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TECHNICAL UNIVERSITY
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Domain: Civil Engineering and Installations

PhD THESIS
– ABSTRACT –

Eco-friendly Concrete Based on Alkaline-Activated Mineral Binders

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INTRODUCTION

1.1. Justification of the topic approach

One of humankind's current problems is global warming, caused by the accumulation of greenhouse gases in the atmosphere. Air pollution is the process of changing the natural characteristics of the atmosphere as a result of the action of chemical, physical or biological agents that have a harmful effect on the environment. The main air pollutants are: carbon dioxide (CO_2), carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matter (PM), volatile organic compounds (VOCs), benzene and heavy metals. Carbon dioxide (CO_2) is a greenhouse gas that is emitted by burning fossil fuels. The major sources of CO_2 production are thermo-electric power generation, manufacturing industry and metallurgical industry.

Consequently, in order to protect the environment, the construction industry must align to the standards of sustainable development and the Circular Economy, by providing alternative, environmentally friendly building materials. The present thesis focuses on the development of an ecological concrete (geopolymer) based on alkaline-activated mineral binders, which does not contain Portland cement, itself a massive source of pollution.

1.2. Topic framing within international and national approaches

The construction industry is the fastest growing in the world. Current world statistics have shown that 260,000,000 tonnes of cement are needed annually [1].

According to Davidovits (1994) [2], the cement industry is responsible for the production of CO_2 emissions, because for the production of one tonne of Portland cement, approximately one tonne of CO_2 is released into the atmosphere, resulting into atmospheric pollution.

Nowadays, environmental protection is a global issue. Over time, energy resources and subsoil wealth have been depleted, some of which are expected to run out rapidly in the near future, whereas some essential living conditions such as water and air have been showing signs of poisoning.

In order to protect the environment, the construction industry must align to sustainable development and circular economy standards by providing sustainable materials using industrial waste as raw material. An alternative to traditional Portland cement concrete is the geopolymer concrete.

Worldwide, geopolymers have been the subject of interest for many researchers, among which the best known are: Davidovits, Hardjito, Rangan, Palomo, Fernandez-Jimenez, etc. At the national level, they started to be studied at the Technical University "Gheorghe Asachi" of Iași by Burduhos-Nergis D. D., at the University "Dunărea de Jos" of Galați, by Spătaru I., and at the Technical University of Cluj-Napoca, by Lăzărescu A. V.

1.3. Title, premises and the research objectives

The subject of the present research is highly topical, concerning the circular economy and environmental protection, through the production of new, innovative materials. The title of the PhD thesis is: *Eco-friendly concrete based on alkaline-activated mineral binders*.

The PhD thesis approaches the development of an environmentally friendly "green concrete" based on alkaline-activated mineral binders, which does not use Portland cement, as an alternative to traditional concrete. This concrete is made from silica and aluminium-rich industrial waste, such as fly ash from thermal power plants, blast furnace slag or marble dust, which, when alkaline-activated with a sodium hydroxide and sodium silicate solution, produces a geopolymerisation reaction, leading to the hardening of the material and the production of geopolymer concrete. A property of geopolymer concrete is that it hardens rapidly, reaching 90% of its compressive strength after seven days, compared to traditional Portland cement concrete, which reaches maturity in terms of strength only after 28 days.

The research methodology required for the production of alkaline activated geopolymer concrete was based, in addition to the identification of methodologies presented in the literature, on a coherent research programme, which involved a trial-and-error analysis in order to establish its own methodology for the production of these types of materials.

This concrete is made using as raw materials industrial waste (from our country) rich in silicon and aluminium, which, when alkaline activated using a mixture of sodium hydroxide and sodium silicate solutions, produces a geopolymerisation reaction, leading to the hardening of the material. By adding sort 0-8 mm aggregates, geopolymer concrete is obtained. The green binders and concretes resulted by two methods, namely: with a heat treatment (70°C, 24H) or without a heat treatment (ambient temperature 23°C).

The cost of making geopolymer concrete varies according to the raw materials that are used and the concentration of the alkaline solution used. Thus, the aim is to obtain geopolymer concrete with very good, more convenient mechanical properties, by finding a cheap raw material, rich in Si and Al, using the lowest concentration of alkali activator.

The necessary documentation for the research project was obtained with the support of the PhD coordinator and the committee members. Naturally, I also had access to the library of the Technical University, as well as to various international databases.

The research activity was carried out in the INCD URBAN INCERC Cluj-Napoca Branch and in the laboratories of the Technical University of Cluj-Napoca.

After the identification and analysis of local raw materials, I proceeded to the development of ecological binder recipes. Based on the literature, alkaline activated geopolymer pastes based on fly ash were made and considered as control samples. Geopolymer pastes were also obtained by substituting fly ash in the proportions of 10%, 25% and 50% with blast furnace slag, aluminium slag or marble dust, all being industrial wastes/subproducts and characterised by an oxide and mineral composition favourable to the development of the geopolymerisation reaction. Iron trioxide, silicon oxide, magnesium oxide and calcium hydroxide were used in the production of geopolymer pastes with different additions and percentages to fly ash. Based on the 7-day compression results of the binders with and without substitution and with different additions, the recipes with the best results were selected. Thus, the ecological concrete based on mineral binder by adding aggregates to geopolymer pastes with the best compressive strengths was achieved.

Eco-friendly binders and eco-friendly concrete based on alkaline activated mineral binders were made by two methods, namely with a heat treatment (70°C, 24H) or without heat treatment (23°C ambient temperature).

In order to ensure a coherent scientific pathway, four scientific research reports (progress reports) were produced within the research programme and were presented to the PhD supervisor and the supervising committee.

1.4. Contents of the doctoral thesis

The present doctoral thesis is structured in seven chapters, which will be briefly presented below:

Chapter 1, the introduction, justifies the approach to the topic and its framing within international and national approaches, and presents the structure of the paper.

Chapter 2 refers to the current state of research on geopolymer binder/concrete with different raw materials, substitutions and additions, reported by various researchers (Davidovits, Temuujin, Baykara, Allahverdi, Anuar etc.).

Chapter 3 discusses the objectives proposed in the realization of the PhD thesis: identification of raw materials, determination of alkaline activators and the ratio of sodium silicate and sodium hydroxide solution, realization of green binders and green concrete based on alkaline activated mineral binders by two methods (with a heat treatment (70^{o}C, 24H) or without heat treatment (23^{o}C ambient temperature).

Chapter 4 presents the general methodology for making environmentally friendly binders and concretes based on alkaline-activated mineral binders and the equipment used in making and testing them.

Chapter 5 provides the results of the research into the production of alkali-activated ecological binders based on fly ash, by substituting fly ash with marble dust and blast furnace slag in the proportions of 10%, 25% and 50% or with aluminium slag in the proportion of 25%. This chapter also presents the physical and mechanical performance of the environmentally friendly binders made by introducing various additions to the raw material mix such as iron trioxide, calcium oxide, silicon dioxide, magnesium oxide and perlite. The green binders were obtained by two methods – with a heat treatment (70^{o}C, 24H) or without heat treatment (23^{o}C ambient temperature).

Chapter 6 presents the production of ecological concrete based on alkaline activated mineral binders with substitution of fly ash with marble dust in percentages of 10 and 25%, as well as the results obtained from the tests carried out. Ecological concretes were made both with heat treatment (70^{o}C, 24h) and without heat treatment.

In **Chapter 7** the conclusions based on the research results and the author's personal contribution are centralised.

PERSONAL CONTRIBUTION

3. Research hypotheses

Regarding how to make geopolymer materials worldwide, some things are known such as that the raw materials used must be rich in silicon and aluminum and the most used alkaline activators used are based on Na_2SiO_3 and NaOH, but there are and numerous controversies regarding the molar concentration of the NaOH solution, the temperature and duration of the heat treatment as well as the optimal ratio between Na_2SiO_3/NaOH.

4. General methodology

The general methodology consisted of a theoretical and an experimental research. The theoretical research was carried out based on the analysis and synthesis of more than 200 bibliographic references.

The experimental research presented in this doctoral thesis was carried out both within the INCD-URBAN-INCERC laboratory, Cluj-Napoca branch, as well as in different laboratories within the Cluj-Napoca Technical University.

The experimental program consisted of:

- identification of local raw materials rich in Si and Al
- identification of potential fly ash substitutes and possible additives used
- identifying the types of alkaline activators and their ratio
- identifying the molarity of the NaOH solution
- identifying and determining how to make geopolymers with or without heat treatment, as well as determining the temperature of the heat treatment and its duration
- testing methods
- experimental tests on raw materials: analysis and characterization of local raw materials to be used to obtain ecological paste/concrete (monitored parameters: appearance, composition, volumetric mass, granulometric distribution)
- ecological binders with or without heat treatment, with fly ash substitution or with different additions
- ecological concrete based on alkaline activated mineral binder
- experimental tests on binder and ecological concrete based on alkaline activated mineral binder, in order to establish the influence of raw materials, compositional and technological parameters on the performance of the binder and concrete.

For the production of the binder and the eco-friendly concrete, the physical-mechanical tests, the Fourier transform infrared (FTIR) analysis, the microscopic evaluation and the compositional evaluation by the x-ray diffraction (XRD) method, different equipment were used, such as paddle mixers, balances analytical and hydrostatic, thermo-adjustable ovens, sieve set, digital bending and compressive strength testing machine, Jasko FT/IR -6200 Fourier Infrared Spectrometer, 5 bar vacuum press, optical stereomicroscope and diffraction apparatus with X rays. Metal patterns, graduated cylinders, berzelius glasses, morjar, glass rods, etc. were also used.

The raw materials used in the production of binders and ecological concrete were of local origin, in order to study the possibility of producing this type of material in our country.

5. Eco-friendly alkaline activated binder (geopolymer paste)

5.2. Objectives

The objectives of this chapter refer to preliminary research for the realization of alkaline activated ecological binders, their design and realization with different substitutions of fly ash or with different additions, as well as their characterization.

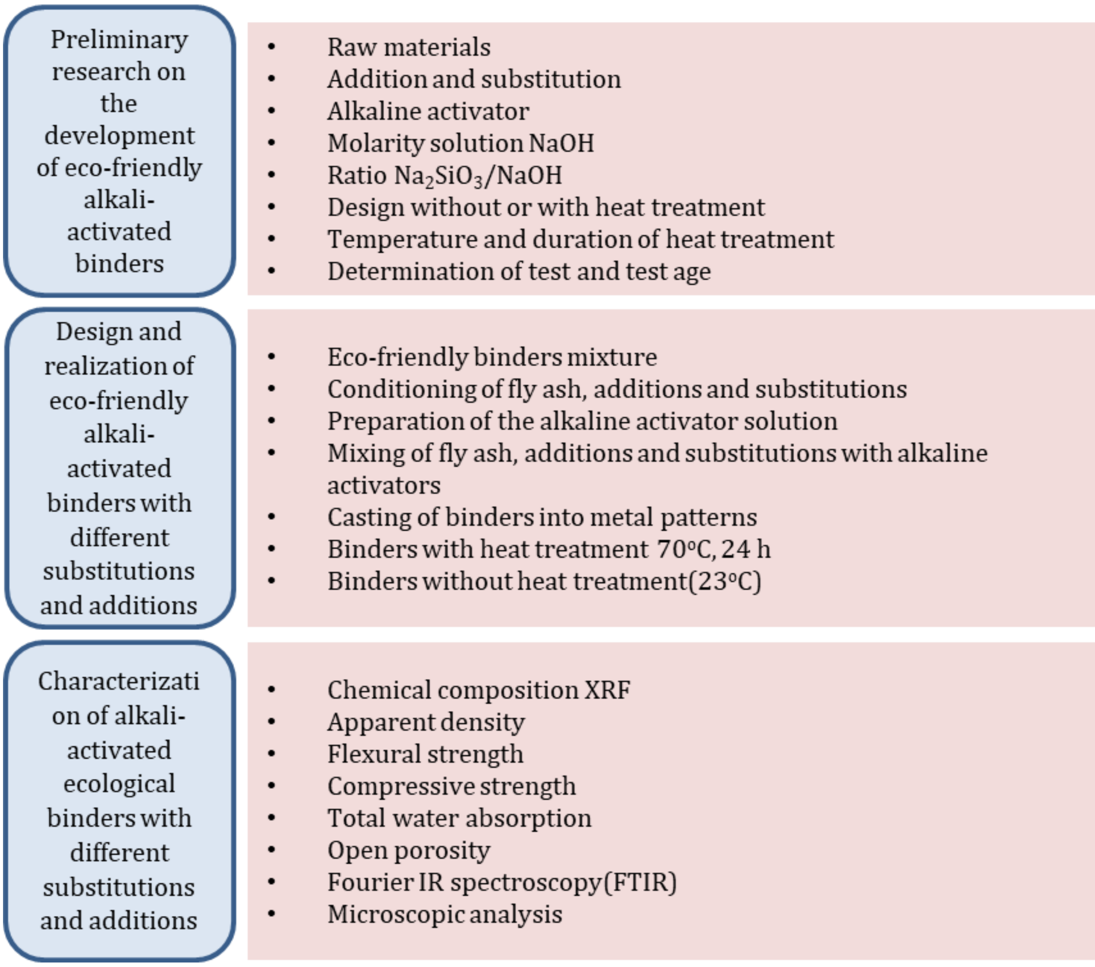

Fig. 5.1. The research methodology of alkaline activated ecological binders and the steps taken

5.3.1.2. Determination of fly ash substitutes and additions

In order to create an ecological binder, the aim was to identify some raw materials from local industrial waste, rich in Si and Al, which can generate the geopolymerization reaction and create resistant and durable materials, comparable to traditional concrete that uses Portland cement.

