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Proiect POSDRU/159/1.5/S/132397 – Excelență în cercetare prin burse doctorale si postdoctorale – ExcelDOC

“Dunarea de Jos” University of Galati
Doctoral School of ENGINEERING

UNIVERSITAS
GALATIENSIS

DOCTOR OF PHILOSOPHY DEGREE (PhD) THESIS

ABSTRACT
Contributions concerning the obtaining of geopolymers by using production residues

PhD Student,
Eng. Ilenuța Spătaru (Severin)

Scientific Coordinator,
Prof. dr. Eng. Maria VLAD

Seria I 5. Material’s Engineering Nr. 9

GALAŢI
2016

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Scientific References:
Prof. univ.dr.Eng. Raluca Daniela Isopescu
Prof. univ. dr. Eng. Cristian Predescu
Prof. univ.dr.fiz. Mirela Praisler

Seria I 5 Material’s Engineering Nr.9

GALAŢI
2016

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Foreword

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Ilenuța Severin, Octombrie. 2016
„Dunărea de Jos” din Galați, România

Keywords

Geopolymers
Slag
Red mud
Wheat straw ash
Microstructures
Compression strength

ROMÂNIA
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DECIZIA

nr. 3341 / 25.11.2016

Conform modificărilor aduse Codului studiilor universitare de doctorat prin Hotărârea Guvernului României nr. 134/2016 și de Regulamentul de organizare și funcționare al CNATDCU aprobat prin Ordinul Ministrului Educației Naționale și Cercetării Științifice nr. 3482/24.03.2016;

având în vedere referatul conducătorului științific Prof.dr.ing. Maria VLAD nr. 38298/24.11.2016, privind propunerea comisiei de susținere publică a tezei de doctorat;

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Art. 1. Se numește comisia pentru evaluarea și susținerea publică a tezei de doctorat de către doctorand/a/ul **ing. SPĂTARU Ș. ILENUȚA (SEVERIN)**, domeniul **Ingineria materialelor,** în următoarea componență:

1. Președinte	**Prof.dr. Viorica-Domnica MUȘAT** Universitatea „Dunărea de Jos” din Galați
2. Conducător de doctorat	**Prof.dr.ing. Maria VLAD** Universitatea „Dunărea de Jos” din Galați
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Art. 2. Școala doctorală de Inginerie, Secretariatul doctorat, Compartimentul salarizare și Serviciul financiar vor duce la îndeplinire prevederile prezentei decizii.

RECTOR,
Prof. dr. ing. Iulian Gabriel BIRSAN

RECTORAT

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Introduction

Industrialization on a global scale affects the environment not only in terms of natural resources usage by reducing their quantity, but also regarding the big amount of the generated industrial waste. Considering the fact that some of the natural resources are non-renewable, in many industrial sectors the capitalization of production residues is required regarding waste resulted from various process streams, mainly from the industrial sector of obtaining and processing metallic materials. Since the development of civil and industrial constructions sector has expanded, demand for construction materials increased proportionally. Thus, in order to satisfy the demand for raw materials for construction materials, without negatively affecting the environment, the possibility of using resources which replace those raw materials while respecting at the same time the initial core standards of the construction materials was taken into account.

The challenge of obtaining new materials with binding properties, such as geopolymers or materials containing geopolymers formed through the process of geopolymerization, and known as non-polluting materials (‘green’), preserving natural raw/auxiliary materials and at the same time comparable to the properties of classic construction materials, at a low price and a low impact on the environment, have been the reasons why research into the production waste recovery through the method of geopolymerization has been addressed in this thesis.

An extensively studied issue is obtaining alternative products made from waste, this being a positive way of recycling by eliminating storage problems, and also achieving additional income sources.

This PhD thesis aimed to obtain and characterize geopolymers with binding properties and resulted materials containing geopolymers formed as a result of alkaline activation of production waste with different contents of alumino-silicate, silicates, aluminates, like: ground granulated blast furnace slag, red mud and wheat straw ash, in order to use them in the construction sector.

Recently, a new group of materials, called geopolymers, has been extensively studied for use in various applications. This class of materials are synthetic mineral products that combine the properties of polymers, ceramics and cements, and which have a number of special properties, like: resistance to fire/heat (stable up to 1200°C); resistance to chemical attack by acids and organic solvents, non-toxic 'green materials', because through their synthesis energy is saved and they do not produce CO_2 emissions like the case of Portland cement. Geopolymers can be made from a variety of cheap aluminum-silicate materials or even waste with a high content of SiO_2 and Al_2O_3, like: metakaolin [1], fly ash [2], slag [3], red mud [4] or construction waste [5, 6].

These polymers with inorganic with a three-dimensional spatial structure do not have hydration water in their structure like in the case of calcium-based cements, so they are impermeable and waterproof and have excellent mechanical properties, (in particular high compressive strength) compared to Portland cement-based materials. Obtaining new materials through the technology based on geopolymerization lately caught researchers' attention, because it has been found to be a viable solution for recycling industrial waste (industrial produce) thus avoiding critical treatment and storage conditions[7].

This innovative technology can be a solution in solving environmental and economic challenges faced by the industry of obtaining metallic materials, following that large amounts of slag, red mud and ash are resulted. Geopolymerization is based on reactions between a solid, rich in silica and alumina, with a concentrated alkaline which results in the alumino-silicate polymers with a semi-crystalline to amorphous structure, where cations of Si^+ and Al^+ in the network of the geopolymer have tetrahedral coordination and are bridged by oxygen. According to data from special literature, geopolymerization is a complex process, which can be divided into the following stages: solubilizing the amorphous phase (SiO_2 and Al_2O_3) in alkaline solutions; transport, orientation and condensation of precursor ions into monomers; polycondensation and polymerization of monomers into silica-alumina amorphous polymers or semi-crystalline [8, 9]. Geopolymers are actually, inorganic polymers, which, generally have excellent physical and chemical properties and can be successfully used in applications such as: insulation materials, cementitious materials and securing radioactive metals, heavy metals, similarly to glass. Geopolymers chemical composition is similar to that of the silica-alumina natural zeolites, but they are usually amorphous instead of crystalline [10]. Generally, materials containing for the most part amorphous silica and alumina are a possible source of producing geopolymers. It is remarkable that, initial feedstock plays a significant role in the specific processes of geopolymerization and influences physical, chemical, structural and mechanical properties of geopolymers.

Geopolymerization as a means of obtaining a new material that can be either a geopolymer or a material which has in its structure a geopolymerical gel is a versatile technique that uses not only natural raw materials but also industrial waste: slag, sterile, red mud, coming from the extractive industry, and from other industries: ashes, slurries or powders, in order to obtain materials for the construction sector. The advantages of using geopolymerization as a way of obtaining new materials are : the use of large quantities of production waste instead of natural raw materials; low obtaining temperature; relatively short hardening time; saving natural resources; saving heat; competitive product thanks to a series of special physical, chemical and mechanical properties.

The experiments were carried out in the laboratories of' Dunărea de Jos' University in Galați, in the laboratories of the Catholic University in Leuven, Belgium (Department of Materials Science and Environment and the Department of Geology), at the Research Centre and Eco-Metallurgical Expertise from the Polytechnic University of Bucharest and in the laboratories of the National Institute for Research and Development and Environmental Protection in Bucharest.

This thesis is developed in six chapters which include, in order, the following:

Chapter 1- presents the current state of research on the use of production residues containing alumino-silicates to obtain geopolymers.

Chapter 2 – presents the materials from which the geopolymers have been obtained and the materials obtained from the geopolymerization process, methods, experimental procedures and means of investigation to determine the physical, chemical, structural, thermal and mechanical properties of the resulted final products. After conducting the specific tests of a construction material, samples of the studied materials had mechanical properties (compression strength), pasty material stability (Le Chatelier stability test), determination of the setting time (the Vicat test), varied depending on the residue characteristics, alkaline activation solution concentration and work conditions (temperature, time).

Chapter 3 – presents research on alkaline activation of residues: granulated slag, red mud, wheat straw ash, production residues deemed of interest for experimental research in this thesis. The results of the experiments have revealed that through the alkaline activation of slag, we can obtain materials with similar properties to the classic concrete obtained from raw materials.

Chapter 4 – presents experimental research regarding the obtaining and characterization of geopolymers and of the resulted materials, containing the geopolymer formed through the alkaline activation with a mixture of NaOH with a solution of Na_2SiO_3, in equal quantities, a mixture of two production residues (granulated slag, straw ash, red mud, mixed two by two based on recipes). The materials resulted from the process of geopolymerization have been characterised chemically, structurally, thermically and mechanically.

Chapter 5 – presents the experimental results regarding the obtaining and characterisation of geopolymers and resulted materials containing the geopolymer formed through the alkaline activation of a mixture containing three residues that contain silicates, aluminates and aluminum silicates (granulated slag, straw ash, red mud) mixed based on recipes.

The materials resulted from the process of geopolymerization have been characterised chemically, structurally, thermically and mechanically, in order to compare their properties to those of the classic concretes and to analyze the possibilities of using them as construction materials.

Chapter 6 – presents general conclusions, original contributions and future research directions.

CHAPTER 1. CURRENT STATE OF RESEARCH ON THE USE OF PRODUCTION RESIDUES CONTAINING ALUMINO-SILICATES TO OBTAIN GEOPOLYMERS

1.1. General Notions

1.1.1. Polymers

Polymers are macromolecules made by bindings of a very large number of small molecules called mers. Polymers are a special category of materials of particular importance as they are found in most of the objects that surround us: rubber; plastics; resins and other, and the reaction through which the monomers combine forming the macromolecule is called polymerization [11].

1.1.2. Geopolymers

Geopolymers are inorganic polymeric materials obtained as a result of alkaline activation of a mixture from a dry, solid material (rich in silica and alumina) with a strongly alkaline solution. The preparation time is relatively short, the work temperature is low and the resulting material has a three-dimensional structure, similar to the natural silico-aluminous zeolites [13]. The term of „geopolymer" was given to a binding material and was first introduced in academic language by French researcher J. Davidovits [14]. The general chemical formula of a geopolymer is $M_n[-(SiO_2)_Z-AlO_2]_nwH_2O$, where M is a cation of Na, K, Ca or Li;; *n* is the degree of polycondensation; *w* represents the number of water molecules in the system and *z* is 1, 2, 3, or a number much bigger than 3 [14]. These chemical bonds (-Si-O-Al-O-) unite to form the specific three-dimensional structure of a geopolymer based on polisialates.

The block diagram of obtaining a geopolymer is described in Fig. 1.2 [18].

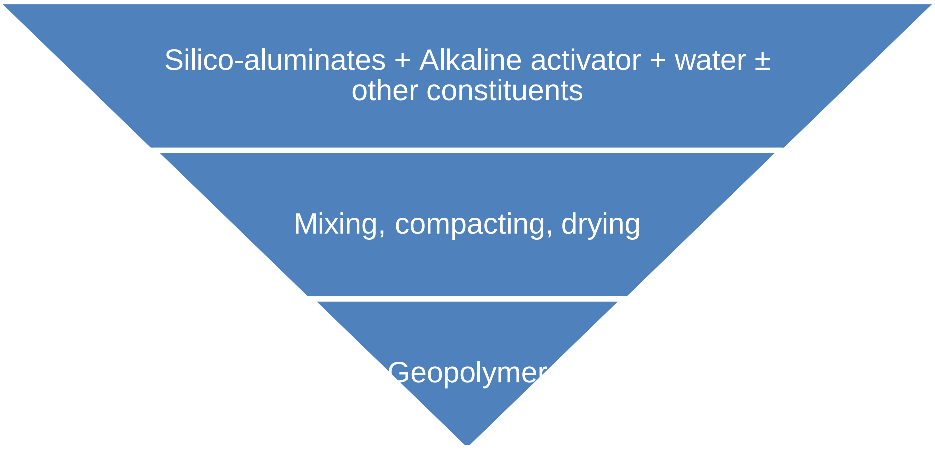


Figura 1.1 The block diagram of obtaining a geopolymer [18]

1.1.3. The mechanism of the chemical reactions of geopolymerization

The geopolymer resulted from the chemical reactions of geopolymerization is actually an inorganic polymer with a very long, crosslinked network, in which, the tetrahedral networks specific to the alumina structures contain groups (AlO_4), and in case of the silicates groups of (SiO_4) that are placed in the three-dimensional structure and the connection between these tetrahedra is balanced by alkaline ions: Na^+, K^+ sau Li^+ [46-48].

Until the present, the mechanism showing the existence of alkaline ions into the molecular structure of the resulted geopolymeric material is not well known, but, it is considered that these metal ions are trapped in structure to balance the negative electronic charge or are trapped to the existing network effectively.

Fig 1.3. describes the geopolymerization chemical reaction mechanism in the case of fly ash [49].

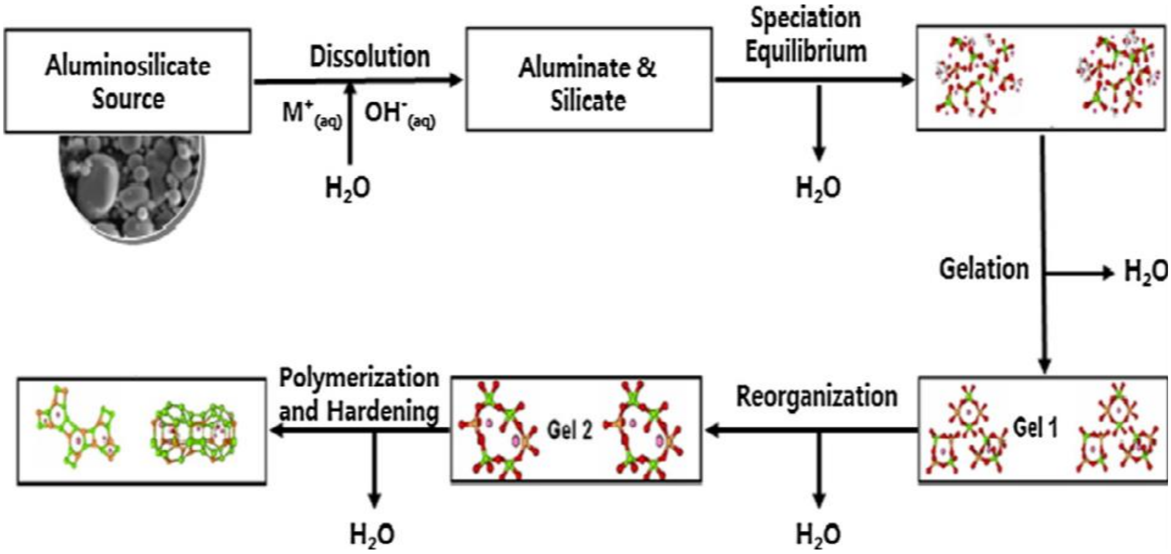


Fig 1.2. The geopolymerization chemical reaction mechanism in the case of fly ash [49].

1.4. Factors influencing physical, chemical and mechanical properties of geopolymers

In the case of geopolymers, the factors influencing their physical, chemical and mechanical properties are: particle size; ratio of silicon and aluminum content (Si/Al); the amount of calcium; nature and concentration of the alkaline activator; curing time; temperature (of maintenance, resistance to high temperature).

1.4.1. Average particle sizes

In many specialized studies, average particle size is a determining factor in the case of compression strength, this setting the difference between a geopolymer with medium-sized small particles, with a high compressive strength and one with medium-sized big particles which results in high porosity, so a low compressive strength value.

1.4.2. Si/Al ratio

Theoretically, the influence of the Si/Al ratio and the link with the mechanical properties of the geopolymers should be positive because an increase in the quantity of silica also increases the content of Si-O-Si links, that are stronger than the links formed of Si-O-Al and Al-O-Al [184].

1.4.3. The amount of calcium

In the case of geopolymeric materials made of fly ash [193], cured at ambiental temperature, it was demonstrated that the addition of calcium in the geopolymer network increases its resistance, which is not true for the case wherein the curing is carried out under conditions of elevated temperature [190], because, in this case, the development of the three-dimensional network structure of the geopolymeric gel is prevented by the presence of calcium.

1.4.4. The type and concentration of the alkaline activator

In the case of alkaline activation of the silica-alumina materials (red mud, slag, fly ash, metakaolin, or other precursors), an important role in determining the structural and mechanical properties is played by the type and concentration of the alkaline activator and also the physical and chemical nature of the solid silica-alumina precursor used for making the geopolymer. The typically used activators are: sodium hydroxide or potassium hydroxide and/or sodium or potassium silicate [22-29].

1.4.5. The period of maintenance

The period of maintenance in some conditions (temperature, humidity) is an important factor in obtaining good mechanical properties of the geopolymeric material regardless of the source of silica-alumina material used in its realization.

1.4.6. Temperature

During geopolymerization, water facilitates the workability of the initial pulp but will not be incorporated in the structure of the resulted geopolymer. Although water is not directly involved in the chemical reaction key, it will be eliminated during the curing phase, respectively, drying. This is in contrast to the hydration that occurs in the case of obtaining the portland cement, in which, the cement mixed with water will result in the production of calcium hydrate, calcium hydroxide and silicon. This influences the mechanical and chemical properties of the resulted geopolymeric concrete.

