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Performance of local fly ash geopolymers under different types of acids

D D Burduhos Nergis[1], P Vizureanu[1,*], L Andrusca[1] and D C Achitei[1]
[1]"Gheorghe Asachi" Technical University of Iasi, Blvd. Mangeron, No. 51, 700050, Iasi, Romania

E-mail: peviz2002@yahoo.com

Abstract. A new class of ceramic materials, known as geopolymers, possess comparable or even higher mechanical and chemical properties than ordinary Portland cement-based materials. Because geopolymers can be used in a wide variety of areas, from civil engineering applications to decorative objects manufacturing, they can get in contact with different types of acidic corrosive substances. The degradation degree depends mostly on the acidic solution concentration and the exposure time. Due to the interaction between the geopolymer compounds, Al, Si and Fe ions solubility and the corrosive environment substance, there may follow severe consequences on the material mechanical properties. These consequences are highly related to the geopolymers three-dimensional structure degeopolymerization. The performance of geopolymers under severe environmental condition depends on the raw material, mineralogical composition and activation method. The aim of this paper is to present the effects of nitric acid, sulfuric acid and hydrochloric acid exposure on the local fly ash geopolymers compressive strength and microstructure.

1. Introduction

Large quantities of rich in alumina and silica wastes can be used to create geopolymers with multiple applications, especially in civil engineering or as insulating materials. Because, usually, this high-performance composite is used as an ecofriendly and much resistant replacer of Ordinary Portland cement concrete, these materials must withstand to harsh environments and different types of acids. Geopolymers can be defined as totally ceramic materials based on Si-O-Al tetragonal structure, chemically balanced by metallic ions [1].These are obtained following the geopolymerisation reaction between a material rich in aluminium and silicon oxides and a strong alkaline solution, which can be based on sodium silicate, potassium silicate, sodium hydroxide or potassium hydroxide, but usually a mix of multiple solution is used [2].

The degradation degree of geopolymers under acid condition depends on multiple factors, which are related, first of all, to the acid solution concentration, exposure period and environmental condition, such as pressure and temperature [3]. Also, the type of the alkaline activator and the mineralogical composition of the raw materials used can increase the depolymerization reaction, as can be seen in Figure 1. This can be related with the Al, Si and Fe ions high solubility in strong alkaline solutions as in acidic solutions [4].

When Ordinary Portland cement-based materials are exposed to Na_2SO_4 environments, their mechanical properties significantly decrease due to the gypsum and etching formation. Thus, compounds expand in the structure causing cracks, holes and, eventually, samples fail without being

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under external load [5]. The fly ash based geopolymers do not contain, usually, $Ca(OH)_2$ or mono-sulfoaluminate in the matrix, that can cause the structure expansion [6].

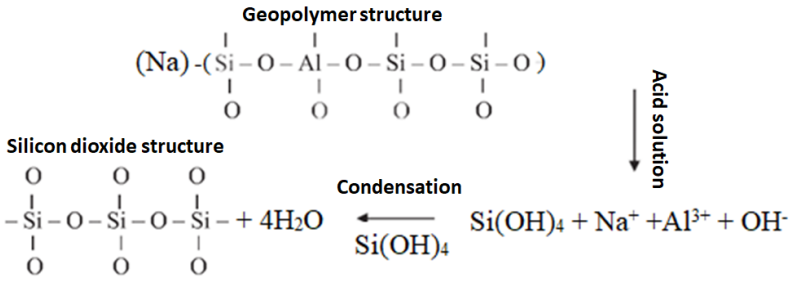


Figure 1. Degeopolymerization reaction of geopolymers exposed to acid environment [7].

According to B. Singh et al. the geopolymer samples presents low degradation in fresh or salt water, in terms of bending strength, but the calcium sulfate dihydrate presents severe consequences on the samples mechanical strength when exposed to $MgSO_4$ environment [8].