The fly ash (F.A.) used in the production of alkaline activated ecological binders was obtained from the Rovinari Thermal Power Plant.

Based on the mixture of alkaline-activated ecological binders based on fly ash, derived mixtures were made by substituting fly ash in percentages of 10%, 25% and 50% with marble dust (mixtures R9÷20) and furnace slag (rmixtures R34÷36).

The marble dust (M.D.) used in the study was obtained from the processing of Ruschița marble, by cutting, and is white in color.

The blast furnace slag is of domestic origin.

Also in this research was studied the influence of different raw materials used as an addition to the basic mixture of fly ash-based alkaline activated geopolymer paste.

Aluminum slag is obtained from waste processing.

Perlite is obtained by grinding commercially purchased perlite granules.

Iron trioxide, SiO_2, $Ca(OH)_2$ and MgO were purchased commercially.

5.3.1.3. Determination of alkali activators and molarity of NaOH solution

According to specialized literature, the most frequent alkaline activators are sodium silicate and sodium hydroxide. Thus, we opted for an alkaline activation solution made by mixing sodium silicate with sodium hydroxide of different molarities. The molar concentration of the NaOH solutions used in the ecological binders was 6M, 8M and 10M.

5.3.1.4. Determination of Na_2SiO_3/NaOH ratio

Also, the influence of the Na_2SiO_3/NaOH ratio on the physical-mechanical properties was studied on these ecological binders. Different ratios of Na_2SiO_3/NaOH =1; 1.5; 2 and 2.5, were used in the study, made at different molarities 8M (Mixture R1, R2, R3 and R4) and 10M (Mixture R5, R6, R7 and R8)

5.3.1.5. Determination of how to make geopolymer binders with/without heat treatment. Temperature and duration of heat treatment

Studying the specialized literature, where the possibility of making geopolymer pastes with or without heat treatment is presented, some of the mixtures were made with a heat treatment of 24h at 70^{o}C, and others were made without heat treatment, at a temperature of 23 ±2^{o}C. The samples made by the two methods with/without treatment were compared to each other in order to study the influence of the heat treatment on the mechanical resistances and to be compared with the specialized literature including the temperature of the heat treatment was chosen based on the existing studies.

5.3.1.6. Determination of test and test ages

The test ages of the alkali activated geopolymer pastes were 7, 14 and 28 days.

A number of 68 mixtures of alkaline activated ecological binders were made, of which 50 were subjected to heat treatment (70^{o}C, 24h) and 18 were made without heat treatment (ambient temperature 23^{o}C).

5.4. Results

A number of 68 mixtures of alkaline activated geopolymer pastes were made from which:

- 9 fly ash based (R1÷R8; R21),
- 26 of recipes by substituting fly ash with different raw materials:
  - 15 replacing fly ash in percentages of 10%, 25%, 50% with marble dus (R9÷R20, R53TT÷R55FTT)
  - 6 replacing fly ash in percentages of 10%, 25%, 50% with blast furnace slag (R34÷R36, R34FTT÷R36FTT),
  - 3 by substitution of 5% and 25% with perlite and marble dust (R1P, R2P, R3P)
  - 2 by substitution of 25% with aluminium slag (R33-1, R33-2).
- 33 mixtures with different additions and percentages
  - Iron trioxide addition Fe_2O_3 R22, R23, R24
  - Iron trioxide addition Fe_2O_3 and aluminium slag R25, R26, R27
  - Iron trioxide addition Fe_2O_3 and perlite R28
  - SiO_2 addition and iron trioxide Fe_2O_3 R29, R30, R31
  - Iron trioxide addition Fe_2O_3, SiO_2, MgO și $Ca(OH)_2$ R37, R45, R46, R47, R45FTT, R46FTT, R47FTT
  - SiO_2 addition and $Ca(OH)_2$ R42, R43, R44, R48, R49, R50, R51, R52, R42FTT, R43FTT, R44FTT, R48FTT, R49FTT, R50FTT, R51FTT, R52FTT

Number of 18 geopolymer paste mixture were made without heat treatment (23°C), both with the addition and substitution of fly ash.

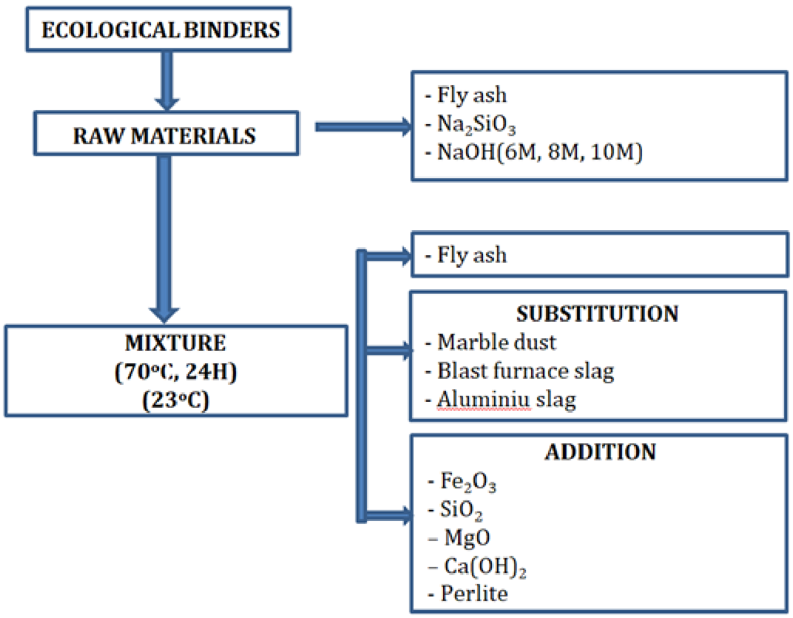

Fig. 5.21. Alkaline activated ecological binder realised

The mixtures of alkaline-activated ecological binders made on the basis of fly ash, considered as control samples for those with substitutions and additions, are presented in the next tables.

Table 5.4. Eco-friendly binder mixtures based on fly ash

Mixture	Solution NaOH	Fly ash		Alkaline activator solution		Alkaline activator solution (A.A.)	Na_2SiO_3/NaOH	AA/FA
				Na_2SiO_3	NaOH			
Nr.	M	%	g	g	g	g	-	-
R1	8	100	800	310	310	620	1,0	0,78
R2	8	100	800	372	248	620	1,5	0,78
R3	8	100	800	414	206	620	2,0	0,78
R4	8	100	800	443	177	620	2,5	0,78
R5	10	100	800	310	310	620	1,0	0,78
R6	10	100	800	372	248	620	1,5	0,78
R7	10	100	800	414	206	620	2,0	0,78
R8	10	100	800	443	177	620	2,5	0,78
R21	6	100	800	414	206	620	2,0	0,78

Geopolymer pastes were made by substituting 10, 25 and 50% fly ash with industrial waste, such as marble dust and blast furnace slag.

Table 5.5. Mixtures of eco-friendly binder with substitution of fly ash with marble dust

Mixture	NaOH	Fly ash (F.A.)		Marble dust (M.D.)		F.A. + M.D.	Alkaline activator solution Na_2SiO_3+ NaOH(8M)		Total alkaline activator solution	Ratio Na_2SiO_3/ NaOH	Alkaline activator solution /(F.A. +M.D.)
-		%	g	%	g	g	g	g	g	-	g
HEAT TREATMENT (70°C, 24h)											
R9	8	90	720	10	80	800	443	177	620	2,5	0,78
R10	8	75	600	25	200	800	443	177	620	2,5	0,78
R11	8	50	400	50	400	800	443	177	620	2,5	0,78
R12	8	90	720	10	80	800	414	206	620	2	0,78
R13	8	75	600	25	200	800	414	206	620	2	0,78
R14	8	50	400	50	400	800	414	206	620	2	0,78
R15	8	90	720	10	80	800	372	248	620	1,5	0,78
R16	8	75	600	25	200	800	372	248	620	1,5	0,78
R17	8	50	400	50	400	800	372	248	620	1,5	0,78
R18	8	90	720	10	80	800	310	310	620	1	0,78
R19	8	75	600	25	200	800	310	310	620	1	0,78
R20	8	50	400	50	400	800	310	310	620	1	0,78
WITHOUT HEAT TREATMENT (23÷2°C)											
R53 FTT	8	90	720	10	80	800	443	177	620	2,5	0,78
R54 FTT	8	75	600	25	200	800	443	177	620	2,5	0,78
R55 FTT	8	50	400	50	400	800	443	177	620	2,5	0,78

Table 5.6. Mixtures of eco-friendly binder with substitution of fly ash with blast furnace slag

Mixture	NaOH	Fly ash (F.A.)		Blast furnace slag (B.F.S.)		F.A+B.F.S.	Alkaline activator solution Na_2SiO_3+ NaOH(8M)		Total alkaline activator solution	Na_2SiO_3/ NaOH	AA /(F.A.+B.F.S.)
-	M	%	g	%	g	g	g	g	g	-	g
HEAT TREATMENT (70°C, 24h)											
R34	8	90	720	10	80	800	443	177	620	2,5	0,78
R35	8	75	600	25	200	800	443	177	620	2,5	0,78
R36	8	50	400	50	400	800	443	177	620	2,5	0,78

Table 5.6. Mixtures of eco-friendly binder with substitution of fly ash with blast furnace slag (continuation)

WITHOUT HEAT TREATMENT (23÷2°C)											
R34FTT	8	90	720	10	80	800	443	177	620	2,5	0,78
R35FTT	8	75	600	25	200	800	443	177	620	2,5	0,78
R36FTT	8	50	400	50	400	800	443	177	620	2,5	0,78

Table 5.14. Mixtures of eco-friendly binder with substitution of fly ash with marble dust and perlite

Mixture	F.A.		P.		M.D.		Na_2SiO_3/ NaOH	AA/(F.A.+P.+M.D.)
Nr.	%	g	%	g	%	g	-	g
R4	100	800	0	0	0	0	2,5	0,78
R1P	95	760	5	40	0	0		
R2P	90	720	5	40	5	40		
R3P	50	400	25	200	25	200		

Eco-friendly binders were also made with different additions, such as Fe_2O_3, SiO_2, $Ca(OH)_2$, MgO, perlite or aluminum slag in different percentages. They were made using a sodium hydroxide solution with a concentration of 6M and a Na2SiO3/NaOH=2 ratio, being made with a heat treatment (70°C, 24h), and some of them were made at an ambient temperature of 23°C

Table 5.7. Eco-friendly binder with different additions and percentage

Mixture	Solution NaOH	Na_2SiO_3/NaOH	FA	Fe_2O_3	SiO_2	MgO	$Ca(OH)_2$	Al slag	Perlite	70°C, 24H	23±2°C
Nr.	M	-	%	%	%	%	%	%	%	-	-
R21	6	2	100	0	-	-	-	-	-	X	-
R22	6	2	100	1	-	-	-	-	-	X	-
R23	6	2	100	5	-	-	-	-	-	X	-
R24	6	2	100	10	-	-	-	-	-	X	-
R25	6	2	100	1	-	-	-	1	-	X	-
R26	6	2	100	1	-	-	-	5	-	X	-
R27	6	2	100	1	-	-	-	10	-	X	-
R28	6	2	100	1	-	-	-	-	1	X	-
R29	6	2	100	-	34	-	-	-	-	X	-
R30	6	2	100	1	34	-	-	-	-	X	-
R31	6	2	100	10	34	-	-	-	-	X	-
R32	6	2	100	10	34	-	-	-	-	X	-
R37	6	2	100	0,4	24,3	3,4	-	-	-	X	-
R38	6	2	100	2,3	24,3	20,2	-	-	-	X	-
R39	6	2	100	-	-	-	-	-	-	X	-
R40	6	2	100	1,1	24,3	10,1	-	-	-	X	-
R41	6	2	100	-	24,3	-	5	-	-	X	X
R42	6	2	100	-	24,3	-	5	-	-	X	X
R43	6	2	100	-	24,3	-	10	-	-	X	X
R44	6	2	100	-	24,3	-	20	-	-	X	X
R45	6	2	100	-	24,3	-	6,2	-	-	X	X
R46	6	2	100	0,4	24,3	3,4	5	-	-	X	X
R47	6	2	100	0,4	24,3	3,4	10	-	-	X	X
R48	6	2	100	0,4	24,3	3,4	20	-	-	X	X
R49	6	2	100	-	24,3	-	7,5	-	-	X	X
R50	6	2	100	-	24,3	-	8,7	-	-	X	X
R51	6	2	100	-	24,3	-	11,2	-	-	X	X
R52	6	2	100	-	24,3	-	12,5	-	-	X	X

The fly ash and additions/substitution used in the laboratory were conditioned for a minimum of 24 hours at a temperature of 23±2°C. The ash and substitutes/additives, as well as the alkaline activator solutions were weighed in the desired ratio.