1.5. The applications of geopolymers in constructions

Geopolymers are considered a green material, futuristic materials. They can be obtained from any source of material rich in silica and alumina, which, mixed with a solution of alkaline activator, can generate the process of geopolymerization. As a result of geopolymerization, a product with special structural, chemical, physical and mechanical properties can be obtained. From a practical perspective, obtaining geopolymers from residues constitutes the way to using silico-alumina production waste as alternative raw material sources.

1.6. Partial conclusions

1) Production waste originating from different technological flows mainly from industry for obtaining and processing of metallic materials (slag and red mud) or other industries (fly ash, slurries, powders) for having in their composition silica, alumina and/or silica-aluminates can be used to obtain geopolymers.

2) The geopolymer is an inorganic polimer showing very good physical, mechanical and chemical properties that can be used in various applications such as: cementitious binder, concrete, bricks, insulating material or radioactive metal sequestration material.

CHAPTER 2 EXPERIMENTAL MATERIALS, METHODS AND PROCEDURES

2.1. Overview

In this chapter, the materials(production residues) and alkaline solutions used in preparing geopolymers are characterised physically, chemically, mineralogically, structurally, thermically and mechanically. Moreover, the methods and procedures of investigation and analysis as well as the way of preparing geopolymers are described.

2.2. Bulk materials used for the synthesis of geopolymers

2.2.1. Ground granulated blast furnace slag (GGBFS)

Fig. 2.1. (a) and (b) highlights the differences between the sample of granulated slag as it was purchased from the vendor and a sample of granulated slag after being subjected to grinding and sieving operations.

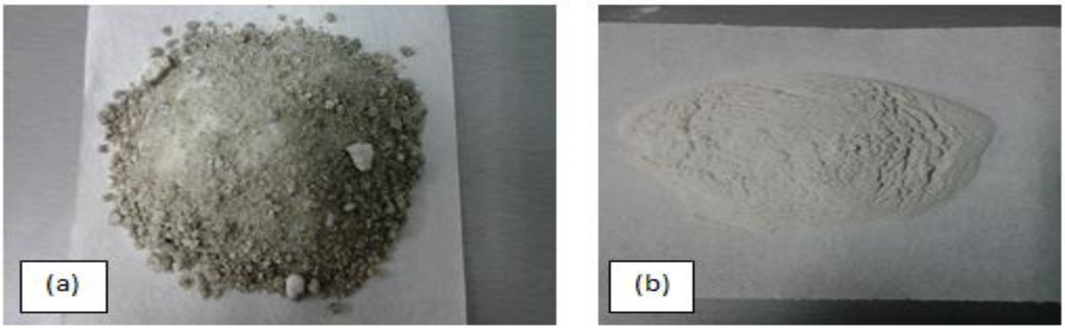


Fig 2.1.Granulated slag sample(a) granulated slag grinded and sieved at 80 µm (b)

2.2.2. Red mud (RM)

The red mud used in experiments was brought from the factory making alumina through the wet alkaline Bayer procedure, from ALUM Tulcea, respectively from the landfill of the factory. The purchased material was brought in a solid-dusty state, of a red-brick colour, color caused by the high amount of oxides of iron, especially Fe_2O_3 (hematite) iron sulfate and silica-alumina, titanium dioxide and other.

Fig 2.3. a) presents a sample of uncalcined red mud, red-brick coloured, and a sample of calcined red mud of an intense red, colour caused by iron oxide concentration in the sample subjected to calcination in Fig 2.3.b).

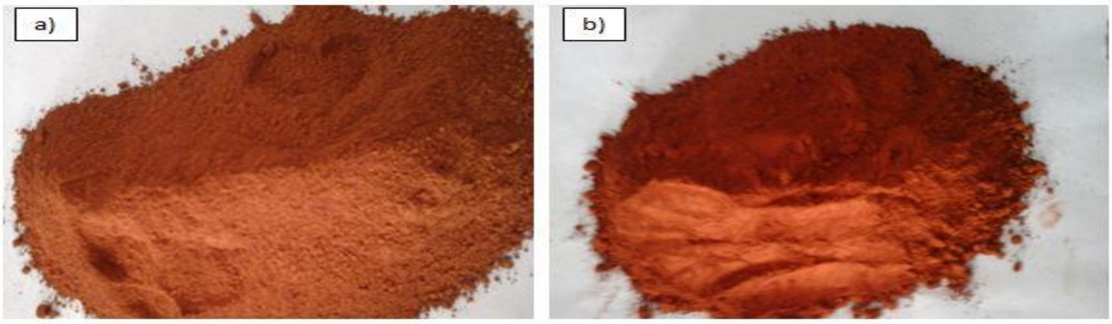


Fig. 2.3.Sample of uncalcined red mud (a) and calcined at 600°C(b)

2.2.3. Wheat straw ash (WSA)

Since Romania is a predominantly agricultural country and cereal crops are high, waste from uncontrolled burning of the wheat straw resulted after harvesting are a source of environmental pollution. The ash used in the experimental research was obtained through the controlled burning of the crop residues resulted after harvesting the wheat(wheat straw).

Fig.2.3. presents a sample of wheat straw ash in unprepared form a) and a sample of grinded ash b).

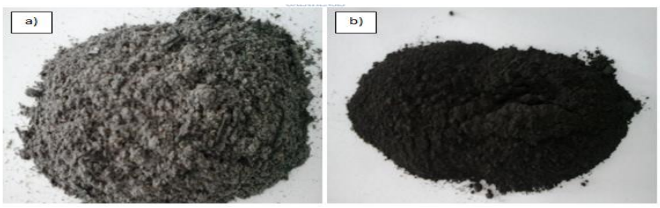


Fig 2.4. Sample of unground ash a) and grinded ash b)

2.3. Alkaline activators used for the geopolymer synthesis

Alkaline solutions used in the study (like NaOH in different concentrations and mixture of NaOH and Na_2SiO_3) were prepared in the laboratory 24 h prior to being used to ensure proper mixing and dissolution of chemicals. The maturation and cooling of the solution of NaOH was carried out in the laboratory at a temperature of 20°C and humidity of about 50%, mixture of Na_2SiO_3/ NaOH (50% weight percent) was kept in an oven at 60°C in order to prevent settling of sodium silicate. Before using the mixture of Na_2SiO_3/NaOH, 50% weight percent each, it was allowed to cool to room temperature.

2.4. Preparation of solid materials

The making of geopolymers involves a series of operations prior to obtaining them. Solid raw materials have undergone initial operations of reducing their size by grinding and sieving. Furthermore, in the case of red mud, it has also undergone the operation of calcination. Calcination was performed to make a comparison between the properties of the geopolymer obtained with uncalcined red mud and the geopolymer obtained with calcined red mud.

2.5. Physical characterization of materials

The solid materials in the recipes for the geopolymers synthesis were characterized physically performing grinding operations, sieving and/or calcination. There have been determined, the bulk density, average particle diameter and specific surface area of the raw materials (slag, ash and red mud) in order to facilitate the characterization of their chemical, mineralogical and morphological structure.

Table 2.2. The average of bulk density and specific surface of the solid materials used for sythesis

Material	Bulk average density (g/cm^3)	Standard Deviation (g/cm^3)	Specific surface (g/cm^2)
Ground granulated blast furnace slag	2,8801	0,0003	4,2653
Ash	2,3813	0,0034	4,1187
Uncalcined red mud	2,6715	0,0029	7,3087
Calcined red mud	2,8019	0,0065	7,3679

From the comparative analysis of the diagrams it is observed that granulated slag has a uniform distribution of particles, about 40% of the total volume of the particles having an average diameter of 45.2 µm, the average diameter of wheat straw ash of 22,06 µm, 50% smaller than that of the granulated slag. In the case of red mud the difference between the calcined red mud and the uncalcined one is obvious by decreasing particle size after calcination due to both physical decay by losing the physically linked water and due to the different chemical reactions such as the decomposition which took place during calcining.

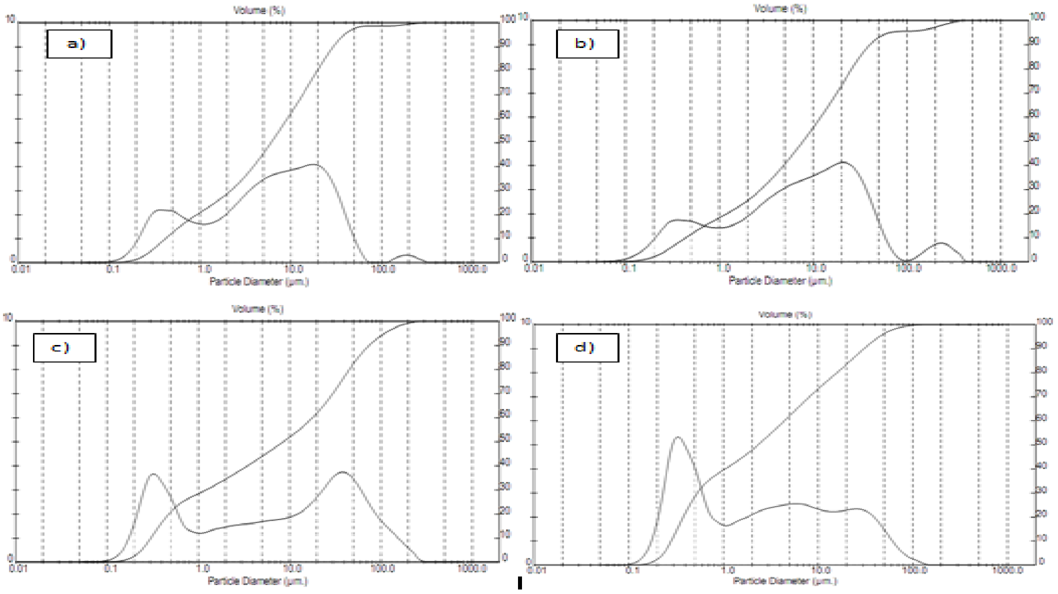


Fig 2.9. Average particle size distribution of: granulated slag (a), wheat straw ash (b); uncalcined red mud (c);and calcined red mud (d)

So, uncalcined red mud has a volume of average particle whose dimensions do not exceed 14,86 µm of 35%, and calcined red mud has a volume of approximately 50% with a mean particle diameter of 10,28µm.

2.6. Chemical characterization

2.6.1. Chemical characterization by X-ray fluorescence (XRF)

In the table 2.3 chemical composition is presented based on the contents of oxides present in those materials.

Table 2.3. Chemical composition of analised production residues

Oxid	GGBFS (%)	ASH (%)	RED MUD(%)
CaO	42,61	5,21	5,86
SiO_2	36,91	53,13	13,86
Al_2O_3	8,27	-	21,7
MgO	6,29	1,2	-
FeO	2,39	2,75	44,50
TiO_2	-	-	6,56
Na_2O	-	-	5,08
K_2O	-	28,27	-
P_2O_5	-	2,15	-
SO_3	-	1,47	-

2.6.2. Chemical characterization by optical emission spectrometry with inductively coupled plasma (ICP-OES)

Fig. 2.13 and Fig. 2.14 present concentration variation (in ppm) of the elements Al and Si solubilized from granulated slag, wheat straw ash and red mud. As one can see, the percentage of chemical element solubilized varies depending on the preexisting amount of Al and Si in the analyzed material, on the forming particles dimensions and on the activating solutions concentration.

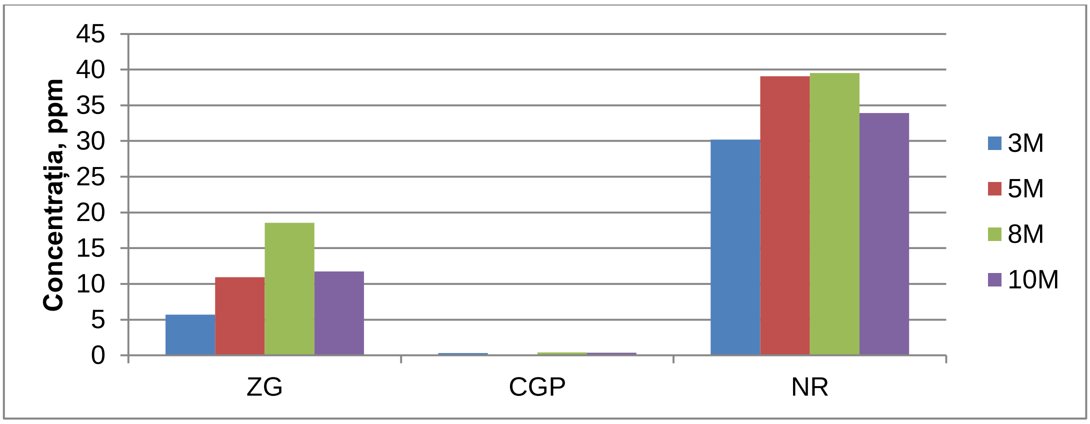


Fig 2.13. The solubilization of Al in a solution of NaOH of different concentrations

Fig. 2.14 presents the quantity of Si solubilized from analyzed materials, in a solution of NaOH of different concentrations.

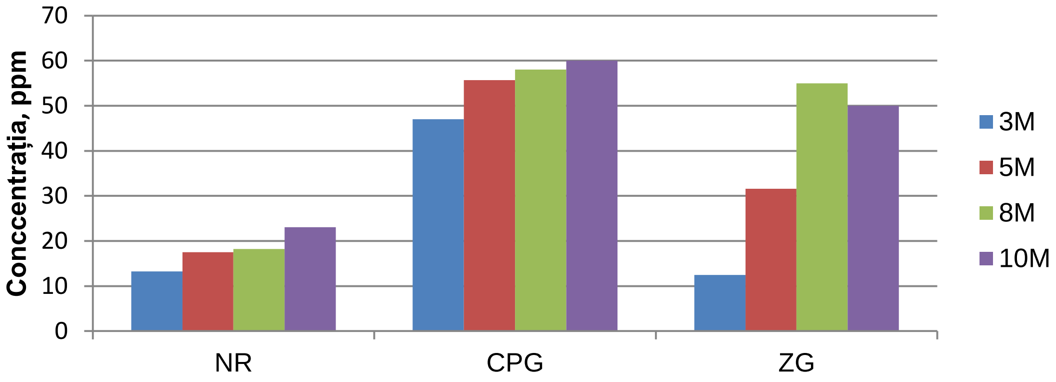


Fig 2.14. Solubilization of Si in a solution of NaOH of different concentrations

2.6.3. Chemical structure characterization of materials by Fourier Transform Infrared Spectrometry

FT-IR spectrums for the samples of granulated slag, wheat straw ash and a sample of red mud, as raw materials are presented in the Fig 2.16.

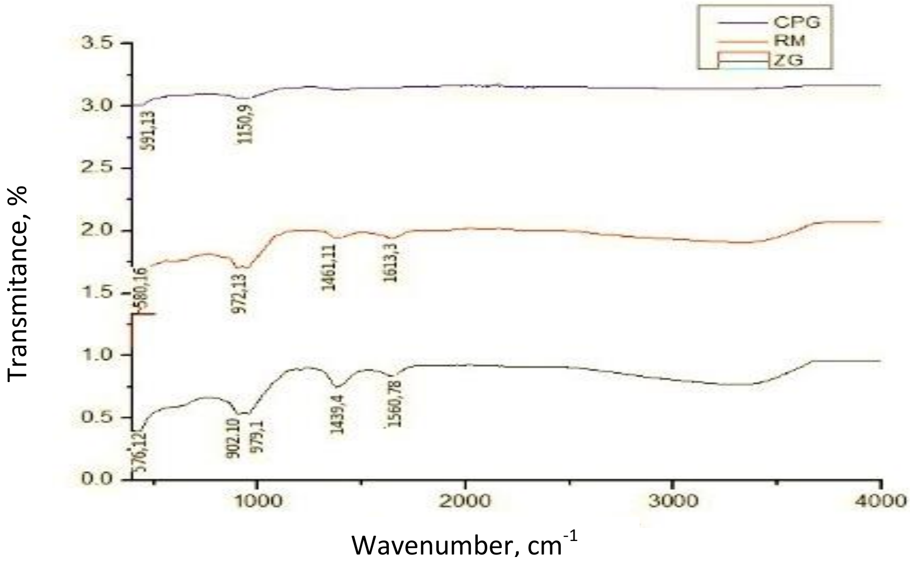


Fig 2.16 FT-IR spectrums of the analyzed samples

In these spectrums the vibration intensity corresponding to certain chemical bonds is observed.

2.7. Thermal characterization

2.7.1. Thermogravimetric characterization

Thermogravimetric analysis curves are presented in the Fig. 2.26 a) and b), and highlight the changes that occur as a result of phase transformations or formation or dissociation of chemical combinations in the sample mass.

