Influence of Iron Trioxide Addition on Alkali-Activated Fly Ash-Based Geopolymer Paste

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Abstract. This paper presents the study conducted in order to study the influence of the use of iron trioxide as an addition to an alkaline activated geopolymer paste on its physical and mechanical performance. The experimental test followed the variation of the flexural and compressive strength of alkali-activated geopolymer pastes at the age of 7 days, which takes place after the introduction as an addition to the preparation of 1%, 5% and 10% (mass percent) iron trioxide powder and compared to the control sample performed without addition. The experimental results showed that the flexural strength increased by 7.2% for a 1% addition of iron trioxide to fly ash, by 30.7% and by 33.7% for cases of addition of iron trioxide 5%, respectively 10% to fly ash. Test regarding the compressive strength revealed an increase of 21.7% for a 1% addition of iron trioxide to fly ash, by 15.3% and 14.8% respectively for cases of addition of iron trioxide 5% and 10% respectively.

Keywords: Geopolymer paste · Alkali-activation · Iron trioxide powder

1 Introduction

In the last years, worldwide, as a result of increasing pollution, there has been the issue of environmental protection, preservation of non-renewable natural resources and the identification of minimally polluting or non-polluting technologies in all areas of activity.

In line with current development strategies, sustainable development and implementation of the concepts of the Circular Economy, the construction industry must align itself with innovative technologies to achieve alternative, environmentally friendly construction materials. This is urgently needed because the construction industry is the fastest growing in the world, with current world statistics indicating that 260 million tons of cement are needed annually [1]. On the other hand, the cement industry is responsible for producing CO_2 emissions because, for the production of one ton of Portland cement, about one ton of CO_2 is released into the atmosphere [2]. An alternative to traditional

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concrete is represented by geopolymer ecological concretes based on alkaline activated mineral binders.

The term of geopolymer was originally introduced by Davidovits [3], representing a wide range of inorganic materials. According to Davidovits [4], nine different classes of geopolymers are defined, geopolymer concrete, with aluminosilicate structure, of particular interest because it could be used to completely replace traditional concrete. In 1999, Palomo identified the possibility of activating pozzolanic materials such as blast furnace slag and power plant ash "using alkaline liquids to form a binder and completely replace the use of Portland cement in concrete production" [5].

The geopolymer is an inorganic polymer composed of two main constituents, namely source materials of aluminosilicates and alkaline activating solutions [6]. In general, sources of aluminosilicates containing high amounts of silicon, alumina and calcium oxide are used in the preparation of geopolymers. The combination of sodium silicate (Na_2SiO_3) and sodium hydroxide (NaOH) has been widely used as an alkaline activator in liquid form [7]. Currently, experimental research has shown that the technology of making geopolymer materials offers the possibility of using industrial waste as raw materials, for example, fly ash, thus responding to the concepts of the Circular Economy. Thus, reports from the literature indicated the obtaining of geopolymer materials which, among other types of cementitious materials fall within the research interest worldwide [8].

The relative types and quantities of coal incombustible matter determine the chemical composition of the fly ash. The chemical composition is composed mainly of oxides of silicon (SiO_2), aluminum (Al_2O_3), iron (Fe_2O_3) and calcium (CaO), while magnesium, potassium, sodium, titanium and sulfur are present in a smaller amount. The major influence on the chemical composition of flying ash comes from the type of coal. However, recent studies have shown that precursors with a higher iron content than those commonly found in fly ash can be activated in an alkaline environment [9–11] with applications in engineering.

Although the presence of iron trioxide (Fe_2O3) could play important roles in the structure and properties of geopolymers, the replacement of aluminum trioxide with iron trioxide has not yet been fully studied.

The compression strength of geopolymers generally increases with increasing specific concentration of alkaline activators [12, 13]. A higher concentration gives rise to a stronger ion pair formation and ensures a more complete and faster poly-condensation process of the particle interface [14] improving the dissolution of silicon and aluminum-containing materials in the presence of activators [15]. However, too high a concentration could lead to an increase in the coagulated structure [16], resulting in lower workability with rapid hardening behavior [17]. According to the literature, the most used NaOH concentrations are 6, 8 and 10 M. The optimum alkaline concentration can also vary depending on a large number of conditions and factors, such as the specific properties of the raw materials, the alkaline activator/raw material ratio, the Na_2SiO_3/NaOH ratio, the curing temperature, or even the age of testing.