Mixing of ash and used additions/substitution took place for ca. 60 s for complete homogenization, with the help of a paddle mixer, used to make mortars in test laboratories.

After mixing the solid raw materials, the alkaline activator solution was gradually poured in at interval of 70s at a low speed at the beginning. A too sudden pouring of the alkaline activator can lead to the effect of flesh setting (rapid – sudden hardening of the geopolymer paste). The mixing of the alkaline activators with the solid raw materials was done for approx. 2.5-3 min.

Fresh density was determined using containers of known volume and an analytical balance.

The casting of the samples was done in prismatic molds, after they had previously been treated with decofrol. The patterns with the prismatic specimens with dimensions of 40x40x160 mm were subjected to a thermal treatment of 70°C for 24 hours, with the help of a temperature-adjustable laboratory oven, or were left in the conditioning room at a temperature of (23±2°C), in the case those made without heat treatment.

After performing the heat treatment and stripping the prismatic samples, their density was obtained by determining the dimensions and weighing with the help of the analytical balance.

The samples were conditioned for 6 days in laboratory conditions (t=23±2, U.R.A.=50%), after which the density was determined at the age of 7 days and physical-mechanical determinations were performed. Flexural tensile strength and compressive strength, the most used tests according to the specialized literature, as well as total water absorption and open porosity for some of them, were also obtained.

5.5. Discussions

5.5.1. Determination of bulk density

5.5.1.1. Eco-friendly binder based on fly ash

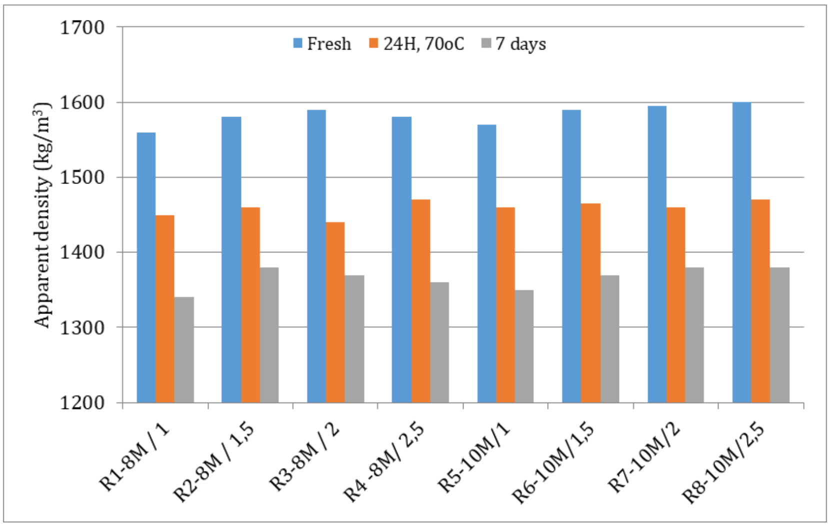

Fig. 5.22. Apparent density of eco-friendly binder with different molarities and ratios Na_2SiO_3/NaOH

5.5.1.2. Eco-friendly binder made by substituting fly ash at 10%, 25% and 50% with marble dust

❖ **Heat treatment**

Table 5.8. Fresh density of eco-friendly binder with marble dust substitution

Raw materials	Molarity	Ratio $Na_2SiO_3/NaOH$			
	8M	2.5	2	1.5	1
	Mixture	Fresh density			
%	Nr.	kg/m^3	kg/m^3	kg/m^3	kg/m^3
F.A. 100%	R4/R3/R2/R1	1580	1590	1580	1560
F.A. 90% + 10% M.D.	R9/R12/R15/R18	1680	1680	1670	1640
F.A. 75% + 25% M.D.	R10/R13/R16/R19	1710	1720	1720	1650
F.A. 50% + 50% M.D	R11/R14/R17/R20	1750	1800	1670	1750

Table 5.9. Apparent density of eco-friendly binder with marble dust substitution after heat treatment

Raw materials	Mixture	$\rho_{24h,\,70^oC}$			
%	Nr.	kg/m^3	kg/m^3	kg/m^3	kg/m^3
F.A. 100%	R4/R3/R2/R1	1470	1440	1460	1450
F.A. 90% + 10% M.D.	R9/R12/R15/R18	1570	1570	1630	1560
F.A. 75% + 25% M.D.	R10/R13/R16/R19	1620	1600	1640	1640
F.A. 50% + 50% M.D	R11/R14/R17/R20	1740	1740	1750	1670

Table 5.10. Apparent density of eco-friendly binder with marble dust substitution at 7 days

Raw materials	Mixture	$\rho_{7\ day}$			
%	Nr.	kg/m^3	kg/m^3	kg/m^3	kg/m^3
F.A. 100%	R4/R3/R2/R1	1360	1370	1380	1340
F.A. 90% + 10% M.D.	R9/R12/R15/R18	1550	1510	1530	1520
F.A. 75% + 25% M.D.	R10/R13/R16/R19	1580	1550	1570	1580
F.A. 50% + 50% M.D	R11/R14/R17/R20	1670	1680	1670	1650

❖ **Without heat treatment**

Table 5.11. Apparent density of eco-friendly binder with marble dust substitution without heat treatment

Raw materials	Mixture	Fresh	7 days	14 days	28 days
%	Nr.	kg/m^3	kg/m^3	kg/m^3	kg/m^3
F.A. 90% + 10% M.D.	R53FTT	1680	1620	1560	1550
F.A. 75% + 25% M.D..	R54FTT	1710	1700	1650	1580
F.A. 50% + 50% M.D.	R55FTT	1750	1740	1720	1650

5.5.1.3. Eco-friendly binder made by substituting fly ash at 10%, 25% and 50% with blast furnace slag

Table 5.12. Apparent density of the eco-friendly binder with blast furnace slag substitution

Molaritate 8M și raport Raport $Na_2SiO_3/NaOH$=2,5				
HEAT TREATMENT (70°C, 24h)				
Raw materials	Mixture	Fresh	24H, 70°C	7days
%	Nr.	kg/m^3	kg/m^3	kg/m^3
F.A. 100%	R4	1580	1470	1360
F.A. 90% + 10% B.F.S.	R34	1620	1550	1460
F.A. 75% + 25% B.F.S.	R35	1650	1570	1520
F.A. 50% + 50% B.F.S.	R36	1730	1710	1630

Table 5.12. Apparent density of the eco-friendly binder with blast furnace slag substitution (continuation)

Molaritate 8M și raport Raport $Na_2SiO_3/NaOH$=2,5					
WITHOUT HEAT TREATMENT (22°C)					
Raw materials	Mixture	ρ_{fresh}	ρ_{7days}	ρ_{14days}	ρ_{28days}
%	Nr.	kg/m³	kg/m³	kg/m³	kg/m³
F.A. 90% + 10% B.F.S.	R34FTT	1620	1615	1610	1610
F.A. 75% + 25% B.F.S.	R35FTT	1650	1640	1630	1620
F.A. 50% + 50% B.F.S.	R36FTT	1730	1700	1680	1630

5.5.1.4. Eco-friendly binder made by substituting fly ash with marble dust and perlite

Table 5.15. Apparent density mixture R1P, R2P and R3P

Mixture	F.A.	Perlite	M.D.	ρ_{fresh}	$\rho_{70oC, 24h}$	ρ_{7days}
Nr.	%	%	%	kg/m³	kg/m³	kg/m³
R4	100	0	0	1580	1470	1360
R1P	95	5	0	1480	1410	1330
R2P	90	5	5	1580	1440	1360
R3P	50	25	25	1680	1540	1500

5.5.1.5. Eco-friendly binder made with different additions and percentages to fly ash

❖ ***Iron trioxide (Fe_2O_3) addition***

Table 5.18. Apparent density mixture R21, R22, R23 and R24

Mixture	F.A.	Fe_2O_3	$Na_2SiO_3/NaOH$	ρ_{fresh}	$\rho_{24h,70oC}$	ρ_{7days}
Nr.	%	%	-	kg/m³	kg/m³	kg/m³
R21	100	0	2	1580	1380	1290
R22	100	1		1620	1390	1330
R23	100	5		1640	1450	1350
R24	100	10		1670	1510	1380

❖ ***Iron trioxide (Fe_2O_3) and aluminium slag additions***

Table 5.20. Apparent density mixture R25, R26 and R27

Mixture	F.A.	Fe_2O_3	Zgură Al	$Na_2SiO_3/NaOH$	ρ_{fresh}	$\rho_{24h,70oC}$	ρ_{7days}
Nr.	%	%	%	-	kg/m³	kg/m³	kg/m³
R25	100	1	1	2	1610	1370	1260
R26	100	1	5		1580	1110	1050
R27	100	1	10		1590	930	880

❖ ***Iron trioxide (Fe_2O_3) and perlite additions***

Table 5.22. Apparent density mixture R28

Mixture	F.A.	Fe_2O_3	Perlit	$Na_2SiO_3/NaOH$	ρ_{fresh}	$\rho_{24h, 70^oC}$	$\rho_{7 days}$
Nr.	%	%	%	-	kg/m³	kg/m³	kg/m³
R28	100	1	1	2	1640	1120	1030

❖ ***SiO_2 and iron trioxide (Fe_2O_3) additions***

Table 5.24. Apparent density mixture R29, R30 and R31

Mixture	F.A.	Fe_2O_3	SiO_2	$Na_2SiO_3/NaOH$	ρ_{fresh}	$\rho_{24h, 70oC}$	$\rho_{7 days}$	$\rho_{14 days}$	$\rho_{28 days}$
Nr.	%	%	%	-	kg/m³	kg/m³	kg/m³	kg/m³	kg/m³
R29	100	0	34	2	1540	1490	1370	1300	1260
R30	100	1	34		1580	1460	1400	1350	1300
R31	100	10	34		1570	1530	1440	1420	1410

❖ ***Iron trioxide (Fe_2O_3), SiO_2, MgO și $Ca(OH)_2$ additions***

Table 5.26. Apparent density of the eco-friendly binder with Fe_2O_3, SiO_2, MgO and $Ca(OH)_2$ additions

Mixture	F.A.	Fe_2O_3	SiO_2	MgO	$Ca(OH)_2$	ρ_{fresh}	$\rho_{24h, 70oC}$	$\rho_{7\ days}$	$\rho_{14\ days}$
Nr.	%	%	%	%	%	Kg/m³	Kg/m³	Kg/m³	Kg/m³
HEAT TREATMENT (70°C, 24h)									
R37	100	0,37	24,34	3,37	0	1620	1530	1400	1290
R45	100	0,37	24,34	3,37	5	1670	1580	1540	1500
R46	100	0,37	24,34	3,37	10	1520	1490	1400	1340
R47	100	0,37	24,34	3,37	20	1510	1500	1360	1330
WITHOUT HEAT TREATMENT (22°C)									
R45FTT	100	0,37	24,34	3,37	5	1670	-	1600	-
R46FTT	100	0,37	24,34	3,37	10	1520	-	1570	-
R47FTT	100	0,37	24,34	3,37	20	1510	-	1550	-

❖ ***SiO_2 and $Ca(OH)_2$ additions***

Table 5.28. Apparent density of the eco-friendly binder with SiO_2 and $Ca(OH)_2$ additions

Mixture	F.A.	SiO_2	$Ca(OH)_2$	ρ_{fresh}	$\rho_{24h, 70oC}$	$\rho_{7\ days}$	$\rho_{14\ days}$	$\rho_{28\ days}$
Nr.	%	%	%	Kg/m³	Kg/m³	Kg/m³	Kg/m³	Kg/m³
HEAT TREATMENT (70°C, 24h)								
R42	100	24,3	5,0	1650	1580	1500	1460	1440
R48	100	24,3	6,2	1590	1580	1560	1520	1500
R49	100	24,3	7,5	1590	1550	1540	1530	1490
R50	100	24,3	8,7	1600	1530	1500	1460	1450
R43	100	24,3	10,0	1570	1540	1510	1480	1460
R51	100	24,3	11,2	1480	1460	1450	1420	1410
R52	100	24,3	12,5	1400	1490	1300	1280	1230
R44	100	24,3	20,0	1510	1510	1510	1450	1480

Table 5.28. Apparent density of the eco-friendly binder with SiO_2 and $Ca(OH)_2$ additions (continuation)

Mixture	F.A.	SiO_2	$Ca(OH)_2$	ρ_{fresh}	$\rho_{24h, 70oC}$	$\rho_{7\ days}$	$\rho_{14\ days}$	$\rho_{28\ days}$
Nr.	%	%	%	Kg/m³	Kg/m³	Kg/m³	Kg/m³	Kg/m³
WITHOUT HEAT TREATMENT (22°C)								
R42 FTT	100	24,3	5,0	1650	-	-	1600	-
R48 FTT	100	24,3	6,2	1590	-	-	1580	-
R49 FTT	100	24,3	7,5	1590	-	-	1570	-
R50 FTT	100	24,3	8,7	1600	-	-	1500	-
R43 FTT	100	24,3	10,0	1570	-	-	1470	-
R51 FTT	100	24,3	11,2	1480	-	-	1370	-
R52 FTT	100	24,3	12,5	1400	-	-	1310	-
R44 FTT	100	24,3	20,0	1510	-	-	1300	-