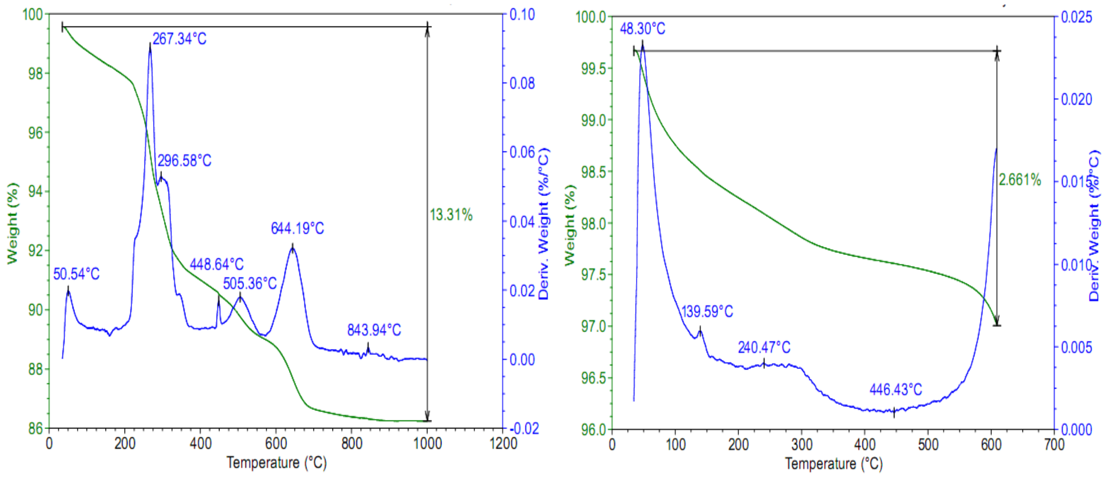


Fig 2.26. a) Curves TGA,DTA of the uncalcined red mud sample and b) of the calcined red mud sample

2.7.2 Thermal characterization by differential scanning calorimetry (DSC)

Through the DSC technique, the differential scanning calorimetric curves were plotted which have determined the thermal effects corresponding to mass transformations and modifications due to the physical and chemical decay of the compounds of the analyzed red mud. Due to this technique the interactions between the components have been rapidly evaluated based on the endothermic and exothermic peaks changes determined by the unit. The resulted curves are shown in Fig 2.29. (a) și (b) .

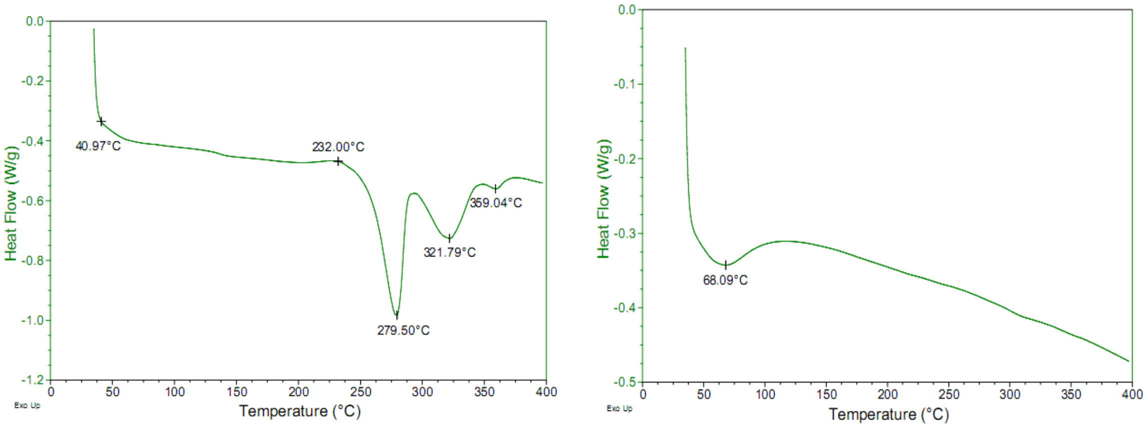


Fig 2.29.a)- The DSC curve of the uncalcined red mud sample and b)- the DSC curve of the calcined sample

2.8. XRD analysis

The resulting powder after milling was placed in a special device (Figura 2.18) and then analysed.

Figure 2.18 Sample support for XRD analysis

2.9. The characterization of materials through the SEM analysis

For the samples subjected to the SEM analysis, additional preparation was needed, as each sample was covered in a conductive layer of Au-Pt in order to facilitate the analysis. In the case of solid samples, for which the analysis is made in cross-section, they needed to be incorporated in resins, then polished and covered in the conductive layer.

In fig 2.32.; 2.33; 2.34; 2.35 we can see SEM images, EDAX spectrums as well as the distribution of elements in the samples of uncalcined red mud and calcined at 600°C.

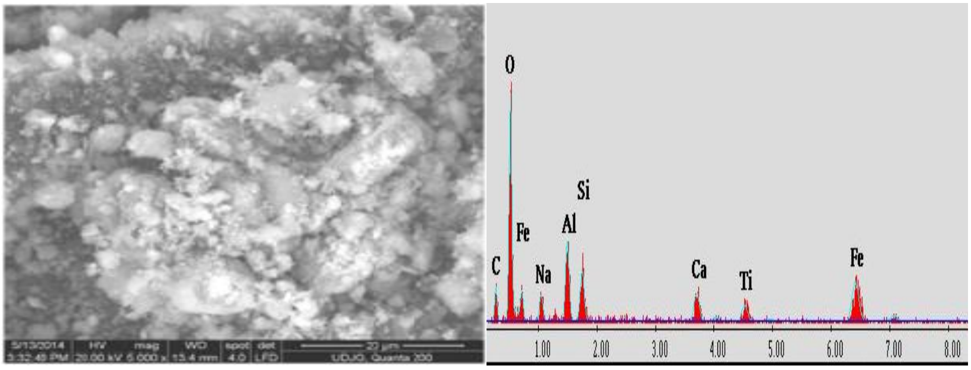


Fig 2.32. SEM Image and EDAX spectrum of the uncalcined red mud sample

Fig. 2.32 presents the SEM image and the EDAX spectrum corresponding to the uncalcined red mud sample. Analyzing the microstructure it appears that the constituent particles have various shapes and sizes, from sub-micron sized to dimensions greater than 20 µm.

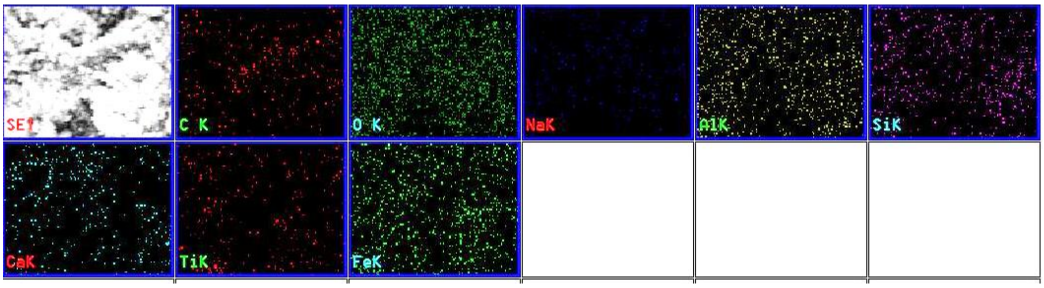


Fig 2.33 The distribution of the chemical elements in the uncalcined red mud sample

In the Fig 2.33 we can see the distribution of the chemical elements in the uncalcined red mud sample. It is observed that the elements are uniformly distributed, the element found in greatest concentration is oxygen, followed by Si and Al, elements that ensure the forming base of the geopolymer structure.

Fig 2.34. presents the SEM image and the EDAX spectrum of the red mud sample calcined at 600°C. It is noted that the particle sizes are much smaller than 20 µm, uniformly distributed, and variously shaped.

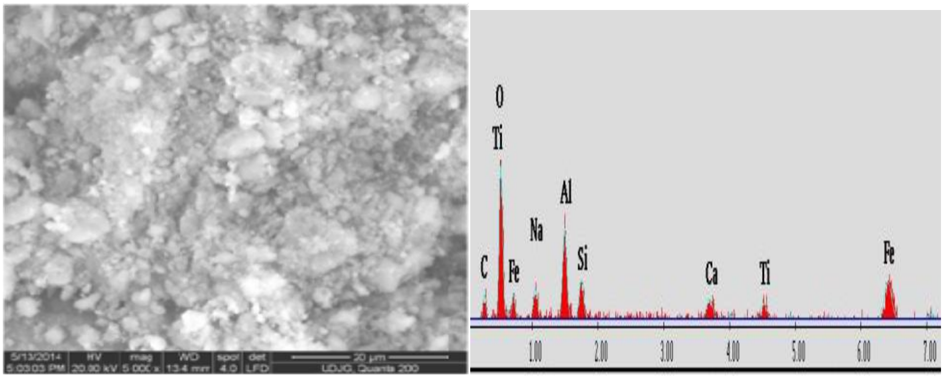


Fig 2.34. The SEM image and the EDAX spectrum of the red mud sample calcined at 600°C

Fig 2.35 presents the distribution of the chemical elements in the red mud sample calcined at 600°C.

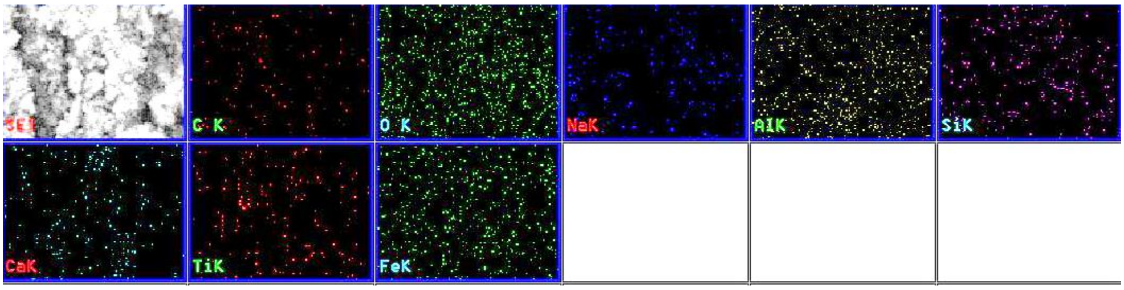


Fig 2.35 The distribution of the chemical elements in the red mud sample calcined at 600°C

2.10. Specific construction materials analyses

2.10.1. The VICAT test

This test was conducted according to the standard SR-EN 196-3 [235] to determine the setting time. While the resulted material is containing the formed geopolymer and this represents the binder that determined obtaining a construction material, this test is necessary.

2.10.2. The Le Chatelier test

Le Chatelier test [235] was carried out with the aid of special devices. The obtained fresh pulp was placed in these devices to determine the stability of the pasty material, in compliance with the STAS for a correct result of the test. The stability of the pulp was determined to appreciate the risk of the obtained material(containing geopolymers), after the alkaline activator's action on the industrial residues used, to hydrate the oxides of calcium and/or magnesium found in their chemical composition. Following the test, all recipes have stability in expansion.

2.10.3. Compressive strength analysis

One of the most important issues about the mechanical properties of the building material is the compressive strength. The test requires that the sample be conducted according to the standard into effect, EN 196-1 [236].

2.10.4. Water Absorption Test

Water absorption is an important parameter for a solid building material especially for the type of bricks. This parameter indicates the permeability of materials and shows the degree of reactivity, as depending on the degree of geopolymerization there will result a sample of material much or less porous. Water absorption increases with soaking time, softening rate decreasing with time.

2.11 Partial conclusions

1) The powdery materials used for the geopolymers synthesis were: granulated slag, red mud and wheat straw ash. Granulated slag used as a basic material in the synthesis process of a geopolymeric binder with cementitious characteristics presented a special interest in this thesis.

2) Red mud used as an additional material in obtaining different cementitious geopolymeric materials, causes a natural resource economy and a step forward in solving the environmental problem posed by storage.

3) Ash obtained by controlled burning of plant waste was used as an additional material in making cementitious geopolymeric binders, because it brings an important share of Si, an element favouring stable structures forming in the geopolymeric matrix.

4) The obtaining of geopolymers involves a series of initial operations of reducing the size by grinding and sieving. Red mud was subjected to the additional operation of calcination at 600°C, aiming to make it easier to analyze the properties of geopolymers depending on the dimensions of the solid particles.

5) In the case of the brick-red coloured mud (due to the high quantity of iron oxides), it changed after the calcination operation into an intense red due to the increased concentration of iron oxides in calcined red mud.

6) The solid materials in the recipes for the geopolymers synthesis were characterized physically performing grinding operations, sieving and/or calcination. There have been determined, the bulk density, average particle diameter and specific surface area of the raw materials.

7) In the case of the red mud sample calcined at 600°C, it was observed that the particle sizes are much lower than 20 µm, evenly distributed, and with various forms.

8) The pasty material used for the Vicat test was conducted in compliance with the required standard, and the obtained results register into the category of fast curing cements,

because the difference between the beginning of the binding and its final period was less than 30 minutes.

9) The stability of the paste was determined to appreciate the risk of the obtained material(containing geopolymers), after the alkaline activator's action on the industrial residues used, to hydrate the oxides of calcium and / or magnesium found in their chemical composition. Following the test, all recipes have stability in expansion.

10) One of the most important issues about the mechanical properties of the building material is compressive strength. The test requires that the sample be conducted according to the standard into effect, EN 196-1.

11) Water absorption is an important parameter for a solid building material. This parameter indicates the permeability of materials and shows the degree of reactivity, as depending on the degree of geopolymerization there will result a sample of material more or less porous. Water absorption increases with soaking time, softening rate decreasing with time.

CHAPTER 3. RESEARCH ON THE ALKALINE ACTIVATION OF RESIDUES GRANULATED SLAG, RED MUD AND WHEAT STRAW ASH

3.1. Motivation and experimental plan

For the obtaining and characterisation of geopolymers it is necessary to know the behaviour of production residues (granulated slag, wheat straw ash and red mud), in alkaline environment and different concentrations.

The experimental plan aimed to investigate those solid materials and the influence of the alkaline activator on the properties of the resulted materials after the alkaline activation. So, it was studied the influence of factors, such as: particle size, density, specific surface area and their distribution on the properties of the materials obtained. In pursuing this objective the raw materials, the residues used in the study, have been subjected to the action of NaOH in different concentrations and then, the resulting materials were analyzed in terms of physical, chemical and structural properties.

3.2. Material preparation

The powdery solid materials used in this study: granulated slag, wheat straw ash and uncalcined red mud were subjected to alkaline activation with sodium hydroxide at various concentrations. For ease of presentation, the following notations were used in the study: granulated slag noted ZG, wheat straw ash CPG and uncalcined red mud NR. Each solid material was mixed with the alkaline activator at a solid/liquid ratio of 0,4. Alkaline activated samples have been obtained with alkaline solutions having the concentration 3, 5, 8 and 10 molar.

3.3. Solid materials characterisation

3.3.1. Physical characterization

Fig 3.1. presents the distribution of the average dimensions as well as the particle volume for granulated slag, red mud and wheat straw ash.

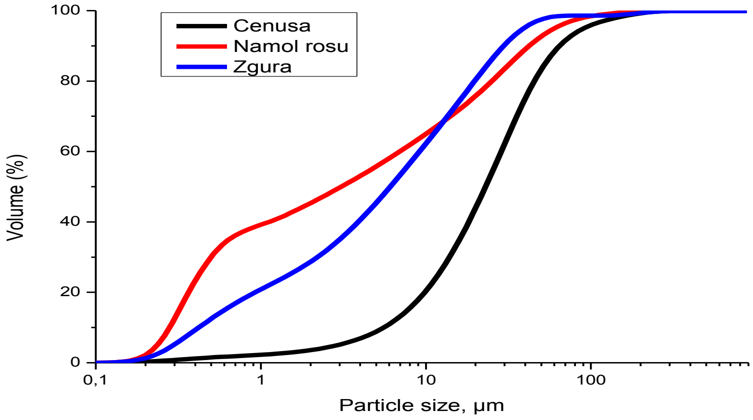


Figure 3.1. Distribution of the particles size of the production residues

3.3.2. Chemical characterization by optical emission spectrometry with inductively coupled plasma (ICP-OES)

To highlight the effect of the concentration of the used activation agent the chemical characterization by optical emission spectrometry with inductively coupled plasma (ICP-OES) was carried out. As a result of the determination there was obtained, in percent, the quantity of Si and Al solubilized in sodium hydroxide in various molarities on conducting those analyzes there have been made for sets of analyzes with 3 samples for each. Fig 3.2. presents, in percent, the quantities of Si and Al solubilized in sodium hydroxide with concentrations: 3, 5, 8 și 10 M (molar) from the used residues (granulated slag, wheat straw ash and uncalcined red mud).

3.3.4. FT-IR spectroscopy characterization

The FT-IR spectra of the samples of granulated blast furnace slag, ash from wheat straw and red mud alkaline activated (each of them) with the solution of NaOH of a concentration of 3M and 10M are shown in figures: 3.9 - 3.14. In the spectra of each activated sample, absorption bands of the vibration of specific chemical bonds in the material analysed appear. Thus, absorption bands appear in the case of asymmetric vibrations meant to deform the oxygen bounds from the corresponding Si-O tetrahedral chains which appear at 915 cm^{-1} and are specific to atoms which have not yet reacted (vibration areas 1091, 1089, 1025, 788, 683-677, 597-574 and 537 cm^{-1}) or have partially reacted, the explanation behind this being similar to other specialised literature analyses which state that it belongs to the quartz in the IR spectra. Another absorption band corresponding to intense vibration is observed at 950 cm^{-1} to 1200 cm^{-1} where it is considered as an area in which the different compounds overlap. In the area of the strip of 1091 cm^{-1} to 1025 cm^{-1}, it is assumed that the gel aluminium silicate is formed due to the formation of the new network of Si-O-T (where T = Al or Si) and a new band is put in the record at 960 cm^{-1}. In the spectrum conducted for the original slag, without the addition of activators, the band 802 cm^{-1} and 1439 cm^{-1} is associated with pure $CaCO_3$ calcium carbonate and attributed to the deformations and, respectively, the vibration plains due to the CO_3^{2-}. The intensity peak in this area is increased and may be due to the presence of calcium carbonate ($CaCO_3$) resulting from activation of the alkali.