Research on geopolymer paste and mortars with heat treatment (between 30 and 90 °C) has shown an increase in the chemical reaction, leading to an increase in compression strength from an early age [18]. Other researchers [19] claim that too high a heat treatment temperature (for example above 90 °C) would lead to a geopolymer with a porous structure due to rapid water loss, causing a negative effect on mechanical properties of the geopolymer.

The optimum temperature of the heat treatment proved to be around 60 to 75 °C, which could accordingly improve the geopolymerization process and an adequate microstructural development [20]. The testing age of geopolymers, according to the literature was 3, 7, 14, 28, 56 and 90 days. However, most reports showed that geopolymer samples gain their strength at the age of 7 days, due to heat treatment [21].

The aim of this paper is to present the study on the influence of the use of iron trioxide as an addition to an alkaline activated geopolymer paste on its physical and mechanical performance. The experimental test followed the variation of the tensile strength by bending and the compression strength of alkaline activated geopolymer pastes at the age of 7 days, which takes place after the introduction as an addition to the preparation of 1%, 5% and 10% (mass percent) trioxide iron powder compared to the control sample performed without addition.

2 Materials and Methods

2.1 Raw Materials

For the design and production of the alkali-activated geopolymer paste samples, the following raw materials were used: fly ash (FA), iron trioxide Fe_2O_3, sodium hydroxide solution NaOH(6 M), sodium silicate solution (Na_2SiO_3) 35% (Fig. 1).

The ash that was used in this study was obtained from Rovinari power-plant, Romania and its chemical composition was established through X-ray fluorescence analysis (XRF analysis) (Table 1). Iron trioxide Fe_2O_3 in powder form was used as an additive. After dry mixing the fly ash with iron trioxide, an alkaline activating solution was added to make the geopolymer paste. A mixture consisting of 35% sodium Na_2SiO_3 silicate solution and a sodium silicate solution (NaOH, 6 M) was chosen as alkaline activator, with mass ratio Na_2SiO_3: NaOH = 2:1. The sodium hydroxide solution was prepared dissolving the NaOH pearls, 99% purity; into water in order to obtain the desired concentration of the solution.

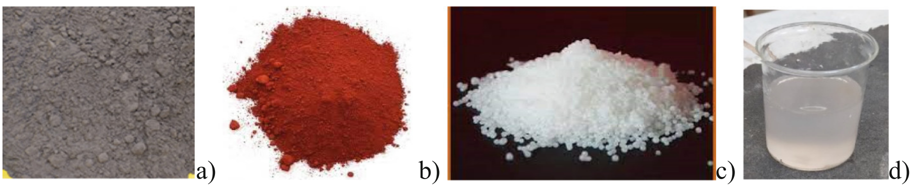


Fig.1. Raw materials used in the production of the alkali-activated geopolymer samples: (a) fly ash; (b) Iron trioxide; (c) NaOH; (d) Na_2SiO_3 solution.

Table 1. Chemical composition of the fly ash used in the production of the alkali-activated geopolymer samples.

Rovinari fly ash										
Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	TiO_2
Wt (%)	46.94	23.83	10.08	10.72	2.63	0.45	0.62	1.65	0.25	0.92

2.2 Mix-Design, Molding and Curing Treatment

Preliminary results obtained on geopolymer paste, using the same type of fly ash, led to an alkaline activator/fly ash ratio of 0.78, because it has shown good workability of the alkali-activated fly ash-based geopolymer paste. In order to study the effect of Fe_2O_3 addition on the mechanical properties of the material, the following mix-design ratios were produced:

– R21: fly ash + solution [35% Na_2SiO_3 + NaOH (6M)], with a Na_2SiO_3/NaOH ratio = 2.0;
– R22: fly ash + 1% Fe_2O_3 + solution [35% Na_2SiO_3 + NaOH (6M)], with a Na_2SiO_3/NaOH ratio = 2.0;
– R23: fly ash + 5% Fe_2O_3 + solution [35% Na_2SiO_3 + NaOH (6M)], with a Na_2SiO_3/NaOH ratio = 2.0;
– R24: fly ash + 10% Fe_2O_3 + solution [35% Na_2SiO_3 + NaOH (6M)], with a Na_2SiO_3/NaOH ratio = 2.0.

