the experimental findings, fly ash can be transformed into a substitute for building materials. After an alkali treatment, fly ash can be valued, lowering the environmental pollution.

The objective of experimental study was to determine the durability of advanced inorganic materials in acidic and alkaline solutions. The materials, by alkaline activated method, are an effective and reasonable substitute for Portland cement, offering significant advantages in terms of energy consumption and carbon dioxide emissions.

In HCl solutions a good behavior had the sample 1, obtained from FA class F, even it has changed the color. In all cases it can conclude that function the raw materials acids (HCl and H_2SO_4) reacts with compounds from its and decomposes them in time (after 14 days the mass loss was higher that after 7 days). In KOH solution the sample had increase losses, the studied samples are recommended for use in acidic media.

The suggested procedure enables the diminution of the thermal power plant's abundant industrial waste, which is present in significant quantities.

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