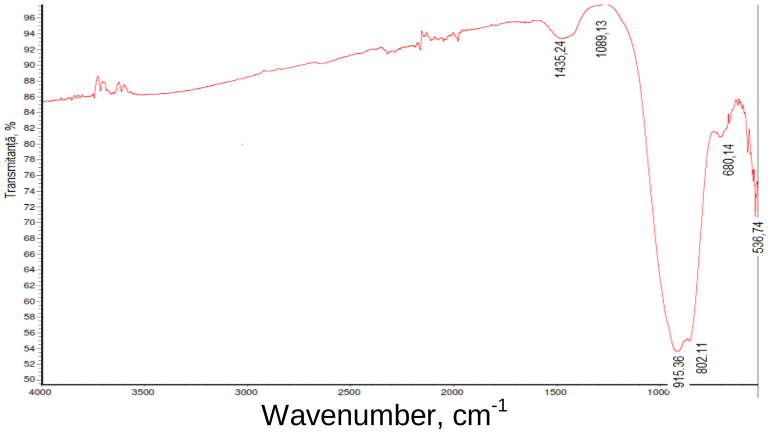


Figure 3.10 FTIR spectrum of the granulated furnace slag sample, alkaline activated with a NaOH 10M solution

In figure 3.12 the FTIR spectrum of the NaOH 10M alkaline activated red mud sample is shown.

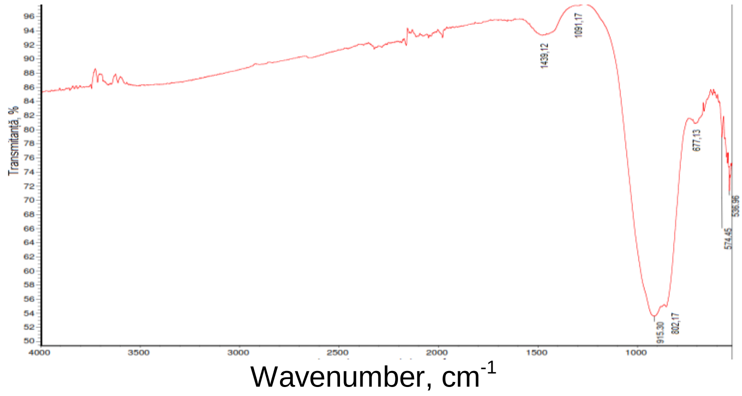


Figure 3.12 FTIR spectrum of the red mud sample, alkaline activated with a NaOH 10M solution

In the 3.14 spectrum, a new absorption band was seen, at a wave number of approximately 3410 cm^{-1} which is attributed to the valence vibration which takes place along the H-O bonds from the obtained reaction products.

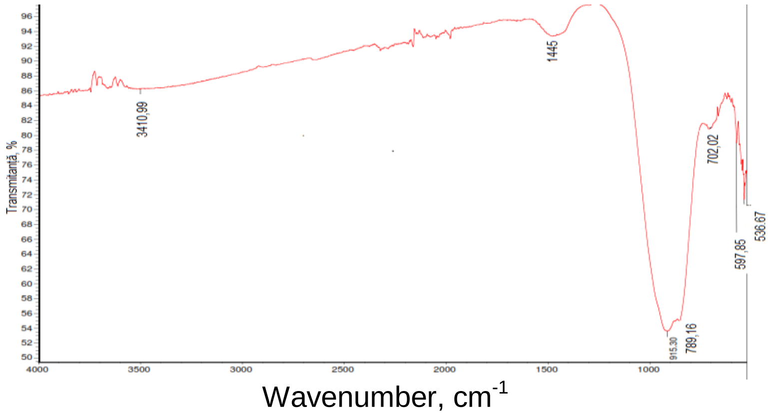


Figure 3.14 FTIR spectrum of the wheat straw ash sample alkaline activated with a NaOH 10M solution

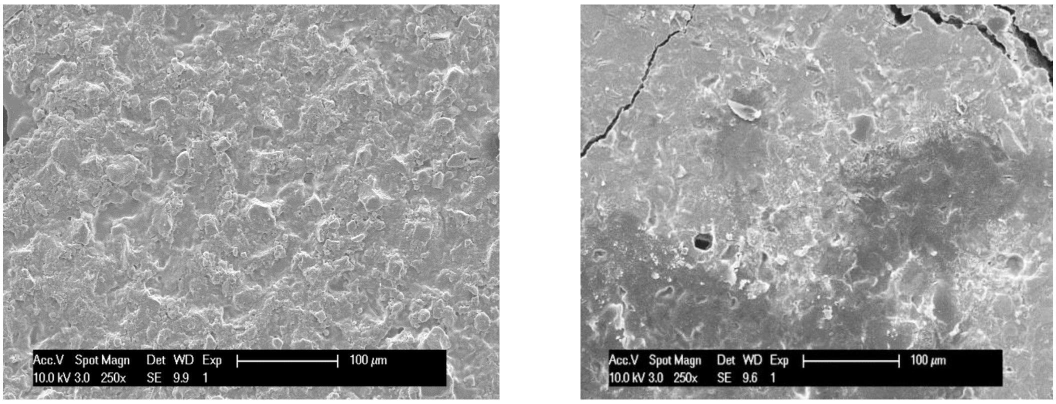
The other absorption bands owing to vibrations are positioned towards higher value wave numbers which shows the formaton of new compounds in the alkaline activated ash with the NaOH 10M concentration solution.

3.3.5. Structure characterization with Scanning Electron Microscopy (SEM)

Another method of analysis very used in the study is the analysis through microscopic electron spectroscopy, due to the accuracy of the results.

The analyses of the microstructures were performed for the samples of solid granulated slag, ash and red mud activated with the solution of NaOH in a concentration of 3M, 5M, 8M, and 10M, after a curing time of 7 days.

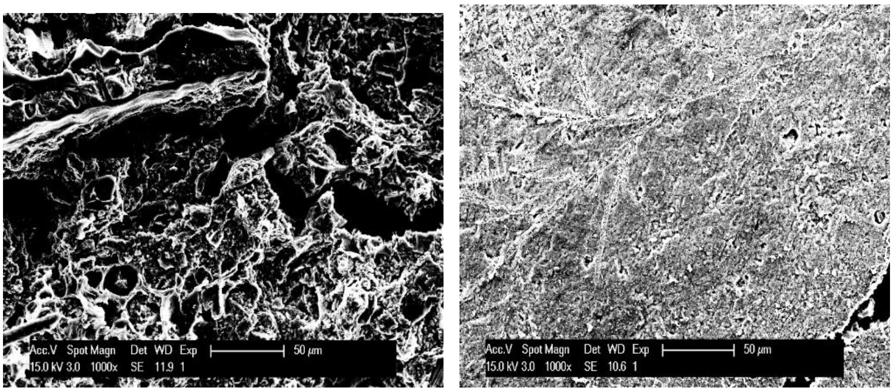
For granulated slag, which has been activated alkaline with NaOH solution of 3M concentration shown in Fig. 3.5., a matrix with homogeneous appearance can be observed.



(a) (b)

Figure 3.15 SEM images of the granulated slag activated with a 3M NaOH solution (a) and a 10M NaOH (b)

For the slag alkaline activated with a 10M NaOH solution a surface with unreacted small particles, microcavities and cracks can be observed. At a lower concentration of the NaOH (3M) alkaline activator, it has been observed that the microstructure contains more pores than the granulated slag sample activated with a 10M solution, as shown in Fig. 3.15.(b).



(a) (b)

Figure 3.16.SEM images of the wheat straw ash activated with a 3M NaOH solution (a) and a 10M NaOH (b)

By scanning microscopic samples of alkaline activated ash the resulting images are shown in Fig. 3.16. (a) and (b) respectively. In Fig. 3.16. (a) the alkaline activated with a 3M NaOh solution ash sample's micrographia is shown. In Fig 3.16. (b) the microstructure of the sample of ash activated alkaline with a solution of NaOH 10 M is represented. The solid/liquid ration in both cases is 0,40.

3.3.6. The compressive strength analysis

To observe the way in which the concentration of the solution of NaOH influence the degree of reactivity of the raw materials the test of compressive strength was performed, according to STAS 196-1 [241]. The results obtained after the completion of the test of compressive strength for samples made of a single residue tested after a hardening period of 7 days, are shown in Fig. 3.18.

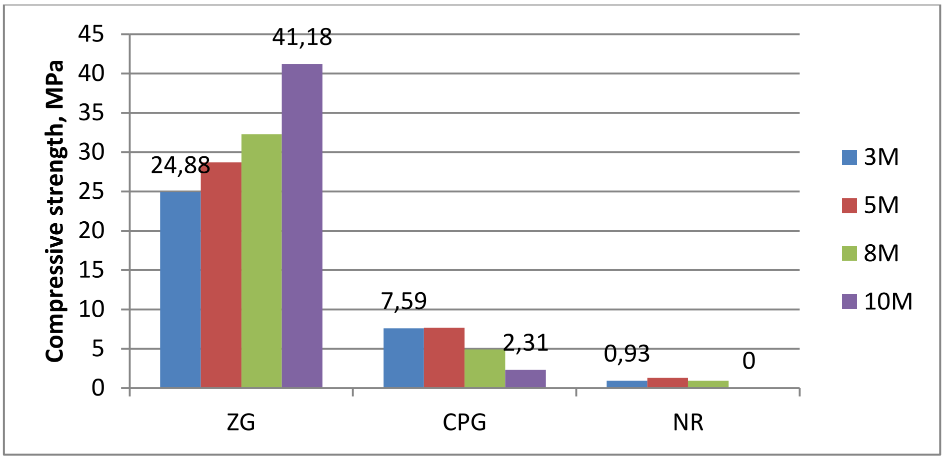


Figure 3.18. The NaOH concentration influence on compressive strength

3.4 Partial conclusions

1) The influence of the concentration of the alkali activator on the properties of the material obtained from industrial waste used in the study (blast furnace slag, uncalcined red mud and wheat straw ash) which have been subjected to the action of the solution of NaOH in different concentrations. The resulting materials were analyzed from the point of view of their physical, chemical and structural properties.

2) The physical characterization consisted of determining the distribution of the average sizes of the particles of the materials under analysis. A notable difference between the percentages of the positive displacement results on the intervals of size has been found. Granulated slag presented a homogeneous distribution in the range of 1-10 µm.

3) To emphasize the effect of the activation agent's concentration used, chemical analysis by optical emission spectrometry with inductively coupled plasma (ICP-OES) was carried out. In connection with the carrying out of the determination, the quantity – in percentage – of soluble Si and Al in sodium hydroxide at different molarities was obtained. It has been found that the percentage of the soluble chemical element differs according to the pre-existent quantity of Al and Si in the analysed material as well as the concentration of the activating solution.

4) Although in accordance with the XRF analysis, aluminum has the largest quantity, 21.7%, it seems that in the uncalcined red mud, it is in stable complex combinations, having a crystalline structure and are solubilized in a small amount of approximately 20 % for a concentration of alkaline solution of 8M. These values of soluble aluminum in red mud are much smaller than the values obtained for the slag, which emphasizes the fact that in the slag there is a high quantity of alumina in amorphous phase.

5) In the case of solubilising Si in the solutions of NaOH at different molarities the conclusion reached was that the percentage of soluble silica is approximately 20% higher in the case of furnace slag in comparison with the values obtained in the case of solubilising, for the same molarities, which is explained by the fact that silicon dioxide, SiO_2, free or linked is in much higher quantity than the content of Al_2O_3 in the chemical composition of slag and because it is present in large quantities in an amorphous phase, which allows solubilisation.

6) The compression strength test of the samples made of productions residue shows that the compressive strength differs from 41,18 MPa in the case of granulated blast furnace slag up to unsolidified samples even after 7 days as is the case of red mud alkaline activated with a NaOH 10M solution.

CHAPTER 4. EXPERIMENTAL RESEARCH ON THE OBTAINING AND CHARACTERISATION OF GEOPOLYMERS AND RESULTING MATERIALS THAT CONTAIN THE GEOPOLYMER FORMED THROUGH THE ALKALINE ACTIVATION OF TWO INDUSTRIAL WASTES MIXTURE

4.1. Motivation and experimental plan

Because during the alkaline activation of a single residue product, it was found that the chemical reactivity of the source material (ground granulated blast furnace slag, wheat straw ash and red mud) was inappropriate, a blending of these materials and a combination of these, respectively, was considered. Taking into account the fact that each of the source material comes with a certain amount of Si and Al, it was to be expected that the combination of GGBFS with wheat straw ash or mixing GGBFS with red mud will result in a geopolymeric binding material with cement-like properties. Thus, a viable technology can be achieved in order to reuse ground furnace slag as well as red mud through geopolymerisation. Because red mud's composition is scarce in silica and has high alkalinity and a high amount of alumina, the reactive silica (usually in an amorphous phase, small in dimension) will be provided by the granulated furnace slag. In the case of granulated furnace slag with added wheat straw ash, through alkaline activation of the resulted material, it was found that it can have cement-like properties because the amount of reactive silica in the ash, according to the XRF analysis is high (53,13%) to which the quantity of Al in slag (8,27%) and Na^+ of the alkaline solution are added. Following the synthesis of these two geopolymers, the influence of the chemical composition and the obtaining temperature on compressive strength of the final geopolymeric product was determined.

4.2. Geopolymer synthesis

The synthesis process of the geopolymers had in sight the blending in twos of the source materials stated in the research program, which were alkaline activated with a 8M NaOH solution and a Na_2SiO_3, so that a solid/liquid ratio of 0,40 was ensured. The mixture was then blended for more than 15 minutes to secure the necessary time for the specific geopolymerisation reactions to develop, having as a result the formation of the geopolymeric material, a paste with the appropriate consistency. The first recipe was carried out by mixing 85% or 95% granulated blast furnace slag (the basis of the geopolymer) and red mud in 15% and 5%, respectively. For the second recipe, granulated furnace slag was used 85% to 95% to which wheat straw ash was added in 15% and 5%, respectively and activated with the same solution.

In table 4.1 the quantities of the source materials and activator used in the formation of the geopolymer as well as the temperatures at which the thermic treatments were carried out for these amples were noted.

Table 4.1 The characteristics of the basic recipe mixtures

Sample	GGBFS (%)	ASH (%)	RM (%)	NaOH/ Na_2SiO_3 (%)	S/L	T (°C)
GGBFS/ASH(15)	85	15	-	50/50	0,4	20, 40, 60
GGBFS/ASH(5)	95	5	-	50/50	0,4	20, 40, 60
GGBFS/RM(15)	85	-	15	50/50	0,4	20, 40, 60
GGBFS/RM(5)	95	-	5	50/50	0,4	20, 40, 60

4.3. Characterising the synthesised geopolymers

4.3.1. Physical characterisation

To characterise obtained geopolymers based on the set recipes in the research plan previously formed, physical analysis was carried out on the solid materials which laid the foundation to the synthesis of geopolymers and whose results are noted in table 4.2.:

Table 4.2 Physical properties of waste used in obtaining geopolymers

Proprieties	GGBFS	ASH	RM
Bulk density (g/cm^3)	2,8801	2,3813	2,6715
Specific surface area (g/cm^2)	4,2653	0,9115	7,5210
Color	White-gris	Black	Red
Main diameter ,D_{50} (μm)	45,2	22,06	10,28

4.3.2. Chemical analysis of source materials

The following table presents the oxidic composition of source materials used in the study determined through XRF:

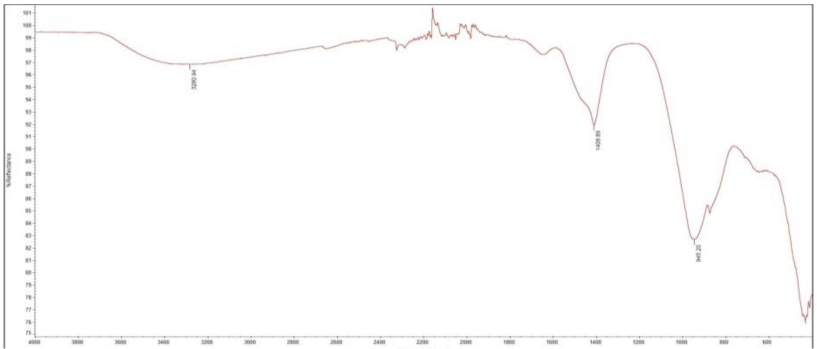
Table 4.3 Oxidic chemical composition of industrial waste

Oxid	GGBFS (%)	ASH (%)	Red Mud (%)
CaO	42,61	5,21	5,86
SiO_2	36,91	53,13	13,86
Al_2O_3	8,27	-	21,7
MgO	6,29	1,2	-
FeO	2,39	2,75	44,50
TiO_2	-	-	6,56
Na_2O	-	-	5,08
K_2O	-	28,27	-
P_2O_5	-	2,15	-
SO_3	-	1,47	-

The chemical composition was determined with the help of XRF spectometry, which indicates a high quantity of calcium oxide in blast furnace slag (42,61%) compared to the quantity in ash (5,21%) as well as in the red mud (5,86%).