According to other studies [9-11] the geopolymers activated with NaOH solution presents higher mechanical properties at early time and higher crystallinity, therefore, this type of geopolymers will present better stability in acidic environments [12]. Also, sodium silicate presents positive influence when used as geopolymers activator, because it contains partially polymerized silicon that improve the geopolymerisation process [13].

This paper presents the effects on local fly ash based geopolymers durability of different types of acid environment: hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3), in terms of compressive strength reduction, macroscopic structure deterioration and weight loss. The samples have been directly immersed in the acid solution after the heat treatment.

2. Materials and methods

Fly ash is a secondary product resulted by coal combustion in city's power plants. This is collected in the upper filters of the installation and ends by being deposited on huge area near places with high human population. Because different dumps present different chemical composition, the activation solution and the ration between the components mush be particularly calculated. In this study a class F fly ash powder with the particle's diameter smaller than 80 μ has been used. The oxidic chemical composition of the powder used analyzed by X-ray fluorescence (XRF) Brucker S8 Tiger means is presented in Table 1.

Table 1. Oxide chemical composition of local fly ash powder [14].

Oxide	**SiO_2**	**Al_2O_3**	Fe_xO_y	CaO	K_2O	MgO	TiO_2	Na_2O	P_2O_5	oth.
w, %	47.8	28.6	10.2	6.4	2.4	2.0	1.3	0.6	0.4	0.1

A certain amount of aggregates with the specific particle distribution presented in [14] has been introduced in the solid component of the geopolymer samples.

Sodium silicate, known as water glass, is one of the most used alkaline activators for geopolymers due to its aggregation capacity. Sodium silicate is produced during a multiple stage process, through the first stage the Na_2CO_3 and SiO_2 are fused at high temperatures above 1100 º in order to obtain an amorphous solid glass, during the following step the product obtained is mixed with water in reactors under high pressure. High purity Na_2SiO_3 solution commercially purchased with 1.37 g/cm^3 density and pH lower than 11.5 has been used.

Sodium hydroxide (NaOH) solution possess small dimension sodium cations which can migrate easily through the binder network, increasing the dissolution capacity. Because the dissolution chemical reaction of NaOH 97% purity flakes in distilled water is exothermic, the heat released by the

reaction can influence the geopolymerisation process. The NaOH solution has been prepared at the desired molar concentration of 10M 24 hours prior using.

2.1 Samples preparation

In this study three type of fly ash base geopolymers samples have been prepared, cured at slightly high temperature and immersed in three types of acids or stored in empty containers (control sample) immediately after the curing period. As can be seen from Table 2, the samples include a solid component and a liquid one. The solid component of the 100FA samples is based on fly ash microparticles, that of the 50FA_50S samples consist in 50 % fly ash and 50% of fine aggregates by mass and that of the 25Fa_75S samples consist in 25 % fly ash and 75% of fine aggregates by mass. All the samples have been activated under alkaline condition with a solution of sodium silicate and sodium hydroxide in the ratio of 1. The solid component has been mixed with the alkaline solution by means of an adjustable speed mixer, until homogeneous binder has been obtained, in this case for 10 minutes. The binder has been poured in molds and subjected to vibrations in order to eliminate the air pores.

Table 2. Samples constituents.

Sample	Solid component		Liquid component
	Fly ash, wt. %	**Aggregates, wt. %**	**Sodium silicate to Sodium Hydroxide ratio**
100FA	100	0	1.5
50FA_50S	50	50	1.5
25Fa_75S	25	75	1.5

2.1.1 Curing process. One of the most important factors that influences the final properties of the geopolymers samples is the curing temperature. During the heat treatment the geopolymerisation reaction take place at higher or lower rate, depending on the setting time and temperature. In this study the curing process has been done at 70 ºC for a 36 hours period.