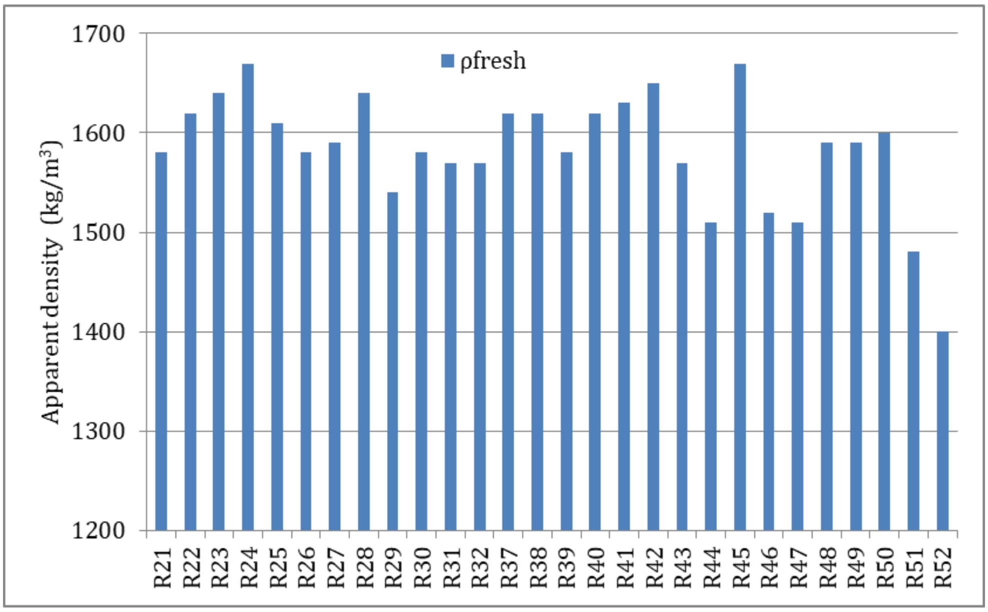

Fig. 5.39. Fresh densities of alkaline activated eco-friendly binders with different additions

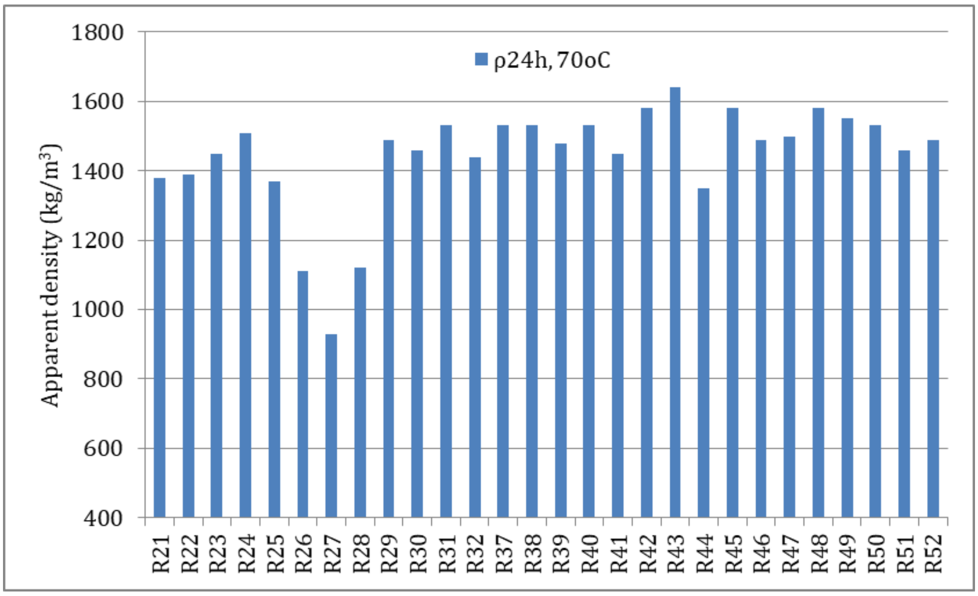

Fig. 5.40. Apparent densities of alkaline activated eco-friendly binders with different additions after heat treatment

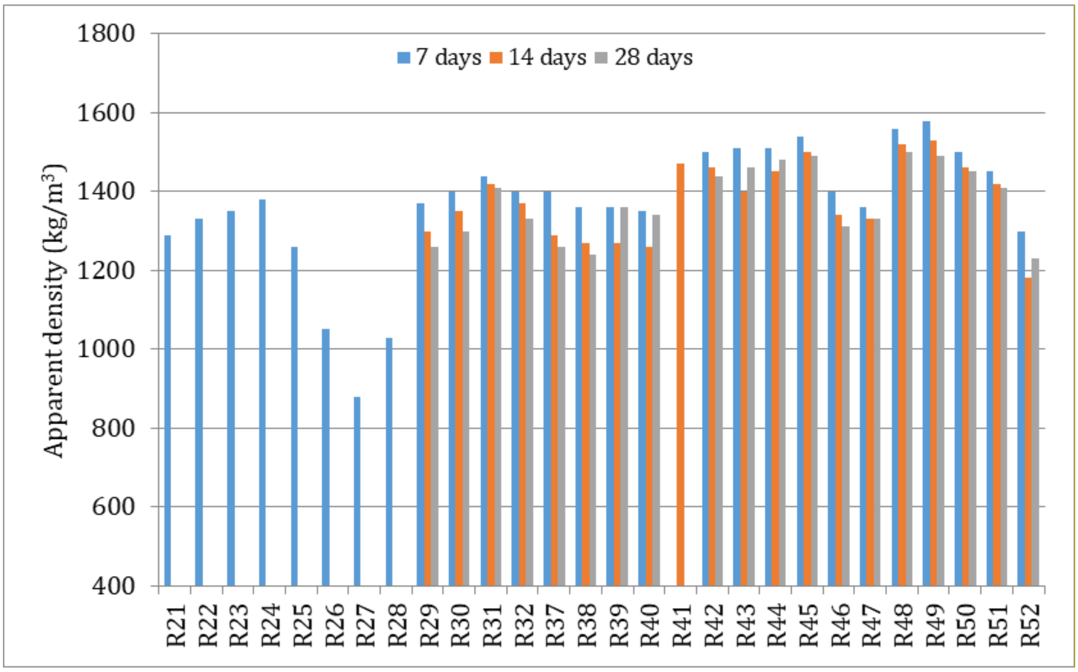

Fig. 5.41. Apparent densities of alkaline activated eco-friendly binders with different additions and test ages

5.5.2. Bending tensile strength

5.5.2.1. Eco-friendly binder based on fly ash

The flexural tensile strength for the geopolymer paste made with an 8M NaOH solution varied between 2.49 N/mm^2 for mixture R2 and 3.45 N/mm^2 for mixture R4. It is observed that the flexural tensile strengths increased linearly with increasing alkaline activator ratio from 1.5 to 2.5. The exception was mixture R1, which had a higher resistance than mixture R2 and R3, although it had the lowest alkaline activator ratio, $Na_2SiO^3/NaOH=1$. For those made with a 10M NaOH solution, the bending tensile strength varied between 2.57 N/mm^2 for mixture R6 and 3.65 N/mm^2 for mixture R7. Better values were obtained for fly ash based binders with a higher molar concentration of NaOH solution.

5.5.2.2. Eco-friendly binder made by substituting fly ash at 10%, 25% and 50% with marble dust

❖ **Heat treatment**

In relation to the composition considered as a control, R4, it is observed that, by substituting a part of the fly ash with marble dust, respectively the compositions R9, R10, R11, the flexural tensile strength decreases, as the percentage of substituted ash increases, except making the composition with 25% substitution, which is equal to the blank. Thus, there were decreases of 4.1% for a 10% substitution of fly ash with marble dust, respectively with 21.4% for a 50% substitution of fly ash with marble dust.

In relation to the composition considered as control, R3, it is observed that, by substituting part of the fly ash with marble dust, respectively the compositions R12, R13, R14, the flexural tensile strengths decrease as the percentage of substituted ash increases, with the exception of the composition with a substitution of 25%, which had a smaller decrease, namely 1.3%. Thus, there were decreases of 4.1% for a 10% substitution of fly ash with marble dust, respectively with 34.4% for a 50% substitution of fly ash with marble dust.

In relation to the composition considered as control, R2, it is observed that, by substituting part of the fly ash with marble dust, respectively the compositions R15, R16, R17, the flexural tensile strengths decrease as the percentage of substituted ash increases, with the exception of the composition with a 10% substitution, which had an increase of 3.2%. Thus, there were decreases of 1.6% for a 25% substitution of fly ash with marble dust, respectively with 17.7% for a 50% substitution of fly ash with marble dust.

In relation to the composition considered as a control, R1, it is observed that, by substituting a part of the fly ash with marble dust, respectively the compositions R18, R19, R20, the flexural tensile strengths decrease as the percentage of substituted ash increases. Thus, there were decreases of 13.8% for a 10% substitution of fly ash with marble dust, respectively with 25.4% and 41.9% for a 25% and 50% substitution of fly ash with marble dust.

- **Without heat treatment**

It was observed that the strengths at 7 and 28 days of age increased with increasing percentage of marble dust. At the age of 14 days, the tensile strength for the sample graded R55FTT, although it had the highest percentage of marbling (50%), was lower compared to the other samples. It was also observed that the strengths increased with increasing test age from 7 to 28 days, except for the sample graded with R55FTT, having a marble dust percentage of 50%, which had a lower value at the age of 14 days. It is possible that this low strength is caused by the alkaline activator not reacting completely with the fly ash and marble dust, or the mixing time of the geopolymer paste is not sufficient, and the specimens made are not homogeneous.

Comparing eco-friendly binders made with heat treatment with those without heat treatment (TTvsFTT), it was observed that the flexural tensile strengths at the age of 7 days were higher for those with heat treatment, in the case of 10 percent marble dust substitution % and 25%. Tensile strengths decreased by 24.7% and 12.2%. The geopolymer paste rated R55FTT with 50% substitution of marble dust, without heat treatment, had higher flexural tensile strength than that made with heat treatment and rated R11, but also compared to the control sample R4. The geopolymer paste rated R53FTT had an increase of 19.9% compared to that rated R11, having the same 50% marble dust substitution.

5.5.2.1. Eco-friendly binder made by substituting fly ash at 10%, 25% and 50% with blast furnace slag

Comparing the results obtained for the same preparation mixtures, in the case of replacing fly ash (F.A.) with blast furnace slag (B.F.S.), with and without heat treatment (TT vs. FTT), it is observed that the lack of heat treatment determined a reduction in resistance to stretch at the age of 7 days, of 29%, for the sample with a substitution of 25%, but also increases of 13% and 85% depending on the amount of substituted fly ash (10% and 25%). Also, the same is observed in the case of replacing fly ash (F.A.) with marble dust (M.D.), the decrease in tensile strength being between 18% and 33%.

5.5.2.5. Eco-friendly binder made with different additions and percentages to fly ash

- ***Iron trioxide (Fe_2O_3) addition***

Compared to the sample considered as a control (R21), increases were recorded by 7.2% for a 1% addition of iron trioxide to fly ash, by 30.7%, respectively by 33.7% for the cases of 5% addition of iron trioxide , respectively 10% for fly ash.

❖ ***Iron trioxide (Fe_2O_3), SiO_2, MgO și $Ca(OH)_2$ additions***

At geopolymer pastes based on Fe_2O_3, SiO_2, MgO and $Ca(OH)_2$ made with heat treatment, the flexural tensile strengths decrease with increasing $Ca(OH)_2$ addition.

Compared to samples made with heat treatment, although the geopolymer pastes made without heat treatment were cracked due to shrinkage, they had higher tensile strengths at the age of 7 days for those with 10% and 20% addition $Ca(OH)_2$.

❖ ***SiO_2 and $Ca(OH)_2$ additions***

Compared to the control sample, R22, the flexural tensile strengths at the age of 7 days increased for the geopolymer pastes R43, R48 and R50. For the other geopolymer pastes, the flexural strengths decreased. It was observed that for some geopolymer pastes made with heat treatment R49 and R51 the strengths increased with increasing test age from 7 to 28 days. For the other pastes, the strengths fluctuated, due to their inhomogeneity and possibly their partial geopolymerization.

Comparing untreated and heat-treated samples, the tensile strengths for R52FTT and R44FTT samples were significantly higher.