The quantities of raw materials used to produce the alkali-activated geopolymer samples are presented in Table 2.

Table 2. Mix-design ratio of the alkali-activated geopolymer samples.

Mixt.	Fly ash		Fe_2O_3		Fly ash + Fe_2O_3	Alkaline activator			Na_2SiO_3/NaOH	Alkaline activator solution /(FA + Fe_2O_3)
						Na_2SiO_3	NaOH	Total		
	[%]	[g]	[%]	[g]	[g]	[g]	[g]	[g]	–	–
R21	100	267	0	0	267.00	138.7	69.3	208.0	2.0	0.78
R22	100	267	1	2.67	269.67	140.0	70.0	210.0		
R23	100	267	5	13.35	280.35	145.6	72.8	218.4		
R24	100	267	10	26.70	293.70	152.5	76.3	228.8		

After the preparation of the alkaline activator by combining the sodium silicate solution with the sodium hydroxide solution 24 h prior to mixing, the fly ash and/or the Fe_2O_3 addition and the activator were mixed together until a homogeneous mixture was obtained. The samples were then placed in 40 mm × 40 mm × 160 mm molds and heat cured at 70 °C for 24 h (Fig. 2). During the heat treatment a film was put on top of the molds in order to prevent the quick release of the water from the mixtures. After demolding, the samples were kept in the climatic chamber at (20 ± 1) °C and (60 ± 5)% humidity until the test were conducted (Fig. 3).

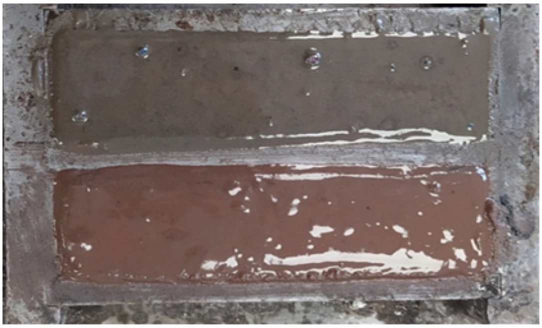
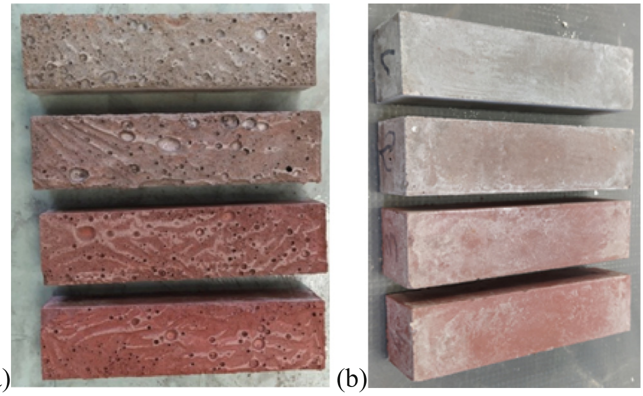


Fig. 2. Alkali-activated geopolymer fresh-state samples: without Fe_2O_3 addition (above); with 1% Fe_2O_3 addition (below).



(a) (b)

Fig. 3. Alkali-activated geopolymer samples after demolding: (a) after heat treatment and (b) prior to the 7 days testing.

2.3 Testing Methods

The apparent density in the fresh state was evaluated according to EN 12,350-1, as the ratio between mass and volume immediately after the mixing finished. The apparent density in hardened state was evaluated according to EN 12,390-7, right after the demolding of the samples and at the age of 7 days.

To obtain the result for the mechanical properties of the samples, for all the alkali-activated geopolymer pastes, minimum three samples were tested to determinate the average value.