2.1.2 Exposure condition. After curing process, the samples have been demolded, cooled at room temperature (up to 1 hour) and immersed in the acids. The acid solutions have been prepared in special health and safety conditions [15,16] at the desired concentrations: hydrochloric acid (HCl) at the concentration of 1N, nitric acid (HNO_3) at the concentration of 1N and sulphuric acid (H_2SO_4) at the concentration of 2N. In order to reduce the acids evaporation, the tanks have been covered until the testing day. After 7 or 28 days, the samples have been dried at 70 ºC for 4 hours and tested at compressive strength.

2.1.3 Compressive strength. Geopolymers are totally inorganic ceramic materials which main mechanical properties is compressive strength. The tests have been performed on 20x20x22 mm samples dimensions, as can be seen in Figure 2, at a punch rate of 1 mm/min.

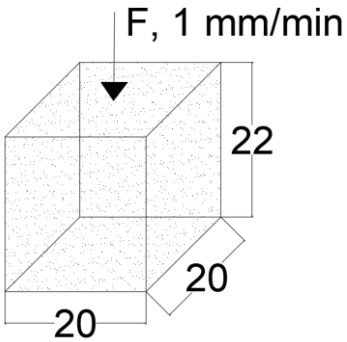


Figure 2. Compressive strength samples dimensions.

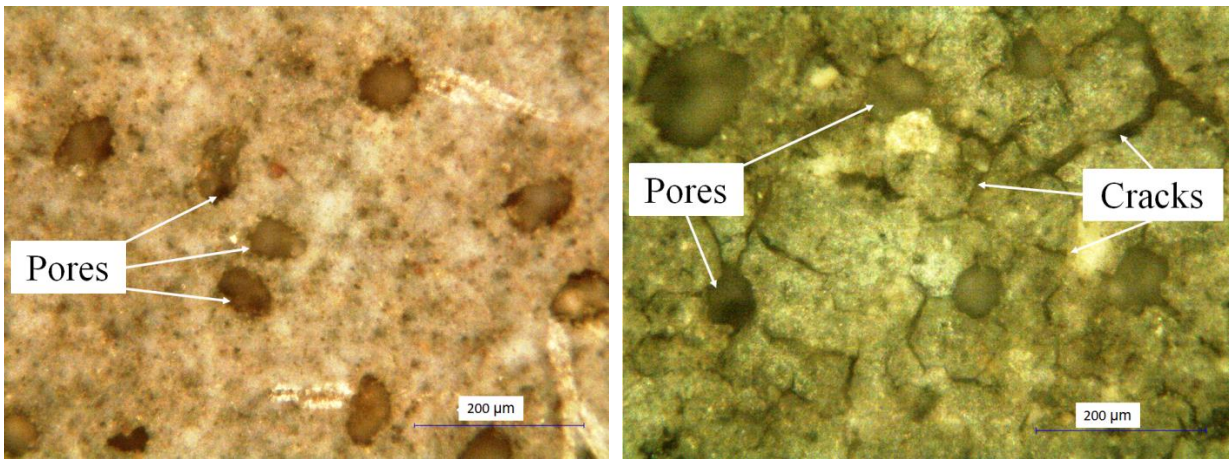
The macrostructural analyses have been performed prior and after compressive strength testing.

In case of composites materials (multi-components materials) the sample homogeneity greatly influences the final characteristics. Therefore, in order to improve the reinforcement particles distribution, the solid component element's have been mixed in a dry state prior alkaline activator introduction.

3. Results and discussion

It was decided that the best procedure for investigating the effect on geopolymers materials used in applications where the product comes in contact with different types of acids immediately after the curing process, i.e. without aging at room temperature for long periods, is to immerse the samples in the acid solutions directly after the curing process.

The micro and macrostructural analysis of the samples surface presents important information's about the samples degradation when exposed to acid environments. As can be seen in the Figure 3, prior exposing to the acids, the sample surface presents multiple pores (Figure 3.a) of small dimensions. However, after exposing to HCl acid for 7 days, multiple cracks are formed on the sample surface (Figure 3.b).



a) b)

Figure 3. Optic micrographs of geopolymer samples: a) Optical micrograph of 100FA sample prior exposing to acid; b) Optical micrograph of 100FA sample after exposing to acid.