4.3.4. FT-IR analysis

This study determines the changes that occured because of the physical and chemical processes which take place in the geopolymers, changes which can be seen on the FT-IR spectrum. The FT-IR spectres of alkaline activated (8M NaOH and Na_2SiO_3, in equal quantities) are comparable to previous publishings [114, 121, 246]. From the spectrum in figure 4.7, an absorption band of wide lengths can be observed, whose maximum intensity is associated with the highest peak at a length of 945 cm-1, band which is attributed to the deformation vibration of Si-O bonds, or represent a weak absorption band for Si-O-Al type structures [264].



Wavenumber, cm^{-1}

Figure 4.7 FT-IR spectrum of geopolymer material samples, noted ZG95/CPG5(60)

Figure 4.8 presents the FT-IR spectrum of the geopolymer material obtained with granulated blast furnace slag 95% and red mud 5% alkaline activated with a 8M NaOH mixed with Na_2SiO_3, solution in an equal ratio.

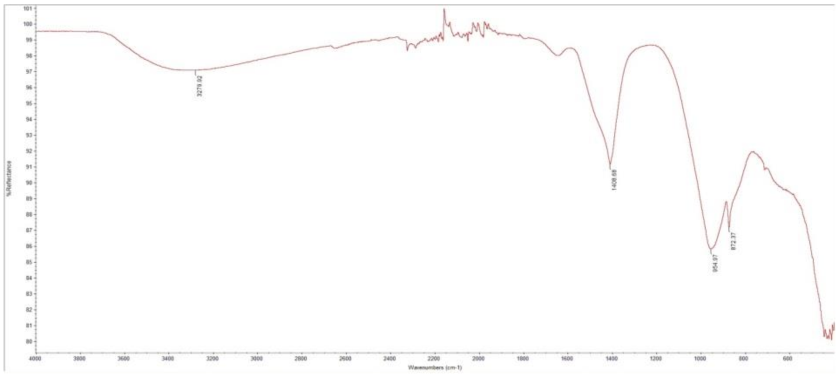


Figure 4.8 FT-IR spectrum of geopolymer material sample, noted ZG95/NR5(60)

Also, the absorption band situated at 872 cm^{-1} wave number is showed to the presence of the appropriate absorption bands and vibrations of the carbon atom composites, CO_2^{3-} ions. These results are in accord with the results obtained in study [36] and the XRD analysis results.

4.3.5. Thermal analysis (TG and DTG)

In the case of ZG85/NR15 made at 20°C and the one treated at 60°C, it was observed that the sample noted ZG85/NR15 cured at 20°C experienced a loss of mass of 15,54% and for the sample noted ZG85/NR15 treated thermically at 60°C the registered mass loss was 17,71%.

The quickness with which the physically and chemically bonded water migrates and evaporates leads to microfisures in the geopolymeric matrix, which induces the degradation of the geopolymer between the temperatures of 100 and 300°C.

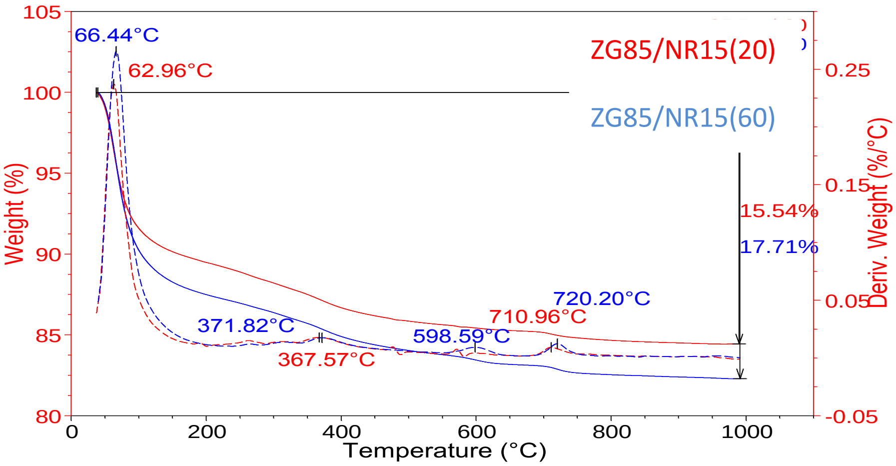


Figure 4.9 Curves regarding the TG and DTG analysis for the geopolymer material sample noted ZG85/NR(15)20 and the sample named ZG85/NR(15)60

For the samples that contain granulated furnace slag (85%) and wheat straw ash (15%) noted ZG85/CPG15 cured at a temperature of 20°C and 60°C the thermogravimetric curves are presented in Figure 4.8. The correspondent temperature peaks of approximately 69°C and 71°C are attributed to the loss of physically bound water in the strucuture of the analysed material.

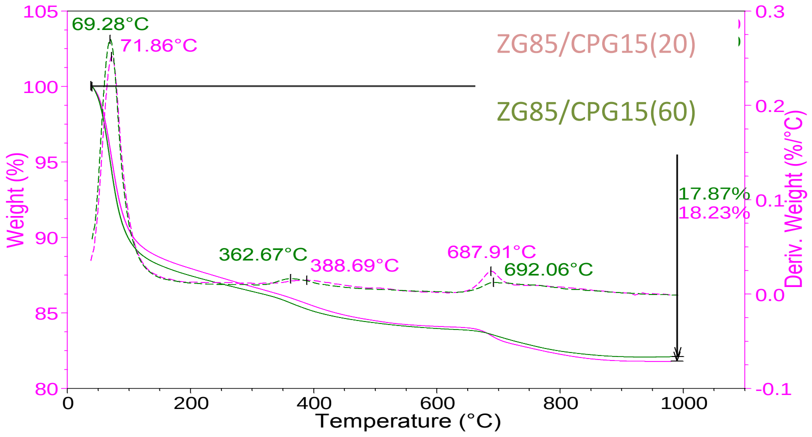


Figure 4.10 Curves regarding the TG and DTG analysis for the geopolymer material sample noted ZG85/CPG(15)20 and the sample noted ZG85/CPG(15)60

4.3.6. Chemical and structural analysis through SEM and EDX

Figure 4.11 presents the SEM image and EDAX spectrum of the geopolymer material sample named ZG85/CPG15 at 20°C. As observed in the figure, the gel matrix has a rough surface and some partially reacted particles leading to the formation of the geopolymer gel and presents minor fisures and pores.

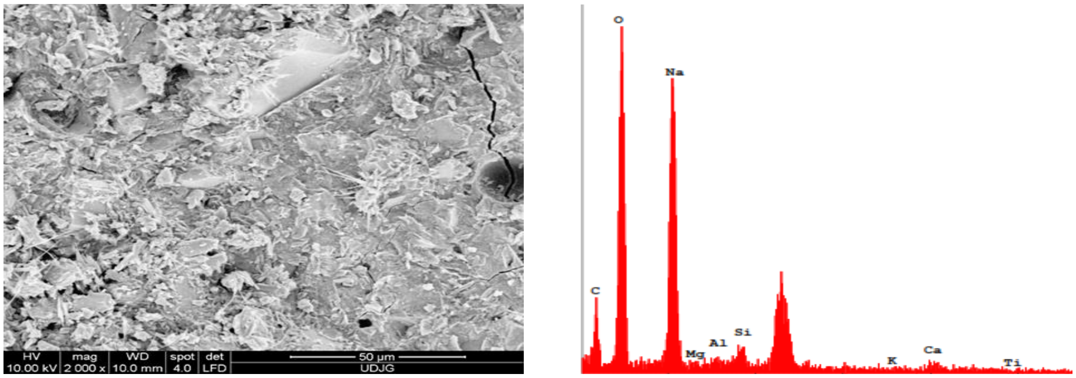


Figure 4.11 SEM image and EDAX spectrum of the geopolymer material sample noted ZG85/CPG15 at 20°C.

Figure 4.12 depicts the distribution of chemical elements for the geopolymeric material sample noted ZG85/CPG15 synthesised at room temperature, 20°C. It can be observed that the chemical elements are uniformely distributed in the gel matrix. In this case the Si/Al ratio was 5,99 which influenced the compressive strength of the sample which lead to it having the lowest value.

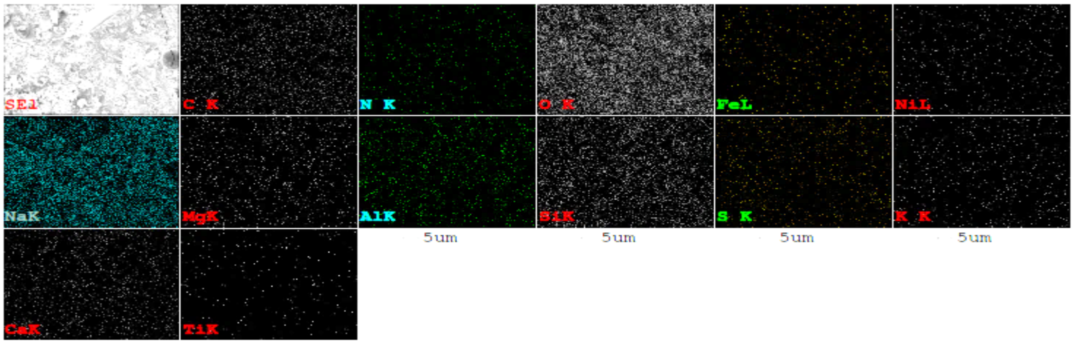


Figure 4.12 Distribution of chemical elements for the geopolymeric material sample noted ZG85/CPG15 at 20°C

Figure 4.13 presents the microstructure and EDAX spectrum of the geopolymeric material sample obtained with 85% granulated furnace slag and 15% ash thermically cured at 60°C. The image presents an unhomgenious microstructure of the sample and unreacted particles caught in the geopolymeric matrix which contains the resulting reaction products after the alkaline activation. A continuous gel microstructure with fisures and microcavities created by the evaporated water during the curing treatment can be observed.

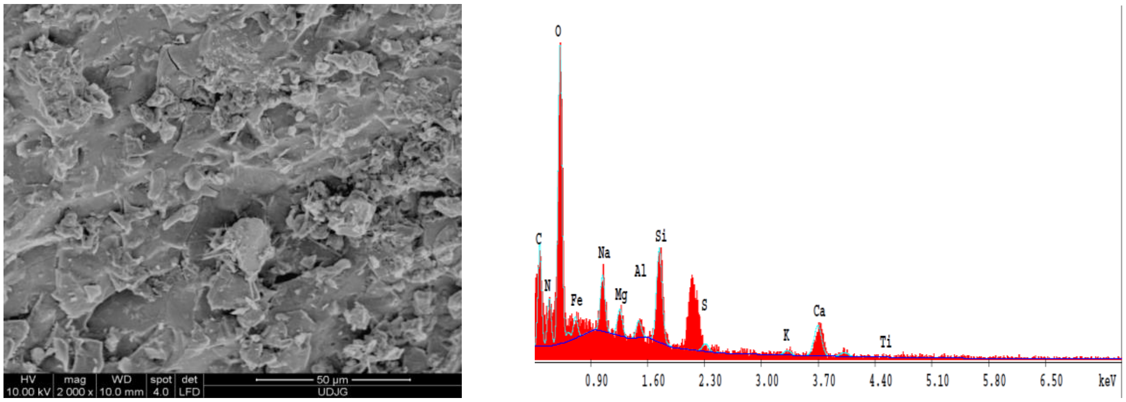


Figure 4.13. SEM image and EDAX spectrum for sample with geopolymer material noted ZG85/CPG(15), at 60°C

As far as the EDAX spectrum is concerned, the oxygen in the resulting matrix is predominantly next to important quantities of Si, Al and Na. In that case, the Si/Al ratio from the reacted product is 5,25 which means weak geopolymerisation of the blend that is in accordance with results obtained by other researchers. [254]

Figure 4.14 represents the distributon of the chemical elements for the geopolymeric material sample noted ZG85/CPG15(60).

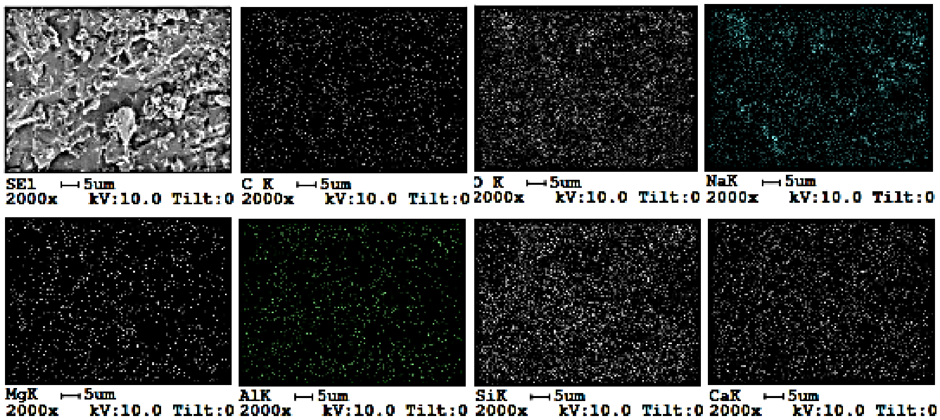


Figure 4.14 The distribution of the chemical elements for the geopolymeric material sample noted ZG85/CPG15 at 60°C

The map of chemical elements distribution in the analysed sample shows that oxygen is dominant, followed by Si and Al. In this case the Si/Al ratio is 5,10 which is reflected in the rate of geopolymerisation, significantly higher than the one cured at 20°C.

In figure 4.15 the SEM image and EDAX spectrum for the geopolymeric material obtained with 95% granulated furnace slag and 5% wheat straw ash at a temperature of 20°C.

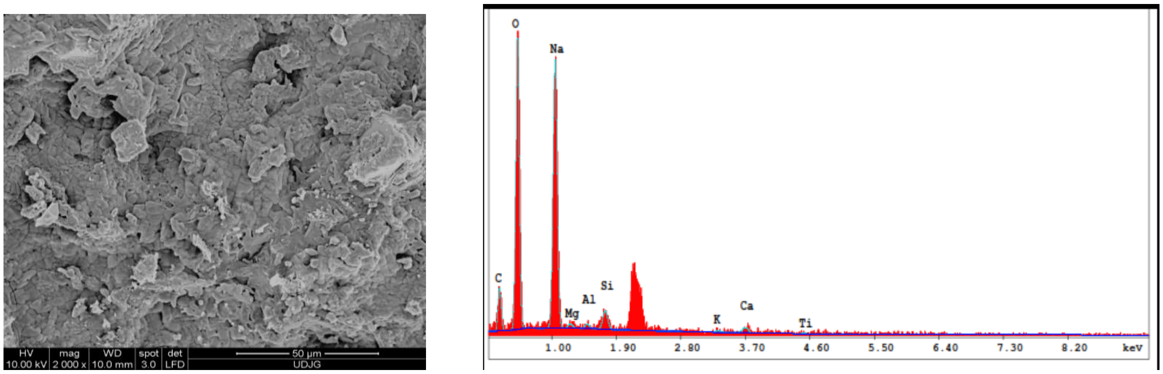


Figure 4.15 SEM image and EDAX spectrum of the geopolymeric material sample noted ZG95/CPG5 at 20°C(2000x)

Figure 4.16 represents the distribution of chemical elements for the geopolymeric material obtained with granulated furnace slag (95%) and wheat straw ash (5%) at a temperature of 20°C.

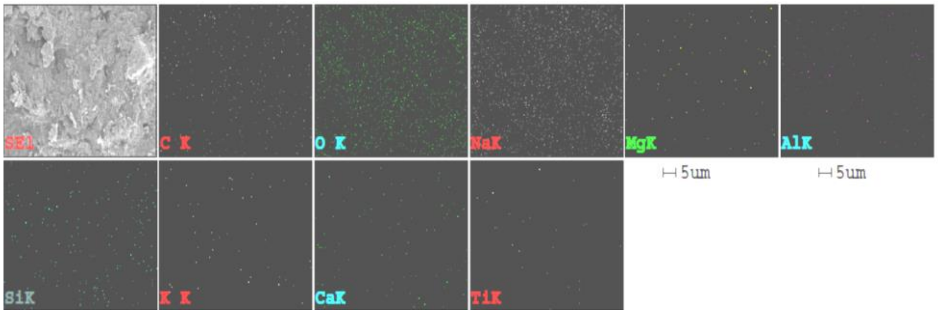


Figure 4.16 Distribution of chemical elements for the noted ZG95/CPG5(20) geopolymeric material

Figure 4.17 shows the SEM image and EDAX spectrum for the geopolymeric construction material obtained from granulated furnace slag(95%) and wheat straw ash(5%) thermically treated at a 60°C temperature.