Conclusions

The highest bending resistance, 4.7 N/mm^2, was obtained for the ecological binder denoted by R50 made with the addition of SiO_2 (24.3%) and $Ca(OH)_2$ (8.7%). This binder had an increase of 2,3 N/mm^2, comparing with the blank denoted by R21 made only on the basis of flying ash and a molarity of 6M, which had a tensile strength of 2,4 N/mm^2. The lowest bending resistance for eco-friendly binders made with different additions was 1.8 N/mm^2 and was obtained for the geopolymer paste denoted R52 with the addition of SiO_2 (24.3%) and $Ca(OH)_2$ (12.5%).

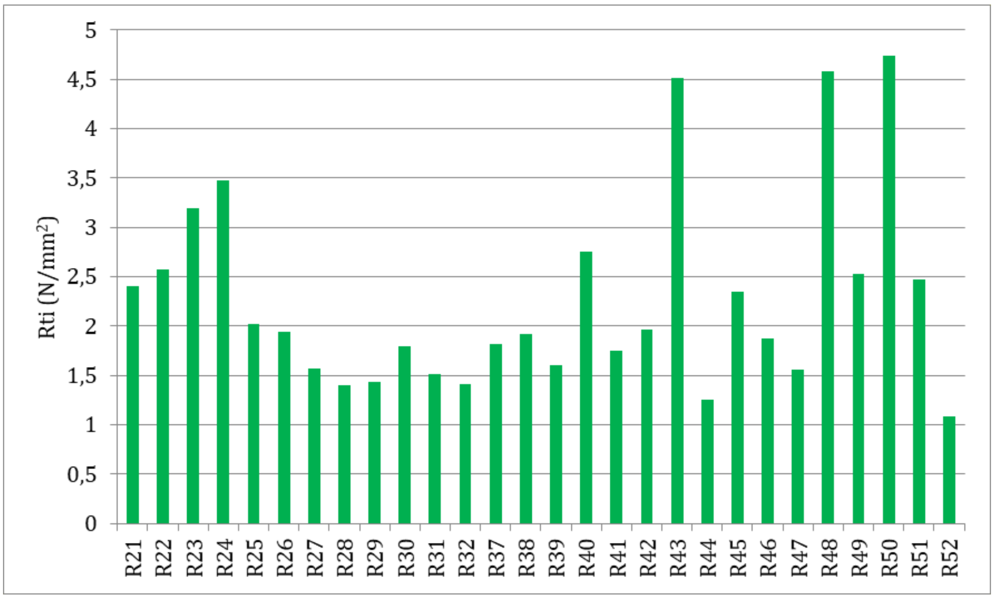

Fig. 5.52. Eco-friendly binders made with heat treatment, with different additions, 7 days age

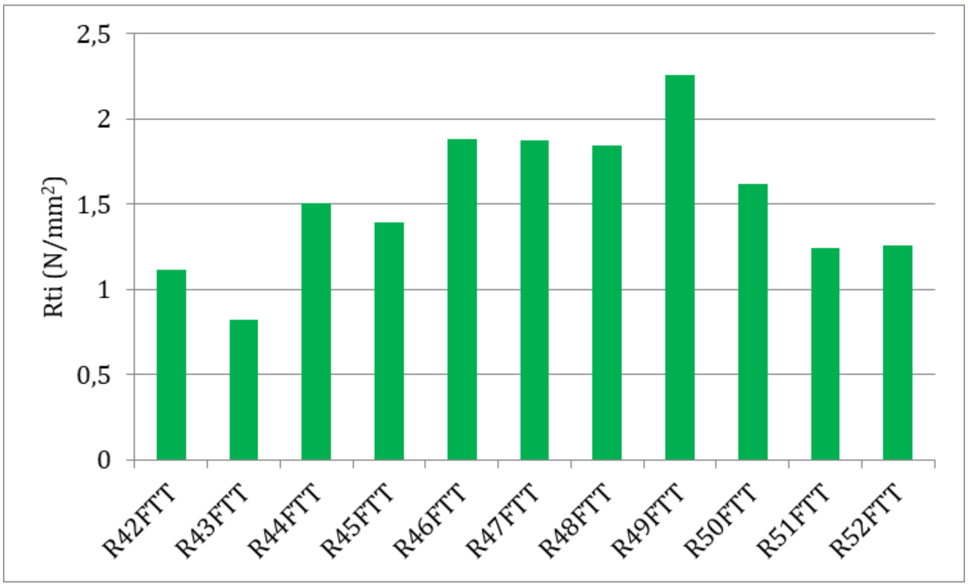

Fig. 5.53. Eco-friendly binders made with heat treatment, with different additions

Environmentally friendly binders made without heat treatment were tested at 14 days, as they were not totally hardened, and the demoulding was done only after 7 days. As for geopolymer pastes made with different additives, without heat treatment, the tensile strength by bending, at 14 days, the highest value Rti = 2.6 N/mm^2 was obtained for the R49FTT mixture. The R49TT mixture had an addition of SiO_2 (24.3%) and $Ca(OH)_2$ (7.5%). The lowest bending resistance, for geopolymer pastes made with different additives, was 0.8 N/mm2 and was obtained for the R52FTT denoted geopolymer paste with the addition of SiO2 (24.3%) and Ca(OH)2 (10.0%).

5.5.3. Compressive strength

The compressive strengths were made on 40x40mm square samples, obtained after bending tensile tests.

The compressive strength of six cubes for each recipe was determined and the values obtained were averaged.

5.5.3.1. Eco-friendly binder based on fly ash

Compressive strengths increased with the increase in the Na_2SiO_3/NaOH ratio from 1 to 2.5. This is also stated in the literature studied, namely that the strength of a paste or a geopolymer concrete increases with the increase of the Na_2SiO_3/NaOH ratio. Compressive strength had an increase of 8.62 N/mm^2 over the R1 mixture. Compressive strengths progressively increased by about 3 N/mm^2 with the increase in the Na_2SiO_3/NaOH ratio.

The highest compressive strength, for geopolymer pastes made with a NaOH-10M concentration, was 34.54 N/mm^2 for the R8 mixture with a ratio Na_2SiO_3/NaOH=2.5. The lowest resistance was 26.29 N/mm^2 for the R5 mixture with a ratio Na_2SiO_3/NaOH=1. The increase in compression resistances of 10M geopolymer pastes was linear, with an increase of about 3 N/mm^2 for an increase in the ratio Na_2SiO_3/NaOH=0,5.

5.5.3.2. Eco-friendly binder made by substituting fly ash at 10%, 25% and 50% with marble dust

❖ **Heat treatment**

The compressive strengths of geopolymer pastes with substitution of marble dust were compared with the blank, without substitution, for each Na_2SiO_3/NaOH ratio.

As can be seen in Table 5.45. and Fig. 5.54. in relation to the control composition, R4, by substituting part of the flying ash with marble dust, the compositions R9, R10, R11, the compressive strength at 7 days decreases as the percentage of substituted ash increases. Thus, there were decreases of 11.3% for a 10% substitution of flying ash with marble dust, by 17.2%, respectively by 53.8% for the cases of substitution by 25% and 50% respectively of the flying ash with marble dust.

The decrease in compressive strength occurs due to a decrease in the content of silicon and aluminum oxides, the geopolymer bonds between marble dust particles and alkaline activators are weaker. Also, by migrating the marble dust to the bottom of the metal pattern, by heat treatment, a two-component test tube made of flying ash at the top was formed, respectively marble dust at the bottom. The eco-friendly binder were uneven, inhomogeneous, with more marble dust at the bottom and more ash at the top.

In relation to the control composition, R3, by substituting part of the flying ash with marble dust, compositions R12, R13, R14, compressive strength at the age of 7 days decreases as the percentage of substituted ash increases. Thus, there were decreases of 7.1% for a 10% substitution of flying ash with marble dust, by 13.2%, respectively by 55.5% for the cases of 25% and 50% substitution of flying ash with marble dust, respectively.

Compared to the blank sample and denoted by R2, by substituting part of the flying ash with marble dust, mixtures R15, R16, R17, the compressive strength at the 7 days age, decreases as the percentage of substituted ash increases. Thus, there were decreases of 9% for a 10% substitution of flying ash with marble dust, by 21.7%, respectively by 54.2% for the cases of substitution by 25% and 50% of the flying ash with marble dust, respectively.

Comparing with the control composition R1, by substituting part of the flying ash with marble dust, i.e. compositions R18, R19, R20, the compressive strength at the age of 7 days decreases as the percentage of substituted ash increases. Thus, there were decreases of 7.5% for a 10% substitution of flying ash with marble dust, by 14.8%, respectively by 36.9% for the cases of substitution by 25% and 50% of the flying ash with marble dust, respectively.

❖ **Without heat treatment**

Compressive strengths decreased with the increase in the percentage of marble.

At 28 days age, the highest compressive strength was obtained for the mixture R54FTT with a substitution of 25% marble dust. Compared to the samples made with heat treatment, those made without heat treatment, the compressive resistances at 7 days age are lower. Thus there were decreases of 18.8%, 32.8% and 28% for cases of substitution with marble dust in percentages of 10%, 25% and 50%.

5.5.3.5. Eco-friendly binder made with different additions and percentages to fly ash

❖ ***Iron trioxide (Fe_2O_3) addition***

Following the determinations carried out, it is observed that the compressive strengths at 7 days age increased with the introduction of iron trioxide. Thus, there were increases of

21.7% for a 1% addition of iron trioxide to flying ash, by 15.3%, respectively by 14.8% for cases of iron trioxide addition 5% and 10% to flying ash, respectively.

The results obtained in this study are correlated with those obtained by Zailani et al. (2020) [84] and Kaya et al. (2022) [222], but contrary to those of his Xiong (2012) [223].

❖ ***Iron trioxide (Fe_2O_3), SiO_2, MgO și $Ca(OH)_2$ additions***

It can be seen from Table 5.53. that for R45 samples at 7 days age, 93.3% of the compressive strength was reached at 28 days. This fact shows that heat treatment is beneficial to the geopolymerization reaction, results also obtained in the specialized literature. On the other hand, it can be noted that, as the addition of Ca(OH)2 increases, in order to obtain a satisfactory workability of the compositions it was necessary to increase the amount of alkaline liquid, which led to the achievement of lower mechanical resistances. Moreover, it can be noted that the mechanical resistances of the geopolymer paste have decreased with the increase in the test age. Also, and Temuujin et al. (2009) [65] achieved lower resistances by substituting flying ash with calcium compounds (CaO și $Ca(OH)_2$) for geopolymers made with a heat treatment of 70^oC, but the resistances for those made without heat treatment have increased (20^oC).

Compressive strengths in geopolymer pastes without heat treatment increased at 14 days age, compared to those at 7 days.

Compared to the samples made with heat treatment, although the geopolymer pastes made without heat treatment were cracked due to the contraction, they had higher compressive strengths at 14 days, for the samples with the addition of 10% și 20% $Ca(OH)_2$. The highest resistance of geopolymer pasts at 7 days was obtained for the mixture R47FTT. It can be said that geopolymer pastes with an addition of 20% $Ca(OH)_2$, made without heat treatment, have higher resistances compared to those with heat treatment.

In the first 28 days, it was observed that gopolymer paste with an addition of 1% Fe_2O_3 has the best compressive strength compared to other ecological binders. After 28 days, the resistance of the blank sample doubled at 95 days and was higher than that of geopolymer pastes with the addition of iron trioxide in a proportion of 1% and 10%. It was observed that the addition of MgO to the geopolymer paste did not reduce contraction and cracked in those without heat treatment. The results obtained are not in line with those obtained by Zhaoheng et al. (2019) [83], which have evenly dispersed MgO powders in the geopolymer to compensate for the uniform shrinkage of geopolymer pastes. The results obtained by them indicate that the contraction decreases with the addition of MgO. The addition of MgO may be reduced by the amount of $Ca(OH)_2$.

❖ ***SiO_2 and $Ca(OH)_2$ additions***

Compared to the R22 blank, the compressive compressive strengths of heat-treated pastes at the age of 7 days decreased. The highest strength of 20,53 N/mm^2 was obtained for the geopolymer paste denoted by R50 and the lowest for the R52 paste, 1,55 N/mm^2.

Samples made without heat treatment were tested at the ages of 14 and 28 days, since at the age of 7 days they were not completely hardened. The highest compressive strength of the samples made without heat treatment at the age of 14 days was obtained for the geopolymer paste denoted by R44FTT.

Analyzing the results obtained (TT vs FTT) at the age of 14 days, compression resistances were higher only for R48, R49, R50 and R51 samples. At the age of 28 days only the compressive strength of the binder denoted by R51 was higher than that achieved without heat treatment, the others being lower.

Conclusions – eco-friendly binders with different additions

The compressive resistances of alkaline-activated geopolymer pastes, made with heat treatment (24H, 70°C), with different additions were determined at different ages, namely 7, 14 and 28 days. The highest compressive strength at the age of 7 days was obtained for the binder denoted by R22 (22,1 N/mm^2), which was achieved with an addition of 1 %Fe_2O_3 and was higher than the control sample denoted by R21 (18,2 N/mm^2).