As can be seen from the 3D surface profile of exposed samples (Figure 4), during the exposing period multiple cracks appears in the samples volume, especially close to the contact surface. The degradation presented by the samples is related to the degeopolymerization reaction that occurs depending on the type and concentration of the acid solution. According to the results, the HCl solution presents the highest degradation effect on the fly ash geopolymer samples.

The compressive strength of geopolymer samples decrease significatively after 7 days (Figure 5) exposure in acid solutions. In case of fly ash samples, aged in air, the average value of compressive strength is 8.3 MPa. After exposing the samples in acid solution for 7 days, the compressive strength of 100FA samples decreases up to 33% in case of HCl solution, 21% in case of H_2SO_4 solution and 17% in case of HNO_3 solution, respectively. The values obtained for fly ash with aggregates sample are lower than those of fly ash samples, this difference can be related with the dimensions of aggregates in accordance to samples dimensions [13]. The 50FA_50S air-maintained samples presents an average value of 7 MPa, the compressive strength decreases up to 38% after exposing to HCl acid, up to 36% in H_2SO_4 and 32% in HNO_3, respectively. By increasing the aggregates quantity, the compressive strength decreases to 6.3 MPa for air-maintained sample, but when exposed in HCl

solution the values decrease up to 21%, up to 16 % in H_2SO_4 and 10% in HNO_3, respectively. Therefore, the 25FA_75S samples presents the lowest degradation when exposed to acid solution, due to the fact that the volume of material (the matrix) affected by the acid is smaller. Also, in case of all samples the HCl presents the highest degradation effect, followed by the H_2SO_4 and HNO_3, respectively.