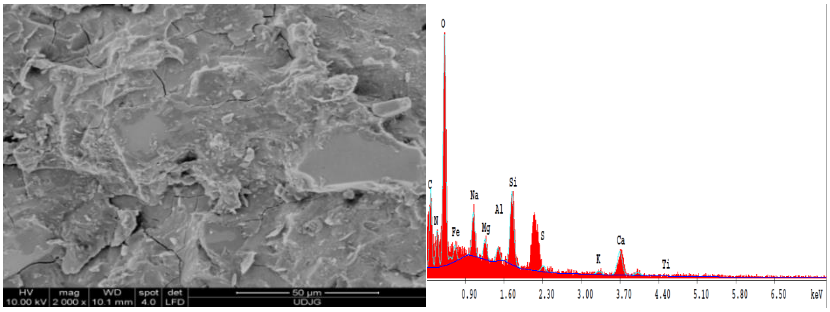


Figure 4.17 SEM image and EDAX spectrum of the noted ZG95/CPG5(60) geopolymeric material sample

In figure 4.18 the main element distribution in the noted ZG95/5CPG thermically treated at 60°C is presented.

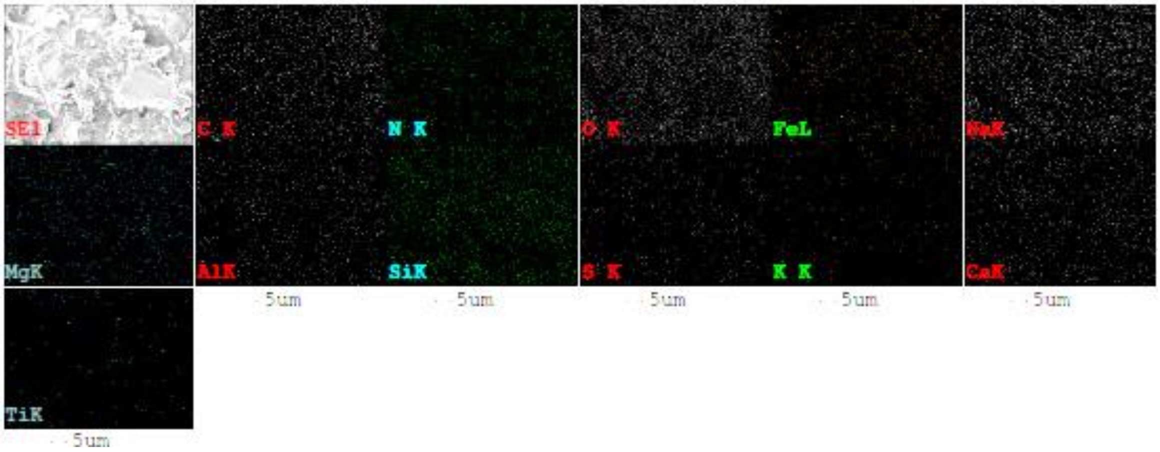


Figure 4.18 Chemical elements distribution for the geopolymeric material sample noted ZG95/CPG5 at 60°C

Figure 4.19 shows the SEM image and EDAX spectrum for the geopolymeric material sample obtained from granulated furnace slag (95%) and red mud (5%) noted ZG95/NR5, synthesised at a temperature of 20°C. The microstructure image presents a rough surface but continuous, containing a gel of unreacted or partially reacted particles.

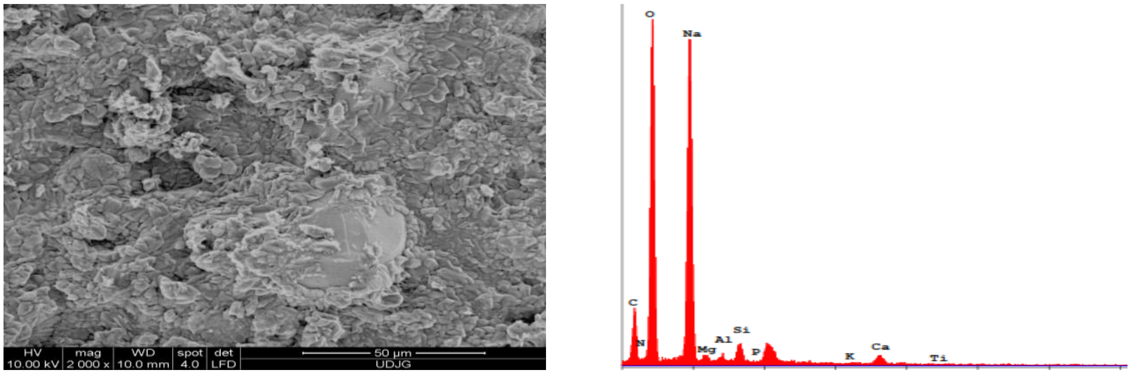


Figure 4.19 SEM image and EDAX spectrum of the geopolymer material sample noted ZG95/NR5 at 20°C.

Figure 4.20 presents the chemical elements distribution in the geopolymeric material sample noted ZG95/NR5, synthesised at a 20°C temperature.

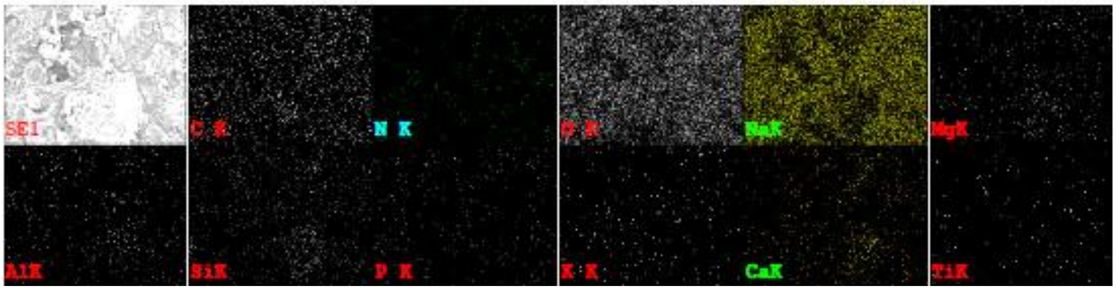


Figure 4.20 Chemical elements distribution for the geopolymeric material sample noted ZG95/NR5 at 20°C.

Figure 4.21 presents the SEM image and EDAX spectrum of the geopolymeric material noted ZG95/NR5, at 60°C.

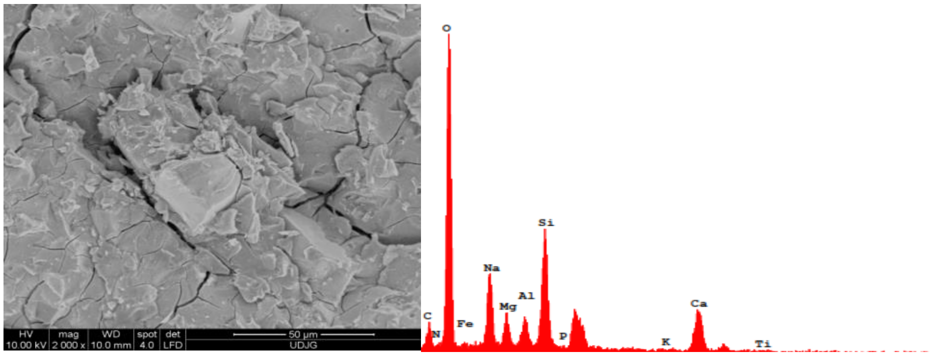


Figure 4.21 SEM image and EDAX spectrum of the geopolymeric material sample noted ZG95/NR5, at 60°C.

In figure 4.21, the matrix can be seen as loose and fisured due to the tension created by the compressive strength test or the vacuum owed to the preparation for the SEM analysis, or thermic treatment.The structure is gel-like and contains little amounts of unreacted particles. From the EDAX spectrum, the main element is oxygen followed by silica, sodium and aluminium, elements directly involved in the formation of the geopolymer structure.

In figure 4.22 the chemical element distribution for the geopolymer material sample noted ZG95/NR5 thermically treated at 60°C can be observed.

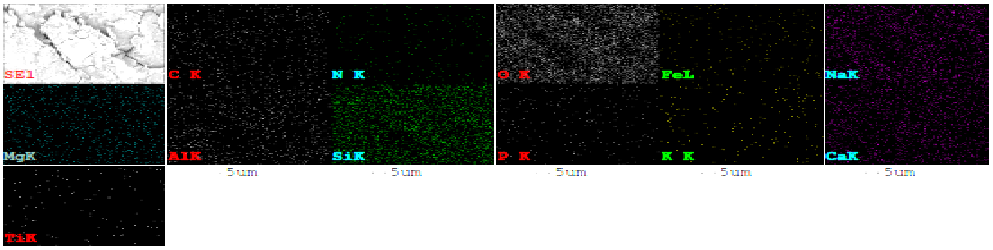


Figure 4.22 Chemical distribution of elements for the geopolymeric material sample noted ZG95/NR5, at 60°C.

On the map of the distribution of chemical elements a smooth dense distribution can be seen, which is in accordance with other studies which assert that a homogenous and dense distribution of elements is characteristic to the structure of gepolymers. [258]

Figure 4.23 presents the SEM image and EDAX spectrum of the geopolymeric material sample, noted ZG85/NR5, synthesised at 20°C. The microstructure of this sample shows a gel-like matrix with small unreacted parcticles, as well as needle-shaped particles owed to the presence of cabon in the structure or the presence of re-crystallised NaOH.

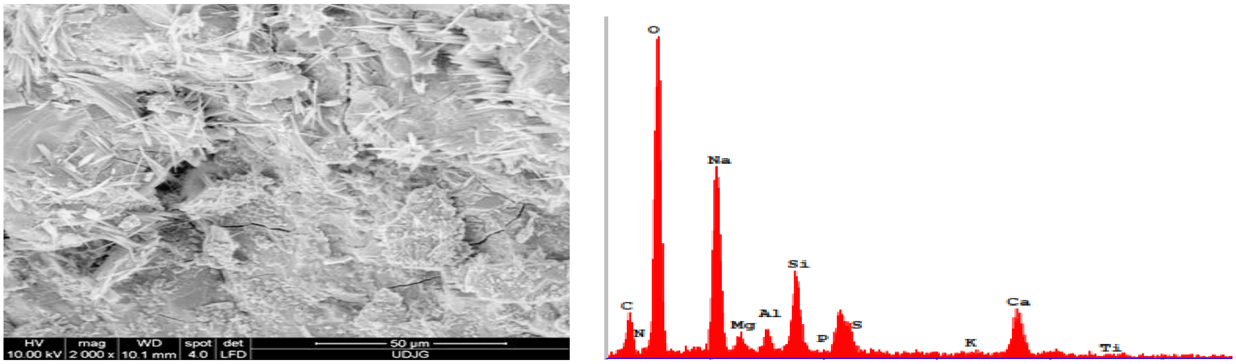


Figure 4.23 SEM image and EDAX spectrum of the geopolymeric material sample noted ZG85/NR15 at 20°C.

As seen in the EDAX spectrum, the sodium amount is substantial, a case encountered in the slag and ash(for the same quantity of ash, 15% and the same synthesis temperature of 20°C). The presence of the carbon phase has not had a negative impact on the compressive strength of the samples, which has been encountered in other studies as well [259]

In Figure 4.24 the chemical element distribution is presented for the geopolymeric material noted ZG85/NR15 obtained at 20°C. It can be observed that the elements are distributed quite uniformely in the created matrix, and the Si/Al ratio is lower, 3,77, which favourises the formation of silico-aluminates in the system.

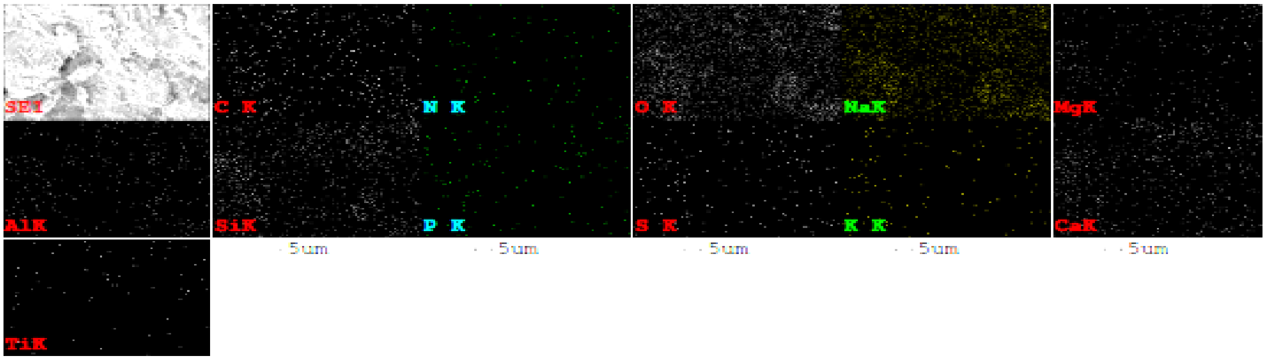


Figure 4.24 Chemical elements distribution for the geopolymeric material sample noted ZG85/NR15 at 20°C

Figure 4.25 describes the SEM image and EDAX spectrum of the geopolymeric material sample noted ZG85/NR15 which underwent thermic treatment at 60°C. In this case the matrix can be observed to be compact, with little unreacted particles and fisures. Also, from the EDAX spectrum it seems that the matrix has a high content of oxygen as a main element as well as others such as sodium and silica.

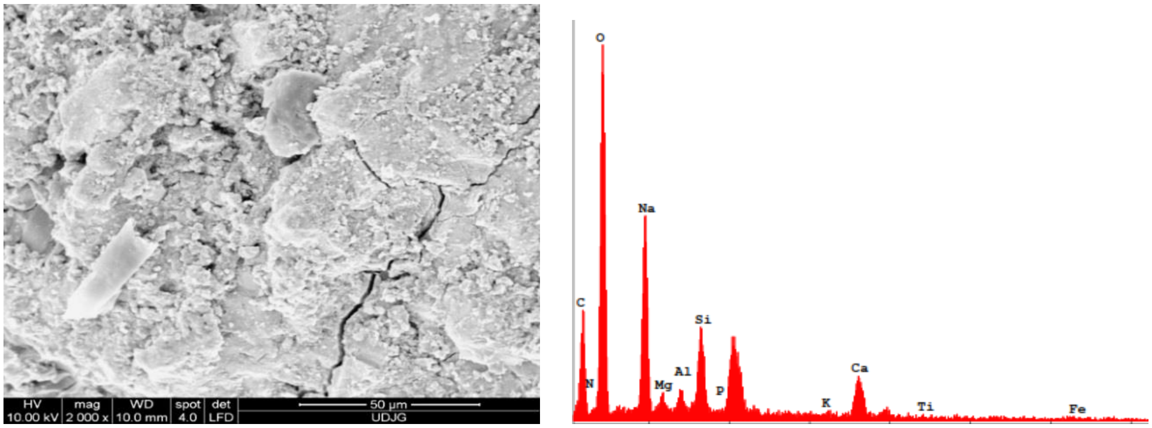


Figure 4.25 SEM image and EDAX spectrum of the geopolymeric material noted ZG85/NR15 at 60°C

In the microstructure in figure 4.25 the presence of carbonates cannot be observed, given the fact that the sample was thermically treated and the geopolymeric reactions have developed quickly within the system making the sodium engage in complexe bonds such as N-A-S-H(N=Na2O, A=Al2O3, S=SiO2 and H=H2O), combinations which are specific to the geopolymeric gel created especially at temperatures over 60°C [259].

Figure 4.26 presents the distribution of chemical elements for the sample noted ZG85/NR15 which went under the synthesising treatment at 60°C.

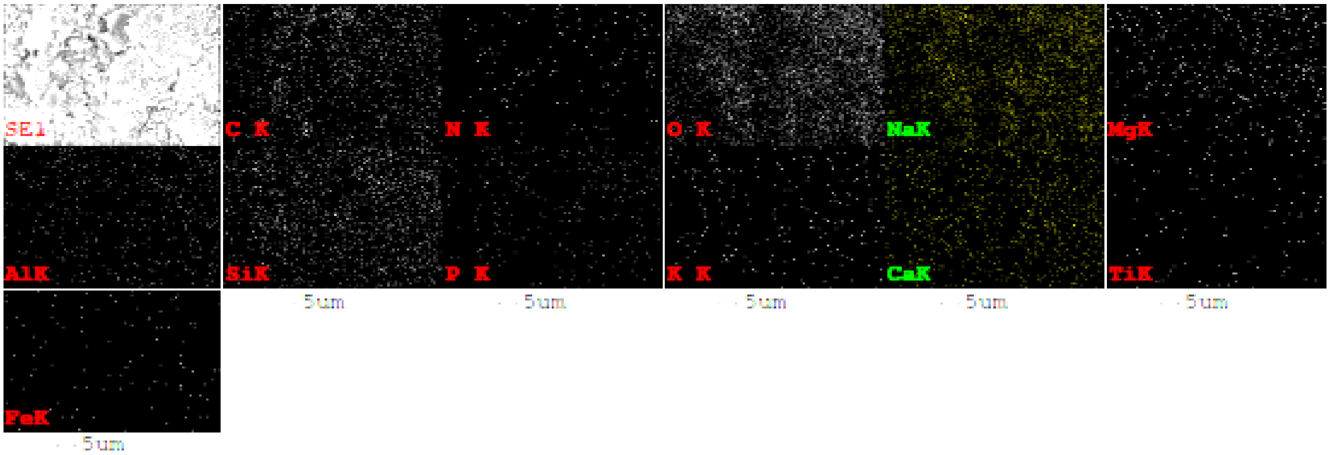


Figure 4.26 Chemical elements distribution for the geopolymeric material sample noted ZG85/NR15 at 60°C

4.3.7. Compressive strength analysis

The highest compression strength value was obtained for the geopolymeric material corresponding to the sample noted ZG95/NR(5)60 is 124,33 MPa which marks a difference of approximately 54% to the sample noted ZG95/CPG(5)60 with only 68 MPa.