The flexural strength (Fig. 4 and Fig. 5) and the compressive strength of the samples were determined according to EN196-1, the standard used for ordinary Portland cement mortars.

Fig. 4. Alkali-activated geopolymer samples during flexural strength test.

Fig. 5. Alkali-activated geopolymer samples after flexural strength test.

The percentage increases of the flexural and compressive strength of the samples with the addition of iron trioxide were calculated by comparing them to the control sample (R21), without the addition of iron trioxide.

3 Results and Discussions

Iron-containing fly ash takes time to react with the alkaline solution in the geopolymer system to form the iron silicate binder gel. This mainly happens due to the high atomic mass and large atomic diameter of the iron contained in silica and alumina [22]. Cannio [23] identified ferro silicate in addition to the sodium aluminum silicate gel in the geopolymer, which contributes to the durability of the geopolymer. Thus, the longer curing time led to an increase in the compressive strength to which iron oxide contributed.

3.1 Apparent Density

The results regarding the apparent density in the fresh and hardened state of the alkali-activated geopolymer samples are presented in Table 3 and Fig. 6.

Table 3. Apparent density of the alkali-activated geopolymer samples.

Mixture	Fly ash	Fe_2O_3	$Na_2SiO_3/NaOH$	$\rho_{fresh\ state}$	ρ_{2days}	ρ_{7days}
–	[%]		–	[kg/m^3]		
R21	100	0	2.0	1580	1380	1290
R22	100	1		1620	1390	1330
R23	100	5		1640	1450	1350
R24	100	10		1670	1510	1380

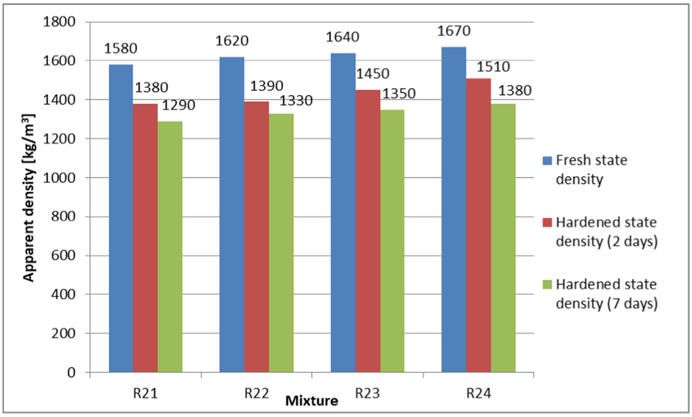


Fig. 6. Apparent density of the alkali-activated geopolymer samples.

In terms of apparent density in fresh state. it is observed that, in relation to the composition considered as control, R21, by the addition of iron trioxide (Fe_2O_3) in percentages of 1, 5 and 10% (compositions R22, R23, R24) to the fly ash, the apparent density in the fresh state increases on as the percentage of Fe_2O_3 added increases. Thus, there were increases of 2.2% for a 1% addition of iron trioxide to fly ash, 3.3% and 5.4% for cases of addition of 5% iron trioxide, respectively 10% to fly ash.

The same behavior was observed for both the 2 and 7 days apparent density in hardened state, with an increase of 0.2% for an addition of 1% iron trioxide to fly ash, by 5.2% and 8.7% for cases of addition of iron trioxide 5% and 10%, respectively (2 days) and 3.1% for an addition of 1% of iron trioxide to fly ash, by 4.5% and 6.7% respectively for cases of addition of iron trioxide 5% and 10%, respectively (7 days).

3.2 Mechanical Properties of the Alkali-Activated Geopolymer Samples

The results regarding the mechanical properties of the alkali-activated geopolymer samples are presented in Table 4 and Fig. 7 (R_{ti} - flexural strength) and Fig. 8 (R_c - compressive strength).

Table 4. Mechanical properties of the alkali-activated geopolymer samples.