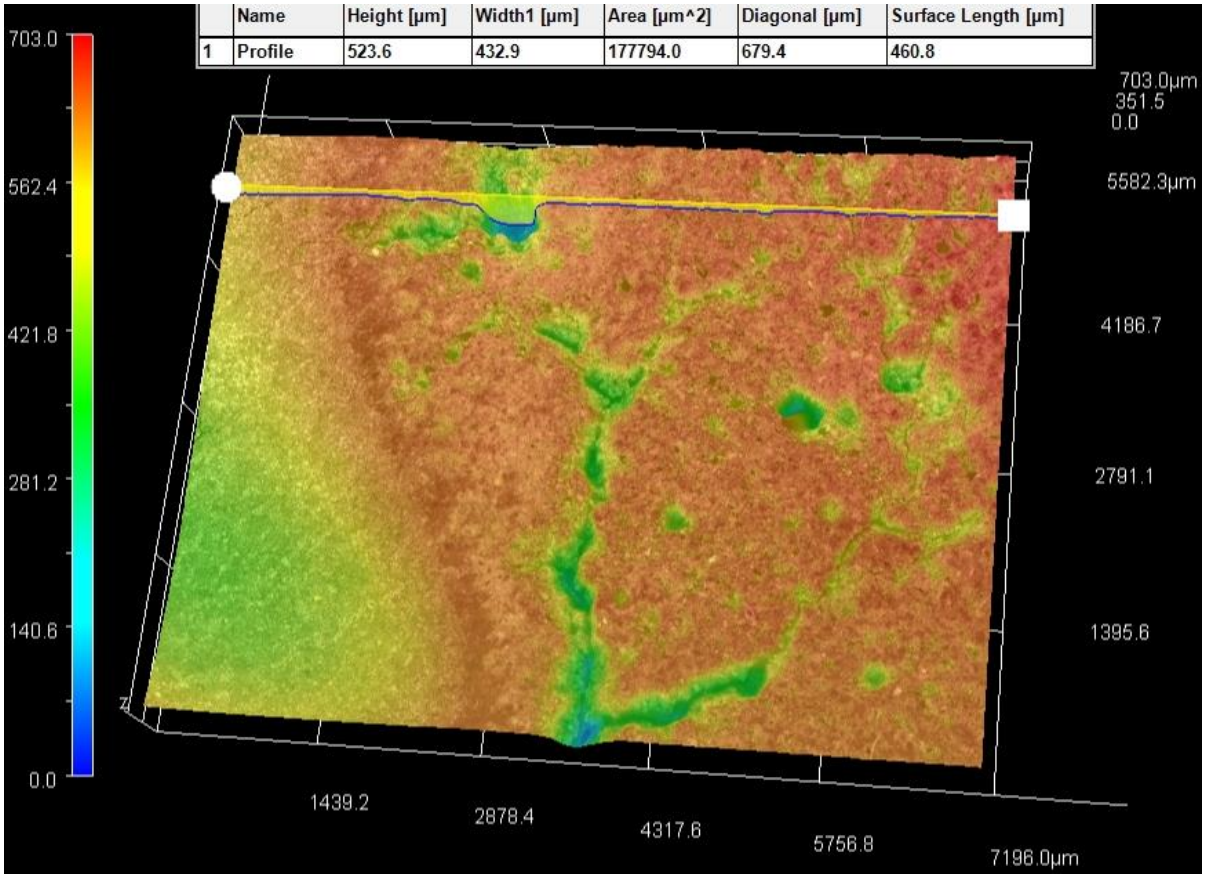


Figure 4. 3D surface profile of exposed fly ash sample.

After 28 days exposure to acids, the compressive strength of geopolymer samples decrease further (Figure 6). However, in case of acid exposed samples the geopolymerisation reaction didn't continued in order to increase the compressive strength, this has been replaced by the degeopolymerisation reaction which presents negative effects on the mechanical properties. Therefore, in order to evaluate the degradation rate, the values for 28 days exposure are compared with those obtained after 7 days. The 100FA samples compressive strength decrease further with 30%, i.e. from 6.4 MPa to 4.5 MPa, when exposed to HCl acid solution, with 7% when exposed to H_2SO_4 acid solution and close to 39% when exposed to HNO_3 acid solution. The 50FA_50S samples values decrease close to 5% after 28 days exposure to HCl, with 2% when exposed to H_2SO_4 and 6% when exposed to HNO_3, respectively. In case of 25FA_75S samples, the compressive strength values present a low decrease which is related with the matrix degradation by the acid solution.

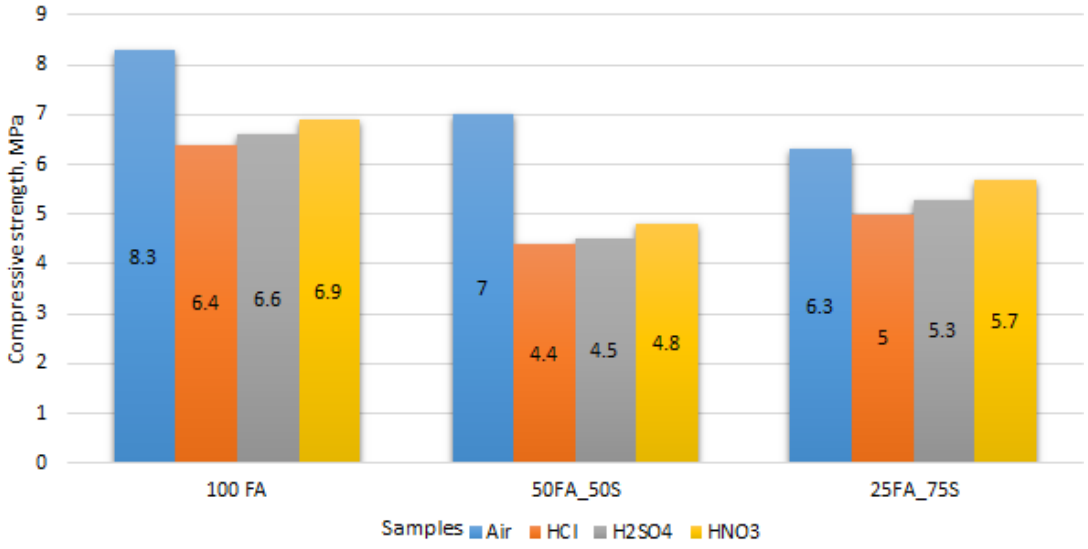


Figure 5. Compressive strength values of geopolymer samples after 7 days.