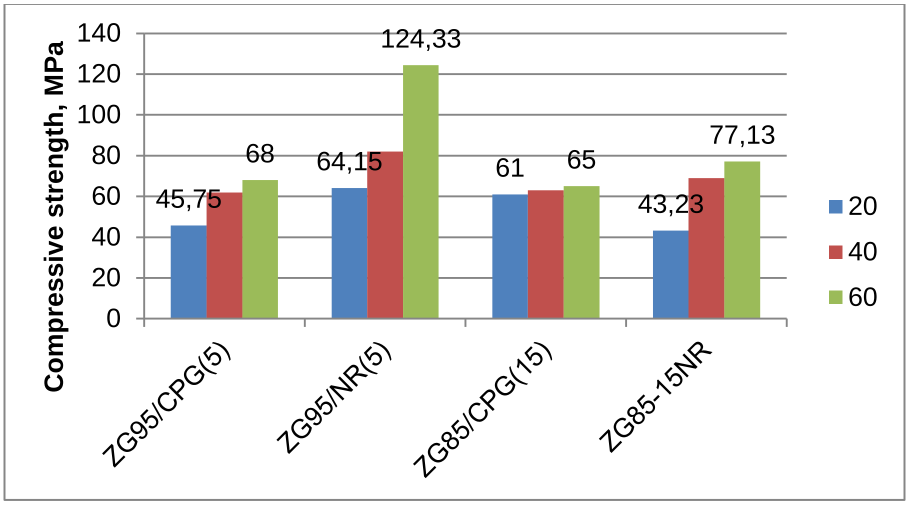


Figure 4.27. The influence of slag quantity and drying temperature on compressive strength

4.3.8. Water absorption analysis

In this study, the water absorption analysis was carried out for the paste obtained with 85% and 95% of granulated furnace slag blended with wheat straw ash (5% and 15%) and red mud (5% and 15%), the resulting values being between 2,13 – 0,9%. The powder blend was alkaline activated with the solution obtained through mixing a 8M NaOH solution with a Na2SiO3 solution at a 50% ratio each (mass percentage). The analysis was done on samples obtained at room temperature (20°C) as well as thermically cured at 40°C and 60°C, respectively. The obtained results after the test drive are presented in figure 4.28.

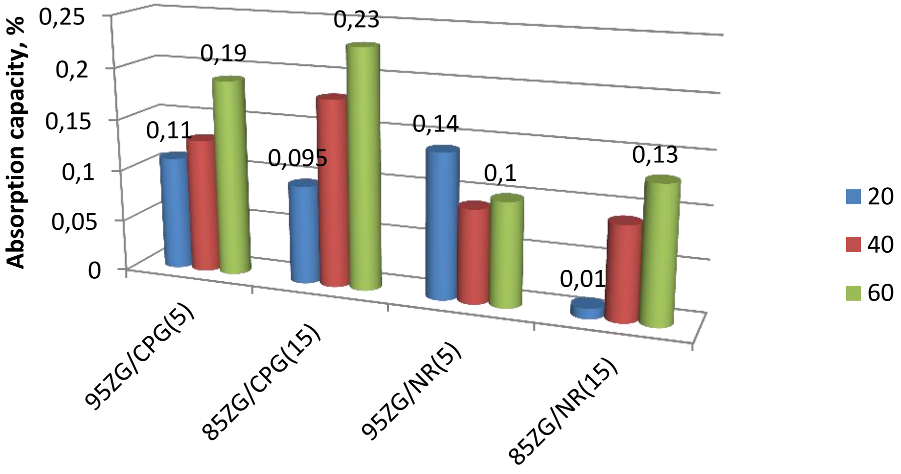


Figure 4.28 Results of water absorption test, 7 days' analysis

In figure 4.28 the water absorption test results are presented, in perecentages which was carried out on the basis of the ASTM C642-13 standards [237].

4.4. Partial conclusions

1) Due to the fact that alkaline activation of a single industrial waste has proven to be of inadequate chemical reactivity to the source materials (granulated furnace slag, wheat straw ash and red mud), the combination of two materials was taken into account.

2) After the synthesising of the two geopolymers by mixing them in pairs of two wastes and alkaline activated with a NaOH solution with a 8M and a Na_2SiO_3 solution so that a liquid/solid ratio of 0,40 is ensured, the resulted products were analysed physically, chemically, minerally, structurally, thermically and their respective compressive strength.

3) Through the chemical characterisation it was found that the granulated blast furnace slag presents a density of 2,8801 g/cm^3, a specific surface of 4,2653 g/cm^2 and an average diameter of 45,2 µm. For the wheat straw ash, the determined values are: the density equals 2,3813 g/cm^3, the specific surface area is 0,9115 g/cm^2 and the average diameter is 22,06 µm. The value of red mud density is 2,6715 g/cm^3, a large specific surface of 7,5210 g/cm^2 for the average particle diameter of 10,28 µm.

4) For the FTIR of the geopolymer material noted ZG95/NR(5)60 the absorption band specific to the corresponding vibration of the 3279 cm^{-1} is owed to the deformation vibration of the covalent bonds, specific to the H-O-H molecules. The wide absorption band situated near the value of 954 cm^{-1}, is characteristic to the geopolymeric gel based on a calcim aluminosilicate hydrate C-(A)-S-H, which confirm the XRD analysis results as well as the high compressive strength.

5) In the case of the geopolymer material noted ZG85/NR15, made at 20°C and the one cured at a temperature of 60°C, following the thermic analysis carried out, it was found that a mass loss of 15,54% for the ZG85/NR15 at a 20°C temperature was registered, while the mass loss for the sample noted ZG85/NR15, thermically treated at a temperature of 60°C was 17,71%. The explanation behind the approximately 2% difference between the samples can be put down to the fact that the sample cured at 60°C had already gone through a loss of physically bound water in a certain amount.

6) For the geopolymeric material noted ZG85/CPG15 at 20°C, the matrix containing the formed geopolymer has a rough aspect and some partially reacted particles with an alkaline solution were higlighted leading to the formation of the polymeric gel with fisures and pores.

7) The microstructure of the geopolymeric material noted ZG85/NR15 at 20°C was observed to have a matrix which contains the geopolymer with small, unreacted particles as well as needle-shaped particles, owing to the presence of cabon in certain amounts in its structure of the presence of re-crystalised NaOH. The presence of the carbon phase did not have a negative impact on the compressive strength of these samples.

8) The microstructure of the geopolymer sample ZG85/NR15 at 60°C was observed to have a compact matrix, with small unreacted particles and cracks. Also, from the EDAX spectrum it seems that the matrix has a high quantity of oxygen as a main element as well as

9) The highest value of compressive strength was registered to be for the geopolymer with the recipe noted ZG95/5NR(60) – 124,33 MPa – and a difference of 54% can be observed between that and the sample noted ZG95/CPG(5)60 with 68 MPa.

10) As far as the capacity to absorb water at a temperature of 60°C, it was observed that both red mud samples scored a lower rate of absorption, by approximately 25% compared to the samples made with wheat straw ash.

CHAPTER 5. THE EXPERIMENTAL RESULTS REGARDING THE OBTAINING AND CHARACTERISATION OF GEOPOLYMERS AND RESULTING MATERIALS WHICH CONTAIN THE GEOPOLYMER FORMED THROUGH ALKALINE ACTIVATION OF A BLEND BETWEEN THREE INDUSTRIAL WASTES

5.1. Motivation and experimental plan

Experimental reseach regarding the obtaining of geopolymers through alkaline activation of two industrial wastes used in the study in different quantities have shown that a geopolymeric material with a compressive strength comparable to those of present-day construction materials can be obtained. In this study, a trial has been done to obtain a geopolymeric material through the blending of the three proposed materials in the research plan, in different combinations and alkaline activated with two types of activators. For the blending based on the recipe of 50% slag, 20% red mud and 30% wheat straw ash, alkaline activated with a NaOH solution, the name used is R50. The geopolymer noted R70 was obtained through the mixing of 70% slag, 20% wheat straw ash and 5% red mud, alkaline activated with a NaOH solution.

5.2. The obtaining of geopolymers through the blending of slag/ash/red mud

In this sense, the possibility of blending the three materials in different proportions alkaline activate with two solutions, the geopolymerised materials later being tested to determine the compressive strength after 7 and 28 days of curing. The labeling of the samples, the industrial waste ratios, the alkaline activator as well as the testing time for compressive strength are presented in brief in table 5.1.

Table 5.1 Sample labelling, waste proportions, alkaline activator concentration and testing period for compressive strength

Sample	GGBFS (%)	ASH (%)	Red Mud (%)	NaOH (Molar)	Testing time (days)
R50Na	50	30	20	3, 5, 8, 10	7
R70Na	70	25	5	3, 5, 8, 10	7

Thus, the geopolymeric materials corresponding the R50 recipes, which was formed by mixing 50% granulated furnace slag, 30% wheat straw ash, 20% red mud; R70 in return is made of 70% granulated furnace slag, 25% ash and 5% uncalcined red mud. Both recipes are activated with a sodium hydroxide solution with a concentration of 3M, 5M, 8M and 10M.

A second set of tests was carried out with the same recipe but alkaline activated with a solution obtained through blending a sodium hydroxide solution with a concentration of 8M and a sodium silicate solution in equal propportions to determine the influence of the alkali activator on the compressive strength. The labelling of the samples, the proportions of industrial waste, the alkali activator used in the activation of the different solutions as well as the testing period of compressive strength is presented in table 5.2.

Table 5.2 Sample labelling, waste proportions, alkaline activator concentration and testing period for compressive strength

Sample	GGBFS (%)	ASH (%)	RED MUD (%)	NaOH(%)	NaOH/ Na_2SiO_3 (%)	Testing time (days)
R50Na7	50	30	20	100	-	7
R50Si7	50	30	20	-	50/50	7
R70Na7	70	25	5	100	-	7
R70Si7	70	25	5	-	50/50	7
R50Na28	50	30	20	100	-	28
R50Si28	50	30	20	-	50/50	28
R70Na28	70	25	5	100	-	28
R70Si28	70	25	5	-	50/50	28

5.3. Characterisation of the samples

5.3.1. Analysis by optical emission spectroscopy with inductive coupled plasma

In this case, the analysis by optical emission spectroscopy with inductive coupled plasma was carried out on samples of industrial waste blending still in their powder state, without being alkali activated, to observe the influence of the alkali activator concentration on the solubilising degree of Al and Si, which are key elements that determine the degree of geopolymerisation of the blending.

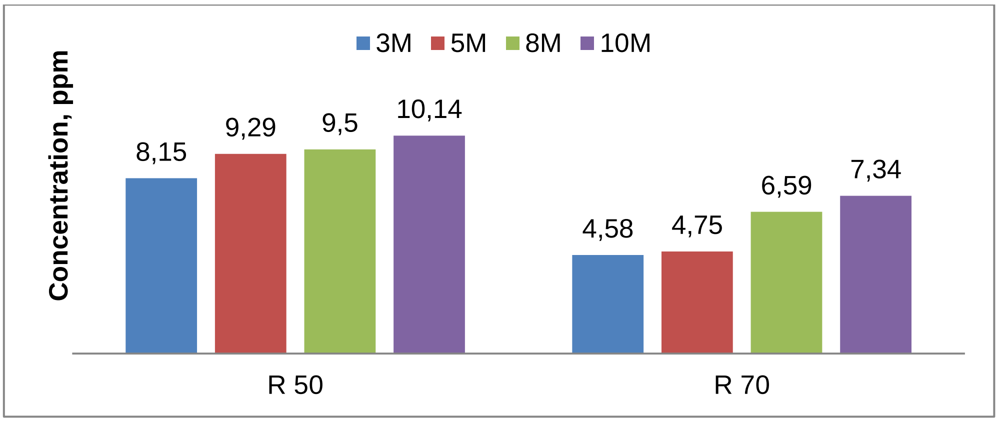


Figure 5.1. Solubilising of Al in geopolymer material samples, noted R50 and R70

Figure 5.2 presents the solubilising of Si in the materials present in the sample corresponding recipe R50 and R70, respectively.

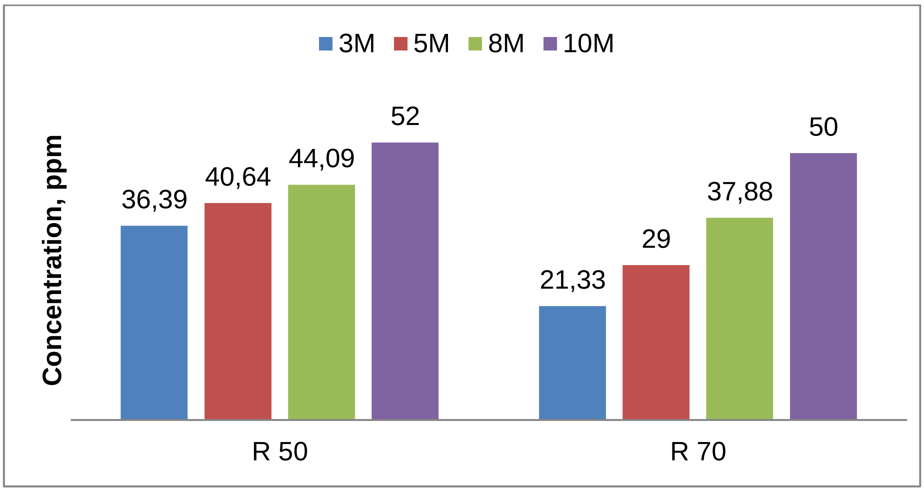


Figure 5.2 Solubilising Si in the geopolymer material samples, noted R50 and R70

By comparison, it is noticed that in the R50 noted sample the Si solubilisation was carried out at a solution concentration of NaOH 3M, 14% more than the sample noted R70 for the same concentration of the activator, while for the 10M concentration, in the case of the R50 sample, the Si solubilisation has reached values of up to 2% higher. It can be considered that the solubilising of both elements is influenced by the concentration of the alkali activator as well as the amount of Al and Si already existent in the solid recipe materials.

5.3.3 Structure analysis by electron scanning electron microscopy (SEM)

The SEM analysis was carried out for the proposed study recipes: R50, alkali activated with a NaOH 3M and 10M and for R70, alkali activated with a NaOH solution with a 3M and 10M concentration. In figure 5.5 the specific microstructures for the R50 samples are presented as follows: a) alkali activated with a NaOH 3M concentration solution and b) alkali activated with a NaOH 10M solution.

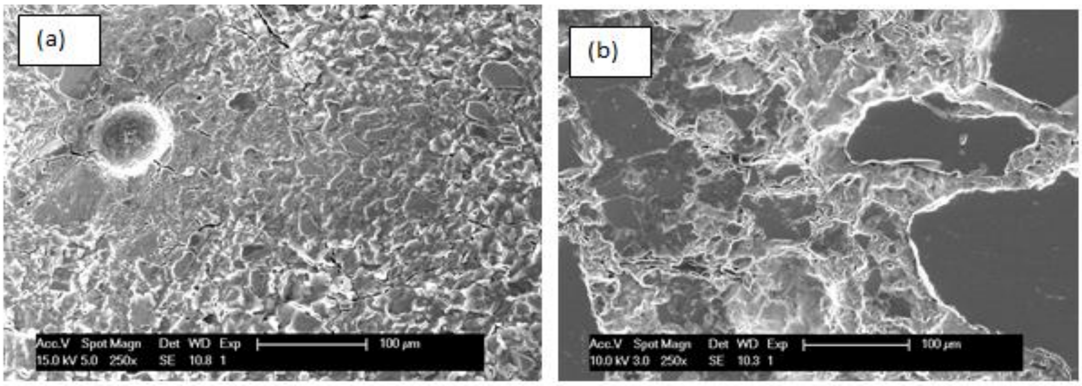


Figure 5.5 SEM images of geopolymer material noted R50Na(a) activated with NaOH 3M and (b) activated with NaOH 10M

In figure 5.5(b) the microstructure of the sample material which contains the R50Na recipe geopolymer, obtained by alkali activating it with a NaOH 3M solution. It is observed that reaction products that form the geopolymeric matrix with its unreacted or not sufficiently reacted particles.

In figure 5.6 the microstructures of the sample noted R70Na alkali activated are presented as follows: (a) with a NaOH solution with 10M concentration and (b) alkali activated with a NaOH solution with 3M concentration.