It is noticed that the compressive strengths at the age of 7 days increased with the introduction of iron trioxide. Thus, there were increases of 21.7% for a 1% addition of iron trioxide to flying ash (R22), by 15.3% and by 14.8% for cases of addition of iron trioxide 5% (R23) and 10% (R24) to flying ash. Also, with the introduction of the addition of aluminum slag, the compressive strengths decrease. Thus, there were decreases of 7% for an addition of 1% of aluminium slag to flying ash and iron trioxide (R25), by 58.5% and 79.5% respectively for cases of addition of aluminium slag 5% (R26) and 10% (R27) to flying ash and iron trioxide respectively.

The compression resistances of geopolymer pastes with the addition of SiO_2 and $Ca(OH)_2$ have demonstrated that those made without heat treatment at an ambient temperature have a better compressive strength than those made with a heat treatment of 70°C. The compressive strength of the geopolymer paste denoted by R44, at the age of 14 days, was 6.61 N/mm^2 in the case of heat treatment, and for the one without heat treatment it was 15.99N/mm2, so that at the age of 28 days it increased from 9.11 N/mm^2 to 20.3 N/mm^2. The results obtained from the research are correlated with the results of other researchers, according to the specialized literature.

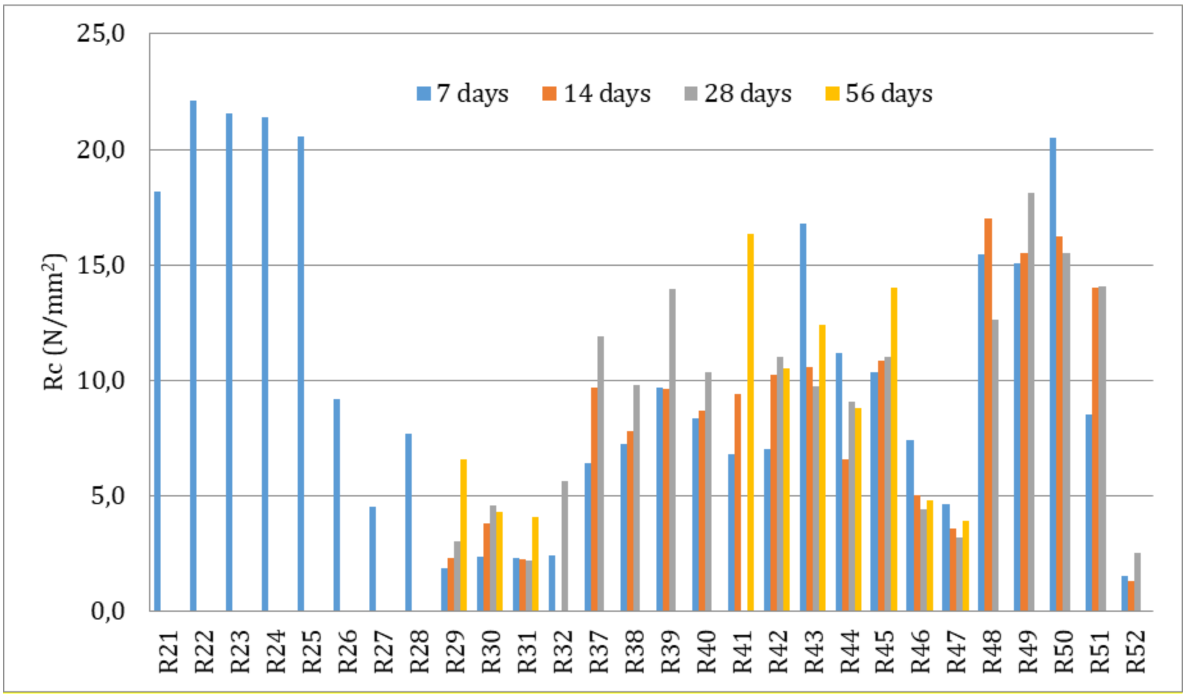

Fig. 5.61. Compressive strengths of eco-friendly binders with different additions made with heat treatment

Analyzing compared to other specialized reports the results obtained, it can be said that the oxide composition and the structural, crystallographic, mineralogical characterizations of the raw materials used, influence the performance of the obtained geopolymer material. Therefore, this research contributes through its degree of novelty to the current level of knowledge.

5.5.6. Microscopic analysis of fly ash-substituted geopolymer pastes made with/without heat treatment

Comparing the geopolymer binder denoted R4, made with a NaOH-8M solution, with the binder denoted R8, made with a NaOH-10M solution, it is observed that the R8 binder is more porous. Fig. 5.67. demonstrates that with the substitution of 10% ash with MD marble dust (R9) and BFS blast furnace slag (R34) in geopolymer binders made with heat treatment (70° C, 24h), the pore size and/or number decreases. There are also differences between binders (R9 and R34) made with heat treatment compared to those made without heat treatment (R53FTT, R34FTT). In the case of those made without heat treatment (23° C), their structure is much more compact and the pores are very small and few.

Concluzii:

The analysis of the microscopic images taken at 1X-2mm resolution showed that the binders contained fewer pores with the substitution of 10% fly ash with marble dust and blast furnace slag. Geopolymer pastes made without heat treatment (23°C) compared to those made with heat treatment (70°C) are more compact. Although the geopolymer pastes are more compact, their mechanical strengths decrease with the substitution of fly ash, and are lower compared to those made with heat treatment. Thus, it can be said that pore size and pore number do not influence their strengths.

The lack of heat treatment leads to non-reaction of the raw materials with the alkali activator, while geopolymerization is incomplete, resulting in decreased mechanical strengths.

5.5.7. Influence of Na_2SiO_3/NaOH ratio on the mechanical strengths of eco-friendly binders based on fly ash with different molarity of NaOH solution

The compressive strengths on cubes with dimensions 40x40x40mm increased with the increasing Na_2SiO_3/NaOH ratio from 1 to 2.5 in both molarity cases, i.e. 8M and 10M. As demonstrated, the compressive strengths increased with the increasing ratio of sodium silicate to sodium hydroxide for the two molarities studied, i.e. 8M and 10M. The compressive strengths had percentage increases of 10%, 11% and 6% for Na_2SiO_3/NaOH ratios of 1.0; 2.0; 1.5 and 2.5 with increasing molarity from 8 to 10M.

Regarding the production of geopolymeric materials, whether we are talking about a paste, a microcrete or a concrete, according to expert studies, it cannot be clearly argued what is the exact ratio and the contribution of each component to obtain optimal results.

According to the literature, compressive strengths on geopolymer pastes and concretes increase with the increasing Na_2SiO_3/NaOH ratio.

Based on the obtained results, it can be stated that the increase in the compressive strengths of geopolymer pastes made from fly ash and alkaline activators (Na_2SiO_3 and NaOH) with heat treatment (70° C, 24h) is influenced by increasing the Na_2SiO_3/NaOH ratio and the molarity of the NaOH solution.

5.5.8. Influence of Na_2SiO_3/NaOH ratio on the compressive and flexural strengths of samples made with marble dust substitution (10%, 25% and 50%) compared to control samples

Analysing the graphs shown in Figure 5.72., it can be seen that the compressive strengths for the control sample and for the samples obtained by substitution with 10% and 25% marble have close values, regardless of the Na_2SiO_3/NaOH ratio, with slight decreases for a ratio value equal to 1.5.

Significant decreases in compressive strength compared to the control sample occur for all samples obtained by substitution with 50% marble from 36.8% for a value of Na_2SiO_3/NaOH ratio=1 to 53.7% for a value of Na_2SiO_3/NaOH ratio=2.5.

The graphs presented in Figure 5.71. prove that the flexural strengths for the control sample and for the samples obtained by substitution with 10% and 25% marble have close values, regardless of the Na_2SiO_3/NaOH ratio, except for the samples obtained for a ratio value equal to 1. Also, a decrease in the flexural strengths is observed for a Na_2SiO_3/NaOH ratio value equal to 1.5.

Significant decreases in flexural strength compared to the control sample are found for all samples obtained by substitution with 50% marble from 41.9% for a Na_2SiO_3/NaOH=1 to 21.4% for a Na_2SiO_3/NaOH=2.5.

Even though the SiO_2/Al_2O_3 ratio is the same for all samples, there are differences in the compressive strengths. The large difference between the compressive strength value for the control sample and the 50% marble substitution sample can be explained by the increase in carbon content from 2.7 in the 25% marble substitution sample to 5.5% in the 50% marble substitution sample.

5.5.9. Influence of heat treatment on the mechanical properties of alkaline activated eco-friendly binder with marble dust substitution

In order to analyze the influence of heat treatment on the mechanical properties of alkaline activated geopolymer paste, the geopolymer paste R9 made with heat treatment (70°C, 24h) and the paste R53FTT made without heat treatment (23±2°C) were compared. The studied pastes were made with 90% fly ash and 10% marble dust, having a molar concentration of 8M and a Na_2SiO_3/NaOH ratio=2.5.

The geopolymer paste denoted R9, made with heat treatment (70°C, 24h) has a higher flexural strength than R53FTT, made without heat treatment (23±2°C).

The compressive strength results showed that heat curing greatly affects the early strength of fly ash-based geopolymer, as the 7-day compressive strength of samples made with heat treatment was about 2.5% higher than that of samples cured at room temperature without heat treatment.

After the bending tensile tests, compressive strength tests were carried out on the geopolymer paste specimen halves on 40 x 40 mm cubes. The compressive strength at the age of 7 days was 28.80 N/mm^2 for recipe R9 (with heat treatment) and 23.40 N/mm^2 for recipe R53FTT (Fig. 5.74.). It is possible that, due to the higher temperature (70°C) and the duration of the heat treatment (24h), the bonds of the compounds formed in the geopolymer paste are stronger than in the geopolymer paste without heat treatment (23±2°C). An influence on the compressive strength is primarily due to the formation of the geopolymer gel which develops faster in the presence of high temperature (between 40-90°C).

The results obtained are in agreement with the literature, according to which the mechanical strengths are higher in samples made with heat treatment compared to those made without heat treatment.

5.5.10. Influence of substitution of fly ash with aluminium slag

In order to obtain alkaline activated geopolymer pastes based on fly ash (75%) and aluminium slag (25%), a $Na_2SiO_3/NaOH$ ratio = 2.5 was used and the molar concentration of NaOH was 8 M. The aluminium slag used in the research originated from a waste processing company.

Comparatively, between samples with heat treatment and without heat treatment, at 7 days of age the bulk density was higher for samples made without heat treatment.

Both bending and compressive strengths were higher for geopolymer pastes without heat treatment.

5.6. Conclusions

The apparent density at the age of 7 days of alkaline activated geopolymer pastes with different molarities NaOH-8 and 10M was between 1340-1380 kg/m^3.

The bending tensile strength at the age of 7 days was carried out on specimens with dimensions of 40x40x160mm. The bending strengths on the NaOH-8M specimens of geopolymer paste ranged from 2.49-3.45 N/mm^2. These strengths are slightly lower than the strengths of geopolymer pastes made with a NaOH-10M solution, ranging between 2.57-3.65 N/mm^2.

Compressive strength on 40x40 mm cubes increased linearly with the increasing $Na_2SiO_3/NaOH$ ratio from 1 to 2.5 for the two types of NaOH solution with different molarities 8 and 10. Compressive strengths at the age of 7 days are influenced by the $Na_2SiO_3/NaOH$ ratio and the molarity of NaOH solution. While for fly ash geopolymer pastes, activated alkaline, using a Na_2SiO_3 and NaOH-8M solution, the strengths ranged from 23.85N/mm^2 to 32.47 N/mm^2, for those with a NaOH-10M solution, the compressive strengths increased, ranging between 26.3N/mm^2 and 34.5 N/mm^2.

<u>Substitution with marble dust</u>

As fly ash (F.A.) was substituted in the proportion of 10%, 25% and 50% with marble dust (M.D.), or blast furnace slag (B.F.S.) compared to the control sample, the following conclusions can be drawn:

- the workability of the pastes in the fresh state when cast decreased with the percentage introduction of marble dust
- the casting density increases by 5.1% to 12.2%.
- the density of the geopolymer paste immediately after 24 hours of heat treatment increases by 6.8% to 20.8%.
- the density of geopolymer paste matured 7 days after casting increases by 7.4% to 23.1%.
- the mechanical strengths of the geopolymer paste 7 days after casting are reduced by up to 41.9% in the case of flexural strength and by a minimum of 7.1% and a maximum of 55.5% in the case of compressive strength.

The best physico-mechanical properties for binders made with different additions were obtained for the addition of iron trioxide, leading to increases of 21.7% for an addition of 1% Fe_2O_3 to fly ash (R21), 15.3% respectively 14.8% for cases of iron trioxide addition of 5% (R23), respectively 10% (R24).

By adding SiO_2 and $Ca(OH)_2$ to the fly ash, better strengths were obtained for green binders made without heat treatment, compared to those realized at 70^{o}C, 24h.