Mixture	Fly ash	Fe_2O_3	$Na_2SiO_3/NaOH$	R_{ti}	R_c
–	[%]		–	[N/mm^2]	[N/mm^2]
R21	100	0	2.0	2.401	18.19
R22	100	1		2.574	22.13
R23	100	5		3.190	21.57
R24	100	10		3.475	21.39

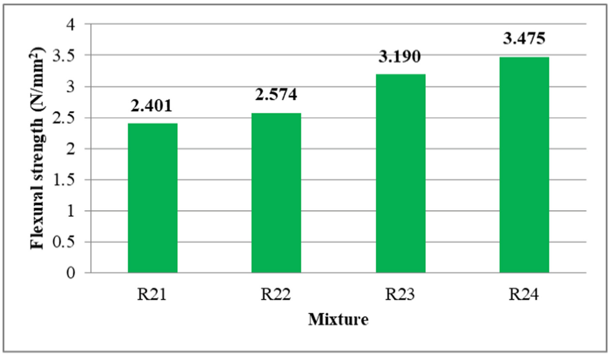


Fig. 7. Flexural strength of the alkali-activated geopolymer samples.

From Table 4 and Fig. 7 it is observed that the flexural strength of the samples increased linearly with the increase of the addition of iron trioxide. Thus, there were increases of 7.2% for an addition of 1% iron trioxide to fly ash, by 32.9% and 44.7% for cases of addition of iron trioxide 5% and 10%, respectively.

The compressive strength of the samples at 7 days increased by the introduction of the addition of iron trioxide. Thus, there were increases by 21.7% for an addition of 1% of iron trioxide to fly ash, by 18.6% and by 17.6% for cases of addition of iron trioxide 5% and 10%, respectively.

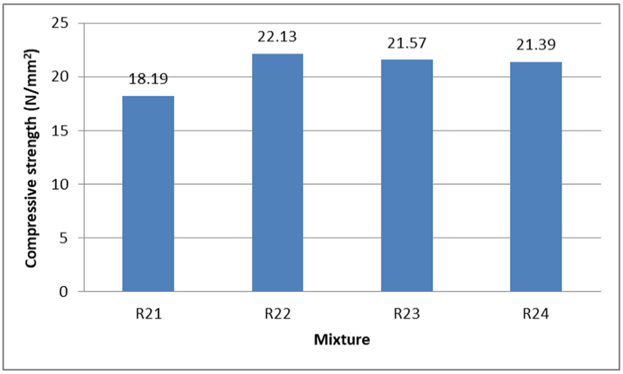


Fig. 8. Compressive strength of the alkali-activated geopolymer samples.

4 Conclusions

Studies have shown that precursors with a higher than usual iron content found in fly ash can be activated in an alkaline environment, a conclusion that is consistent with the literature. This paper aimed to investigate the implications of the presence of iron in the geopolymer structure on preliminary alkali-activated fly ash-based geopolymer materials.

By the addition of iron trioxide in proportions of 1%, 5% and 10% to alkaline activated geopolymer pastes based on fly ash, it was observed that the mechanical properties of the material increased, both in terms of flexural strength and also, compressive strength.

Flexural strength of the alkali-activated geopolymer samples increased with the addition of 1%, 5% and 10% (mass percent) iron trioxide powder compared to the control sample without addition. Thus, there were increases of 7.2% (Mixture R22) for a 1% addition of iron trioxide to fly ash, by 32.9% (Mixture R23) and by 44.7% (Mixture R24) for cases of addition of iron trioxide 5% and 10% respectively to fly ash.

The best compressive strength at 7 days was obtained by adding 1% iron trioxide to fly ash. The mechanical strength for this mixture R22 increased by 21.7% compared to the control sample R21, without the addition of iron trioxide. For mixtures R23 (5% Fe_2O_3 addition) and R24 (10% Fe_2O_3 addition) the compression strengths at the age of 7 days increased by 18.6% and 17.6% respectively compared to the R21 control sample, without the addition of iron trioxide.

Further studies will focus on studying the influence of Fe_2O_3 addition in the production of alkali-activated fly ash-based geopolymer paste by varying several parameters that can affect the mechanical properties of the samples (i.e. raw material ratios in the mix-design) and study the possibility of transition to geopolymer mortars, by adding aggregates into the mixtures.

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