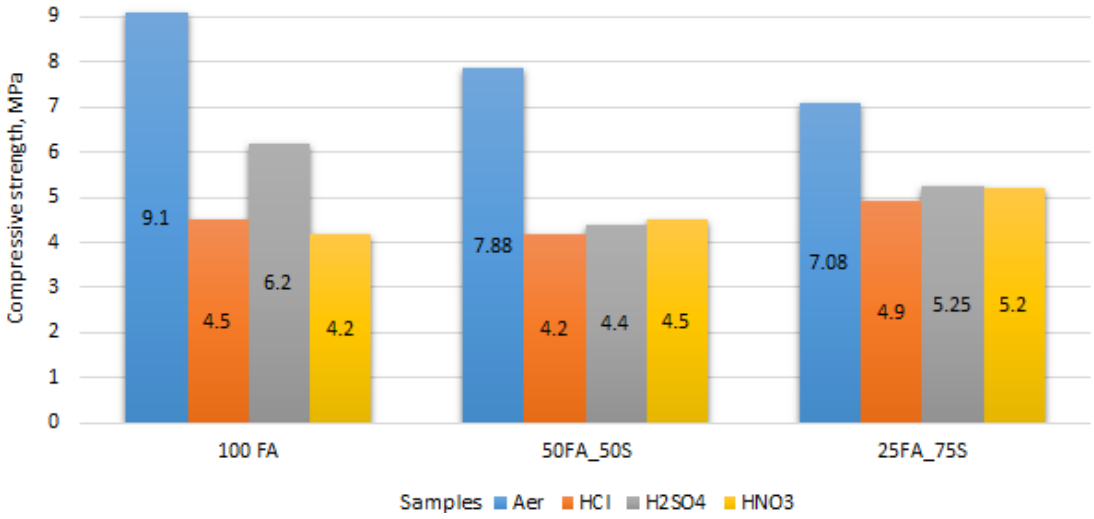


Figure 6. Compressive strength values of geopolymer samples after 28 days.

According to this study, geopolymers materials synthetized from local power plant fly ash chemically activated with sodium silicate solution and sodium hydroxide solution mixed in ratio of 1.5 present good acid exposure behavior. Therefore, this type of materials can be used for metal tank for acids insulating or in applications where acid-resistance is one of the most important factors.

4. Conclusions

Fly ash based geopolymers reinforced with75 % fine aggregates by mass of solid component presents the best behavior in acids environment, in terms of compressive strength and structure degradation, by comparing the values obtained for the samples maintained in air and those exposed to acid.

The 100FA samples presents the highest degradation, from macrostructural point of view, in the HNO_3 acid, because the samples present large and deep cracks. However, by comparting the compressive strength values, the HCl acid has the highest influence despite the exposing time in case of all samples.

The compressive strength of 100FA, 50FA_50S and 25FA_75S samples exposed for 7 days at different type of acid solutions decreases up to 33%, 38%, 21%, respectively, in case of HCl solution,

in case of H_2SO_4 the values decrease with 21%, 36%, 16%, respectively, and in case of HNO_3 acid solution the compressive strength decreases with 17%, 32%, 10%, respectively. The rate of degradation depends on the samples structure, which is mainly influenced by the quantity of aggregates. The samples prepared with 50% by mass of solid component presents the lowest acid resistance, from the compressive strength point of view.

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