6. Eco-friendly Concrete Based on Alkaline-Activated Mineral Binders

6.2. Objectives

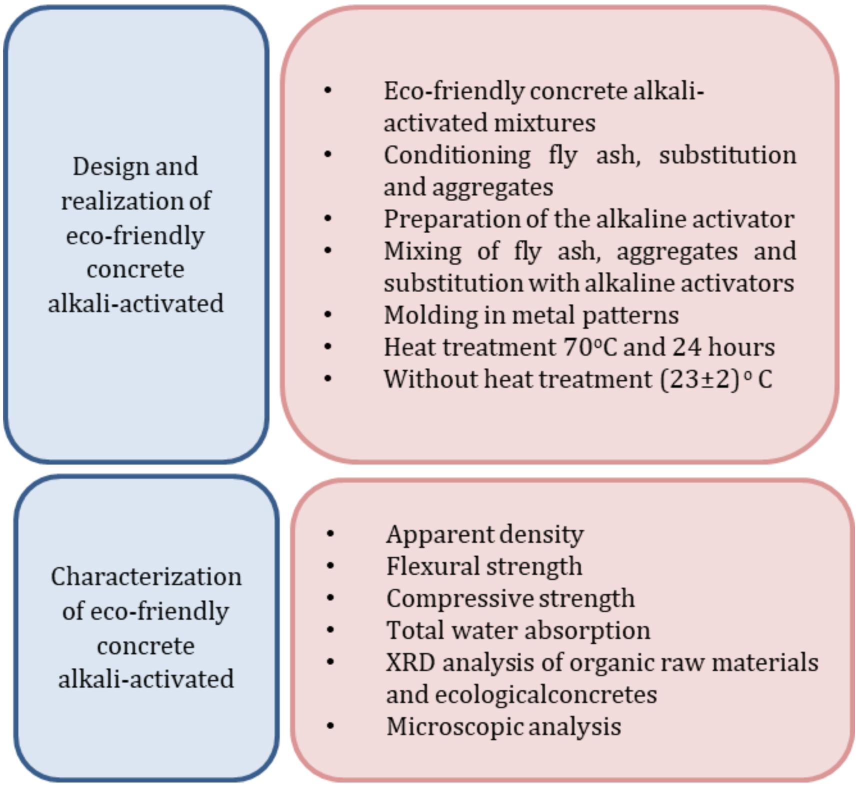

Fig. 6.1. Research methodology of eco-friendly concrete based on alkaline-activated mineral binders

6.3. Materials and methods

Starting from the alkaline-activated eco-friendly binder, realised of eco-friendly concretes based on fly ash and marble dust as a substitute.

The concretes presented in this study were achieved by two methods: with heat treatment (70^{o}C and a duration of 24h) and without heat treatment, at an ambient temperature (23±2^{o}C).

For the design and realization of environmentally friendly concrete, the following component materials were used:

- Fly ash (F.A.)
- Marble dust (M.D.) substitution 10% și 25%
- Aggregate 0-4 și 4-8 mm
- Sodium hydroxide solution (NaOH - 8M)
- Sodium silicate solution (Na_2SiO_3)

As an alkaline activator in the realization of these ecological concretes, a NaOH-based solution with a molar concentration of 8 and sodium silicate was used. Ratio Na_2SiO_3/NaOH was 2,5.

Tabel 6.1. Eco-frendly concrete mixture with and without heat treatment

Mixture	F.A.		M.D.		F.A. + M.D.	Solution Na_2SiO_3	Solution NaOH (8M)	Total solution	Na_2SiO_3 /NaOH	Soluție / (F.A. +M.D.)	Total aggregate 0÷8
Nr.	%	g	%	g	g	g	g	g	-	g	g
Heat treatment (70^{o}C, 24h)											
M2	100	600	0	0	600	428.6	171.4	600	2.5	1.00	1114
M3	90	540	10	60	600	428.6	171.4	600	2.5	1.00	1114
M4	75	450	25	150	600	428.6	171.4	600	2.5	1.00	1114
Without heat treatment (23^{o}C)											
M5	100	600	0	0	600	428.6	171.4	600	2.5	1.00	1114
M6	90	540	10	60	600	428.6	171.4	600	2.5	1.00	1114
M7	75	450	25	150	600	428.6	171.4	600	2.5	1.00	1114

6.4. Results

6.4.1. Determination of the apparent density

With the increase in substitution of flying ash with marble dust in percentages of 10 and 25% also increase the apparent densities. Relative to the control sample M2, apparent densities increased by 2,7 % and 4,3 % fresh, by 3,5 % and 7,6 % at the age of 7 days, respectively by 3,6 % and 9 % at the age of 28 days.

Compared to the M2 blank, the apparent density of the M4 sample (made with 25% marble dust substitution) had a much higher increase than the M3 sample (made with 10% marble dust substitution). Thus, the percentage increase was between 2.7÷3.6% for the M3 sample, and for the M4 sample it was between 4.3÷9%.

And in the case of ecological concretes made without heat treatment, the apparent density increased with the substitution of flying ash with marble dust. Relative to the M5 control, there were increases of 3.8% and 5.4% at the age of 14 days and 4.4% and 6.1%.

Compared to the M4 control sample (performed with heat treatment with 25% marble powder substitution), the M7 sample (made without heat treatment, by substituting flying ash with 25% marble dust), had a lower percentage increase in density. By heat treatment, the surplus of liquid is removed from the concrete matrix.

6.4.2. Determination of flexural strength

6.4.2.1. Mixture M2, M3 și M4 (70^{o}C, 24h)

It is noticed that with the increase in substitution of the flying ash with marble dust in percentages of 10 and 25% decreases the resistances to bending. Relative to the M2 blank, resistances decreased by 20% and 32.7% at the age of 7 days respectively by 19.7% and 30.2% at the age of 28 days.

Compared to the M2 blank sample, the bending tensile strength of the M4 sample (made with 25% marble dust substitution) had a much larger decrease than the M3 sample (achieved with 10% marble dust substitution). Thus, the percentage decrease was between 19.7÷25.8% for the M3 sample and for the M4 sample it was between 30.2÷32.7%.

6.4.2.2. Mixture M5, M6 și M7 (23^{o}C)

In the case of ecological concretes made without heat treatment, the tensile strength by bending decreased with the substitution of flying ash with marble dust. Relative to the M5 blank, there were decreases of 15.8% and 12.8% at the age of 14 days. At the age of 28 days, resistances increased in relation to the blank sample. The increases were 6.7% for the M6 sample and 21% for the M7 sample.

In the case of the M7 sample (made by substituting flying ash with 25% marble dust, without heat treatment) relative to the blank sample, it had a lower percentage decrease in bending resistance at the age of 7 and 14 days compared to the M4 sample (achieved by substituting flying ash with 25% marble powder, with heat treatment).

6.4.2. Determination of compressive strength

6.4.3.1. Mixture M2, M3 și M4 (70^{o}C, 24h)

As with bending resistance, it is observed that with the increase in substitution of flying ash with marble dust in percentages of 10 and 25% compressive strengths decrease. In relation to the M2 blank, resistances decreased by 1,8 % and 24,6 % at the age of 7 days respectively by 4,2 % and 23,0 % at the age of 28 days.

Compared to the M2 blank, the compressive strength of the M4 sample (made with 25% marble dust substitution) had a much greater decrease than the M3 sample (made with 10% marble dust substitution). Thus, the percentage decrease was between 1.8÷4.2% for the M3 sample, and for the M4 sample, between 23.0÷24.6%.

6.4.3.2. Mixture M5, M6 și M7 (23^{o}C)

After determining the compressive strength of ecological concrete cubes made without heat treatment, it was noticed that the resistances decreased with the substitution of the flying ash with the marble dust. Relative to the M5 control, there were decreases of 18.4% and 20.7% at the age of 14 days. At the age of 28 days, the resistance was almost similar to the blank test in the case of substitution of flying ash by 25%.

As can be seen in Fig. 6.12., the compressive strength at the age of 7 days of ecological concretes made without heat treatment, is very low (4.48÷3.18 N/mm^2). This low strength may also be due to the fact that the samples stood in metal patterns and were wet when tested. However, as the material matures, there is a substantial increase in strengths at 28 days, relative to those at 7 days. The increases in resistance at 28 days compared to those at 7 days were 294%, 302% and 452% for ecological concrete denoted by M5, M6 and M7 respectively.

This behavior can signify, on the one hand, the need for heat treatment, and on the other hand, the possibility of achieving the desired mechanical strength, but in a longer period of time. In other words, heat treatment is an accelerator of the geopolymerization processes that take place in the geocomposite matrix.

7. Final conclusions

7.1. General Conclusions

The general conclusions of the present doctoral thesis are highlighted below.

Chapter 1 presents the rationale for the approach of the PhD topic: *An ecological concrete based on alkaline-activated mineral binders*. In order to protect the environment, the construction industry needs to align to sustainable development and circular economy standards by making sustainable materials using industrial waste as raw material. An alternative to the traditional Portland cement concrete can be the environmentally friendly concrete based on alkaline activated mineral binders. An ecological concrete can be considered a 'green concrete', which does not use Portland cement. A property of geopolymer concrete is that it hardens rapidly, reaching 90% of its compressive strength after seven days, compared to the traditional Portland cement, which reaches strength maturity only after 28 days. This concrete is obtained by using silica- and aluminium-rich industrial waste as raw materials, which, activated alkaline using a mixture of sodium hydroxide and sodium silicate solutions, produces a geopolymerisation reaction, resulting in the hardening of the material. The addition of 0-8 mm sort aggregates produces geopolymer concrete. Green binders and concretes were made by two methods, namely: with a heat treatment (70^{o}C, 24H) or without heat treatment (ambient temperature 23^{o}C).

The cost of making geopolymer concrete varies according to the raw materials that are used and the concentration of alkaline solution used. Thus, the aim is to obtain geopolymer concrete with very good, more convenient mechanical properties, by discovering a cheap raw material, rich in Si and Al, using the lowest possible concentration of alkaline activator.

Chapter 2 presents aspects related to the history of geopolymeric materials, the global perspectives in the context of the implementation of the "circular economy" concept, the structure of geopolymeric materials, types and mechanisms of geopolymerisation reactions, raw materials and types of alkaline activators used in making geopolymeric materials, the influence of heat treatment on the geopolymerisation reaction, as well as the factors influencing the properties of geopolymer materials and the compressive strengths of geopolymers made with or without heat treatment at ambient temperature, all reported by various authors in the literature.

The working hypotheses of this PhD thesis are presented in **Chapter 3**.

The general methodology of producing the binder and the green concrete as well as the apparatus used in making and testing this geopolymer material are described in **Chapter 4**.

Chapter 5 goes into more detail on the ecological binder based on alkaline activated mineral binders, how to make this binder, the characteristics of the raw materials, as well as the used additions and fly ash substitutions. Marble dust, blast furnace slag and aluminium slag in different proportions (10%, 25% and 50%) were used as fly ash substitutes. Iron trioxide, magnesium oxide, silicon dioxide, calcium hydroxide or perlite were employed as additives in the raw material mixture. The environmentally friendly binder was obtained by two methods: with a heat treatment (70^{o}C, 24H) or without heat treatment (ambient temperature 23^{o}C).

The molar concentration of NaOH solution used was 6M, 8M and 10M. The Na_2SiO_3/NaOH ratio studied was 1; 1.5; 2 and 2.5. The influence of substitutions and additions in terms of physico-mechanical properties, binder microstructure and water absorption are also presented in this chapter.

Table 7.1 Eco-friendly binders based on fly ash –mechanical properties

$Na_2SiO_3/NaOH$	Apparent density									Flexural strength R_{ti} (N/mm^2)			Compressive strength R_c (N/mm^2)		
	Fresh			Heat treatment (70°C, 24H)			7 day								
	Solution NaOH			Solution NaOH			Solution NaOH			Solution NaOH			Solution NaOH		
	6M	8M	10M	6M	8M	10M	6M	8M	10M	6M	8M	10M	6M	8M	10M
1,0		1560	1570		1450	1460		1340	1350		3,3	2,9		23,8	26,3
1,5		1580	1590		1460	1465		1380	1370		2,5	2,6		26,8	29,8
2,0	1580	1590	1595	1380	1440	1460	1290	1370	1380	2,1	3,0	3,6	18	29,5	32,5
2,5		1580	1600		1470	1470		1360	1380		3,4	3,0		32,5	34,5

Tabel 7.2. Compressive strength of geopolymer pastes based on fly ash

Alkaline solution / Molarity		Rc (N/mm^2)	DAYS	Raw materials (%)	Heat treatment		Ref.	Experimental reults
					°C	ore	-	
FLY ASH (FA)								
NaOH (10)	Na_2SiO_3	42,0	28	FA (100)	65	48	[203]	-
NaOH (10)	Na_2SiO_3	34,5	7	FA (100)	70	24	-	X
NaOH (10)	Na_2SiO_3	34,0	7	FA (100)	65	6	[135]	-
NaOH (10)	Na_2SiO_3	25,4	7	FA (100)	70	24	[61]	
NaOH (10)	Na_2SiO_3	21,6	7	FA (100)	70	24	[61]	
NaOH (8)	Na_2SiO_3	32,5	7	FA (100)	70	24	-	X
NaOH (8)	Na_2SiO_3	25,3	7	FA (100)	70	24	[61]	
NaOH (8)	Na_2SiO_3	20,1	7	FA (100)	70	24	[61]	
NaOH (8)	Na_2SiO_3	25,0	7	FA (100)	70	24	[198]	-
NaOH (6)	Na_2SiO_3	18,0	7	FA (100)	70	24	-	X

Tabel 7.3 Eco-friendly binders with marble dust substitution – mechanical properties

Raw materials $Na_2SiO_3/NaOH$=2,5	Apparent density (kg/m^3)		Flexural strength R_{ti} (N/mm^2)		Compressive strength R_c (N/mm^2)	
	70°C, 24H	23°C	70°C, 24H	23°C	70°C, 24H	23°C
Days	7/14/28	7/14/28	7/14/28	7/14/28	7 / 14 / 28	7 / 14 / 28
100%FA	1360/-/-	-/-/-	3,4/-/-	-/-/-	32,5/-/-	-/-/-
90%FA+10%MD	1550/-/-	1620/1560/1550	3,3/-/-	2,5/2,3/3,5	28,8/-/-	23,4/26,6/20,3
75%FA+25%MD	1580/-/-	1700/1650/1580	3,4/-/-	3,0/3,0/4,0	26,9/-/-	18,1/26,3/26,1
50%FA+50%MD	1670/-/-	1740/1720/1650	2,7/-/-	3,7/1,5/4,1	15,0/-/-	10,8/12,5/15,6

Table 7.4. Compressive strength of geopolymer pastes based on fly ash and marble dust

Mixture	Raw materials (%)		Ratio Alkaline activator/ precursor	NaOH	Ratio Na_2SiO_3/ NaOH	Apparent density (kg/m^3)	Rc $_{7days}$ (N/mm^2)	Ref.	Experimen -tal results
	F.A. Class F	M.D.							
HEAT TREATMENT (70°C, 24H)									
2M-10	90	10	0,22	2M	1	1450	1,82	[57]	
4M-10	90	10	0,22	4M	1	1550	3,34	[57]	
R18	90	10	0,78	8M	1	1550	22,05		X
2M-50	50	50	0,27	2M	1	1550	3,38	[57]	
4M-50	50	50	0,27	4M	1	1680	5,92	[57]	
R20	50	50	0,78	8M	1	1670	15,06		X
WITHOUT HEAT TREATMENT (23°C)									
R53FTT	90	10	0,78	8M	1	1620	20,26		X
R55FTT	50	50	0,78	8M	1	1750	15,58		X

Table 7.5. Eco-friendly binders with blast furnace slag substitution – mechanical properties

Raw materials $Na_2SiO_3/NaOH$=2,5	Apparent density (kg/m³)		Flexural strength R_{ti} (N/mm²)		Compressive strength R_c (N/mm²)	
	70°C, 24H	23°C	70°C, 24H	23°C	70°C, 24H	23°C
Days	7	7/14/28	7/14/28	7/14/28	7 / 14 / 28	7 / 14 / 28
100%FA	1360/-/-	-/-/-	3,4/-/-	-/-/-	32,5/-/-	-/-/-
90%FA+10%BFS	1460	1615/1610/1610	3,3/-/-	3,7/-/-	25,6/25,5/-	8,2/18,6/20,6
75%FA+25%BFS	1520	1640/1630/1620	2,3/-/-	1,7/-/-	21,0/22,1/-	8,2/17,1/22,0
50%FA+50%BFS	1630	1700/1680/1630	1,7/-/-	1,4/-/-	11,6/16,8/-	5,8/11,9/8,1

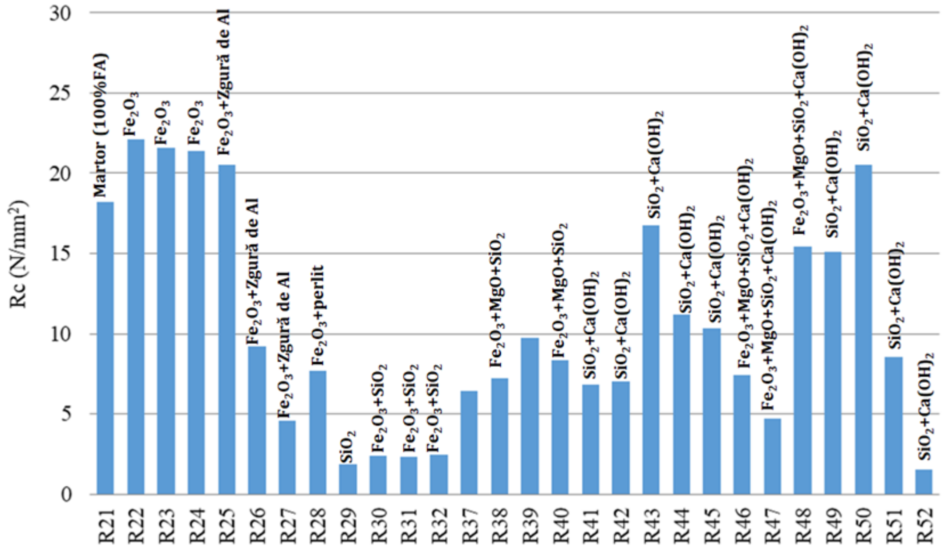

Fig. 7.1 Eco-friendly binders with different additions made with heat treatment (70°C, 24H) Compressive strength al 7 days

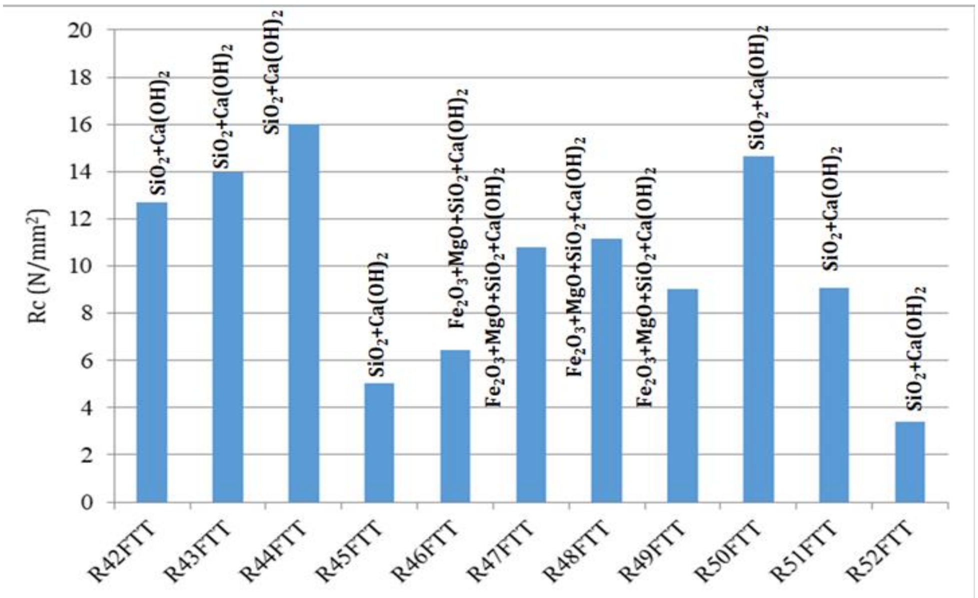

Fig. 7.2 Eco-friendly binders with different additions made without heat treatment (23°C) Compressive strength al 7 days

Chapter 6 focuses on environmentally friendly concrete based on alkaline activated mineral binders. Fly ash and marble dust and river aggregate (sort 0-8 mm) were used as raw materials in the production of this concrete. The alkaline activator made was a mixture of sodium silicate solution and sodium hydroxide (8 M). The ratio of sodium silicate and sodium hydroxide solutions was 2.5. The physico-mechanical properties of ecological concrete made on the basis of fly ash or its substitution with marble dust (10% and 25%), made both with heat treatment (70° C, 24H) or without (23° C) are presented in this chapter, together with the compositional evaluation by X-ray diffraction (XRD) method on raw materials, characterization of ecological concrete made with heat treatment or without, water absorptions of ecological concrete and their microscopic evaluation.

Table 7.6. Physico-mechanical properties of eco-friendly concrete

Raw materials Ratio $Na_2SiO_3/NaOH$ =2,5	Apparent density (kg/m³)		Flexural strength R_{fi} (N/mm²)		Compressive strength R_c (N/mm²)	
	70°C, 24H	23°C	70°C, 24H	23°C	70°C, 24H	23°C
Days	7 / 14 / 28	7 / 14 / 28	7 / 14 / 28	7 / 14 / 28	7 / 14 / 28	7 / 14 / 28
100%FA	1720/1700/1670	1900/1740/1800	3,8/4,5/4,8	1,7/3,3/3,2	22,3/23,3/23,4	4,5/11,9/17,7
90%FA+10%MD	1780/1760/1730	1950/1910/1880	3,1/3,3/3,8	1,7/2,8/3,4	21,9/22,3/22,4	4,2/9,7/16,9
75%FA+25%MD	1850/1840/1820	1980/1940/1910	2,6/2,9/3,3	1,3/2,8/3,8	16,8/17,3/18,0	3,2/9,5/17,6

Table 7.7. Compressive strength of geopolymer concretes based on fly ash

Alcaline solution / Molarity		Rc (N/mm²)	Zile	Raw materials (%)	Heat treatment °C	Heat treatment ore	Ref. -	Experimental results
HEAT TREATMENT 70°C, 24H								
NaOH (8)	Na_2SiO_3	17,0	7	FA (100)	60	24	[71]	
NaOH (8)	Na_2SiO_3	20,0	7	FA (100)	30	24	[71]	
NaOH (8)	Na_2SiO_3	20,3	7	FA (100)	70	24	[61]	
NaOH (8)	Na_2SiO_3	20,5	7	FA (100)	70	24	[61]	
NaOH (8)	Na_2SiO_3	22,3	7	FA (100)	70	24	-	X
NaOH (8)	Na_2SiO_3	57,0	7	FA (100)	60	24	[71]	
WITHOUT HEAT TREATMENT (23°C)								
NaOH (8)	Na_2SiO_3	4,5	7	FA (100)	70	24	-	X
NaOH (8)	Na_2SiO_3	11,9	14	FA (100)	70	24	-	X
NaOH (8)	Na_2SiO_3	17,7	28	FA (100)	70	24	-	X

Chapter 7 summarises the general conclusions of the topic presented, as well as the originality and the innovative contributions of this PhD thesis.

Considering the results obtained in terms of compressive strength (22.3 N/ mm²) at the age of 7 days, the fundamental parameter for establishing the directions of use envisaged, the ecological concrete based on alkaline activated mineral binders based on fly ash, can be assimilated with the classic Portland cement concrete, classified in the concrete class C16/20. By optimising and testing the recipes proposed in the present research, the development of small-scale precast construction elements (slabs, pavers, kerbs, panels, etc.) will be considered.

7.2. Originality and the innovative contributions of the thesis

The originality and innovative contributions of the research programme derive from the following:

- The applied research approach for local raw materials, originating from the Romanian industry, with specific oxidative composition and structural characteristics, gives a strong novelty to this research;

- The compositional design of the geopolymer binder based on the analysis and synthesis of literature reports that were applied in correlation with the specificity of the local raw materials;

- Identification of the Na_2SiO_3/NaOH ratio and the molar concentration of the NaOH solution so that, under the specific conditions of oxide compounds and raw material characteristics, geopolymer materials with the best performance can be obtained;

- Analysis of the possibilities of substitution of fly ash (F.A.) with marble dust (M.D.) in different percentages (10%, 25%, 50%) and their impact on the physical-mechanical performance and microstructure aspects of the new geopolymer composite;

- The study of the possibility of fly ash (F.A.) substitution with blast furnace slag (B.F.S.) in different percentages (10%, 25%, 50%) and study their impact on the physico-mechanical performance and microstructure aspects of the new geopolymer composite;

- Introduction of different additions to the raw material mixture such as iron trioxide (Fe_2O_3), calcium oxide (CaO), silicon dioxide (SiO_2), magnesium oxide (MgO) and perlite and their analysis and impact on the physical-mechanical performance of the geopolymer;

- The production of green binders and alkaline activated green concrete by two methods: with heat treatment (70^{o}C, 24H) and without heat treatment, at ambient temperature (23^o C), is another original element of this study;

- Study of the performance of geopolymers and analysis of the influence of heat treatment on them;

- Compositional design of alkaline activated ecological concrete by substituting fly ash with marble dust (in proportions of 10% and 25%) and introducing river aggregates sort 0-8 mm;

- Analysis of the impact on the physical-mechanical performance of these ecological concretes made with heat treatment (70^o C, 24H) or without it at an ambient temperature of 23^o C.

- Development of the technology for the production of a *cement-free, alkaline activated geopolymer microcrete cladding element type product*, with copyright protection by Patent Application: no. A/00481 of 09.08.2022.

The results of the research were disseminated by:

- Four scientific progress reports presented to the guidance and examination committee.

- Publication of various articles in ISI or BDI indexed journals.

- Participation in different Inventions Salons, where different medals were obtained.

- Application for a Patent of Invention: no. A/00481 of 09.08.2022 *Process of realization and cladding elements of alkaline activated geopolymer micro concrete, without cement content*, holder National Institute for Research and Development in Construction, Urbanism and Sustainable Territorial Development URBAN-INCERC (Annex A).

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