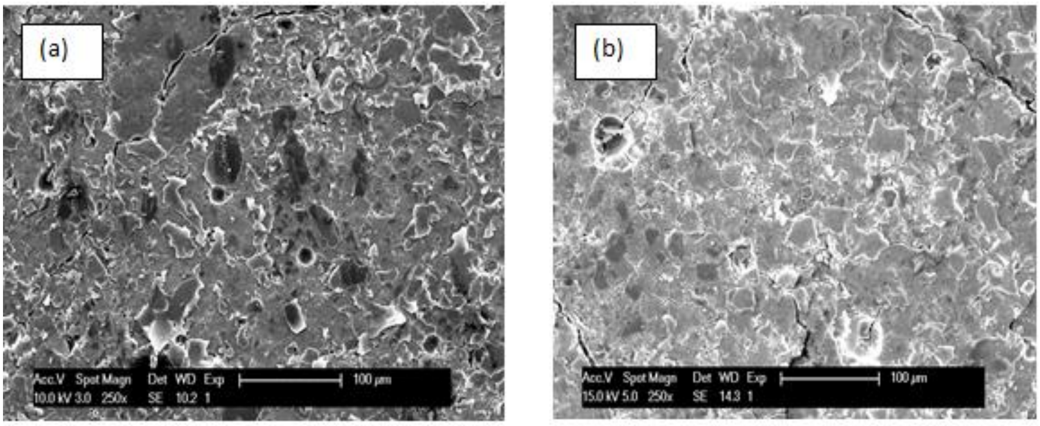


Figure 5.6 SEM images of geopolymer material samples, noted R70Na (a) activated with NaOH 3M and (b)activated with NaOH 10M

The microstructure of the sample 5.6.a) is seen to have formed a dense matrix, less homogeous from a gel which – after curing – has surrounded some of the unreacted particles. Also, the sample presents some microcracks.

5.3.4. Determination of compressive strength

Figure 5.7. presents the variation in compressive strength of geopolymeric materials corresponding to the R50Na and R70Na recipes, obtained through the alkali activation with a NaOH solution at different concentrations, at a constant solid/liquid ratio tested at 7 and 28 days respectively.

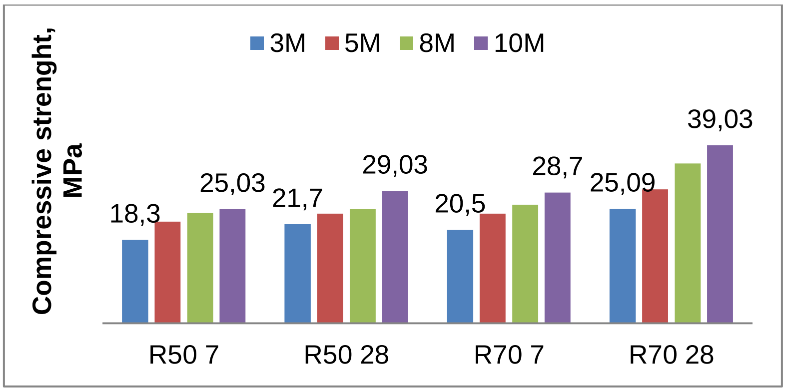


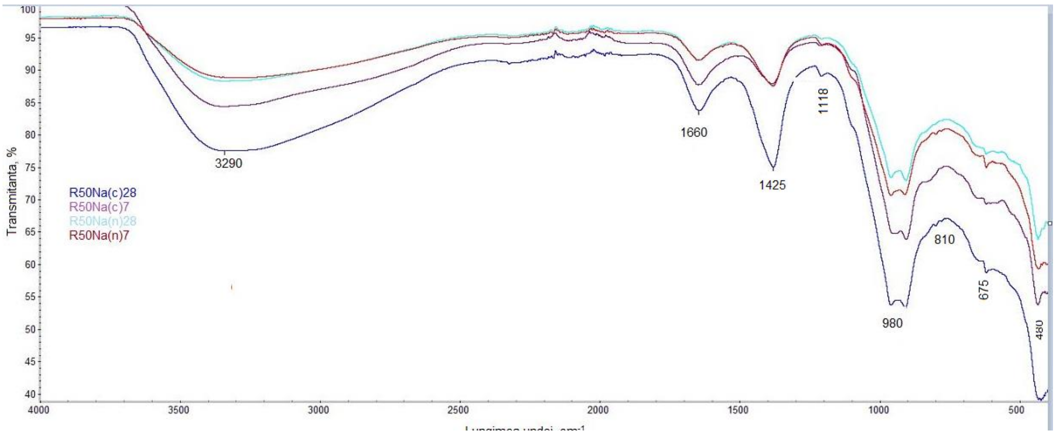
Figure 5.7 Compressive strength of geopolymer materials noted R50 and R70 alkali activated with a NaOH solution at different concentrations tested at 7 and 28 days

5.4. Characterisation of geopolymeric materials from the noted samples R50 and R70

5.4.1. FT-IR spectroscopy analysis

FT-IR spectrums were created for the analysed samples and it was observed that these present the differences in what concerns the position of the absorption band's specific chemical bond vibrations of geopolymers according to the industrial wastes used in the recipes chemical compositions for the synthesis of the geopolymers, the nature of the alkali activator as well as the keeping of final materials which contain a geopolimeric matrix.

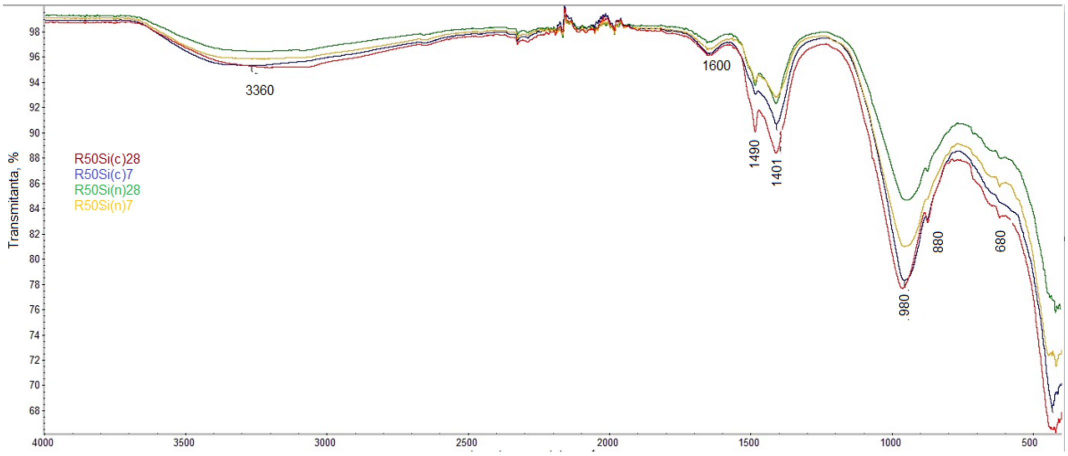
Figure 5.8. presents the FT-IR spectrum of the resulting materials samples after the geopolymerisation process obtained accordint to the recipe noted R50 which contains both calcined and uncalcined red mud, alkali activated with a NaOH 8M solution or with a solution obtained by mixing a sodium hydroxide solution and a sodium silicate one in equal proportions, analysed after a curing period of 7 and 28 days.



Wavenumber, cm^{-1}

Figure 5.8 FT-IR spectrum of the geopolymeric material samples noted R50Na

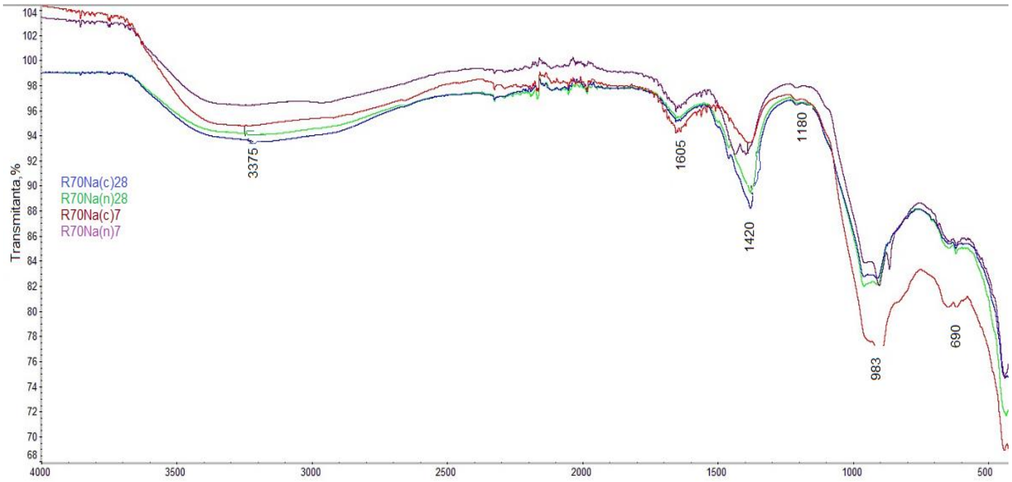
Figure 5.9 presents FT-IR spectres of samples noted R50Si with calcined and uncalcined red mud, alkali activated with a solution obtained by mixing a NaOH solution with 8M and sodium silicate in equal proportions, analysed at 7 and 28 days.



Wavenumber, cm^{-1}

Figure 5.9. FT-IR spectres of geopolymeric material samples, noted R50Si

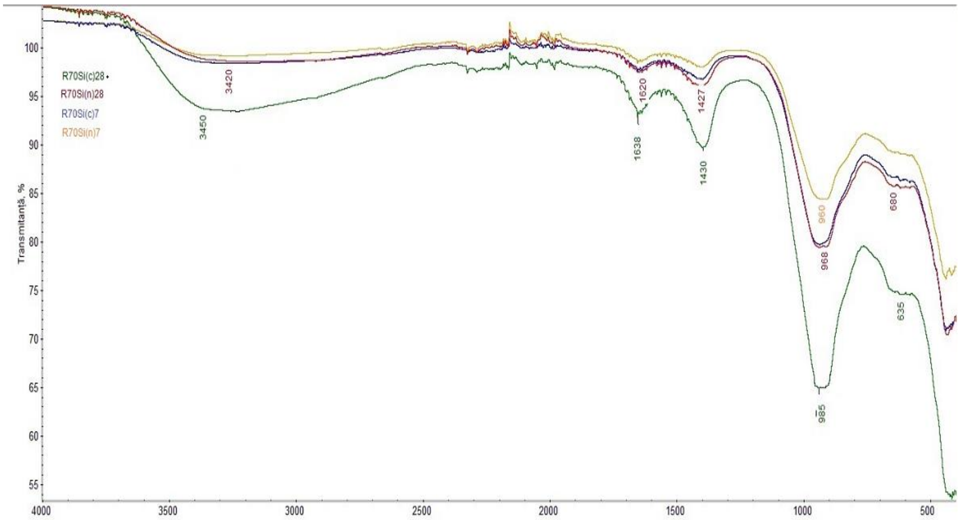
The same ascending trend in what regards the movement of higher wave number peaks is kept for the noted sample materials R70Na(n)28 and R70Na(c)7 or R70Na(c)28, which indicates a high level of geopolymerisation in the structure of obtained geopolymers where, probably, because of polycondesation, N-A-S-H gel is formed, which, in turn is in accordance with the EDAX analysis results, where Si/Al rapport is small. The obtained results are in accordance with the studies carried out by other researchers [275].



Wavenumber, cm^{-1}

Figure 5.10 FT-IR spectrums of geopolymeric material samples

Figure 5.11 presents the FT-IR spectrum of noted samples R70Si which contain 70% granulated furnace slag, 25% ash and 5% uncalcined or calcined red mud, alkali activated with a solution of NaOH, 8M concentration and a sodium silicate solution in equal proportions, which were analysed after a curing time of 7 and 28 days.



Wavenumber, cm^{-1}

Figure 5.11. FT-IR spectrum of geopolymeric material samples, noted R70Si

On the FT-IR spectrums of the geopolymeric material samples noted R70Si vibration absorbing bands can be observed at the following wave number intervals:

a) 677-686 cm^{-1}, vibration absorbing bands owed to the formation of Al-OH in gibbsite;
b) 960-985 cm^{-1}, vibration absorbing bands due to the T-O-Si-type bonds;
c) 1420-1430 cm^{-1}, vibration absorbing bands owed to the carbonate content, of the O-

C-O type bonds present in the materials of the studied samples, as a result of the carboning of the surface during the curing time;

d) 1610-1638 cm^{-1}, vibration absorbing bands owed to the H-O-H bonds as a result of the formation of the N-A-S-H type gel (sodium aluminosilicate hydrate) or C-A-S-H (calcium aluminosilicate hydrate).

e) 3420 cm^{-1} și 3450 cm^{-1}, vibration absorbing bands for the deforming bonds of the correspondent water molecules.

5.4.2. Structure analysis by electron scanning electron microscopy (SEM)

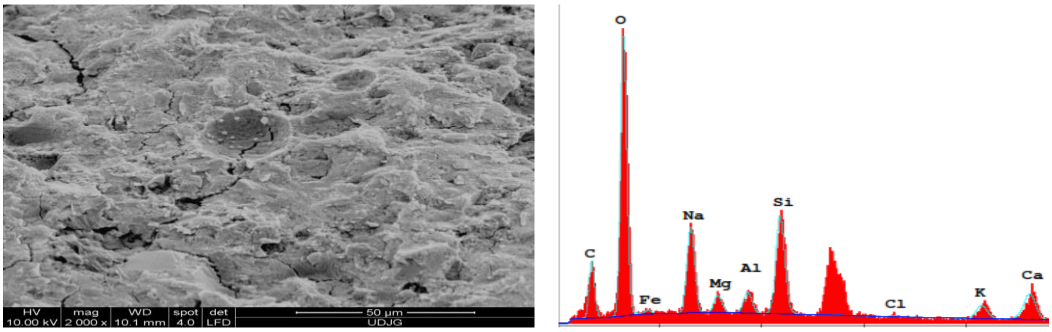


Figure 5.14 SEM image of the R70Na(n)28 after geopolymerisation and EDAX spectrum for the R70Na(n)28

In this case, the Si/Al ratio is lower than 5,44 and the Ca/Si ratio is 0,82, which determines a good compressive strength.

Figure 5.15 presents the distribution of the chemical elements for the R70Na(n)28 sample after geopolymerisation.

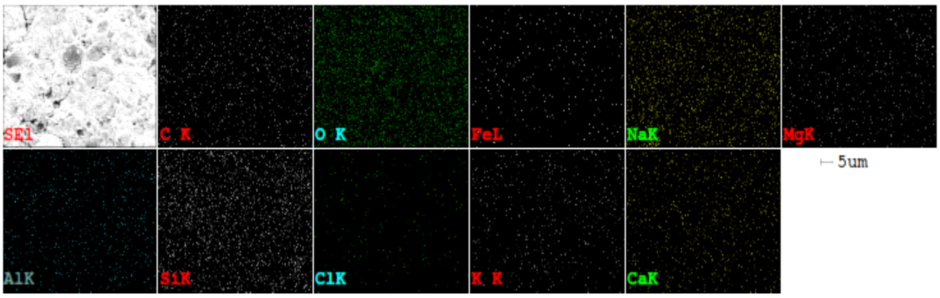


Figure 5.15 Chemical element distribution for the R70Na(n)28 after geopolymerisation

In the map of chemical element distribution present in the analysed sample, oxygen is key factor, followed by Si and Na. In this case, Si/Al ratio is 5,33 which reflects in the level of geopolymerisation higher than the sample at 7 days.

In figure 5.18 the microstructure for the R70Na(c)28 sample is presented after the synthesis of the geopolymer made of industriale waste researched for this purpose. The SEM image observes the reaction products formed after the alkali activation of materials with a high content of Si and Al, forming a dense structure with good homogenity but porous and cracked.

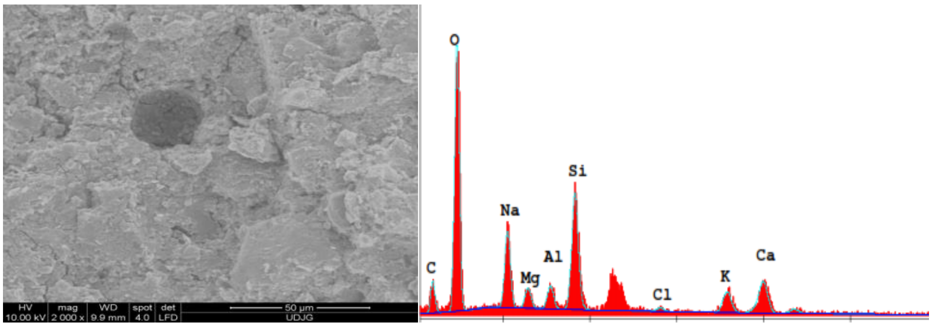


Figure 5.18 SEM image of the R70Na(c)28 after geopolymerisation and EDAX spectrum for the R70Na(c)28

In this case, the Si/Al ratio is 5,74, the Na/Si ratio is 0,05 and the Ca/Si is 0,88 which justifies the presence of C-A-S-H(calcium aluminosilicate hydrate) type composites

Figure 5.19 shows the distribution of elements for the sample noted R70Na(c)28 after geopolymerisation.

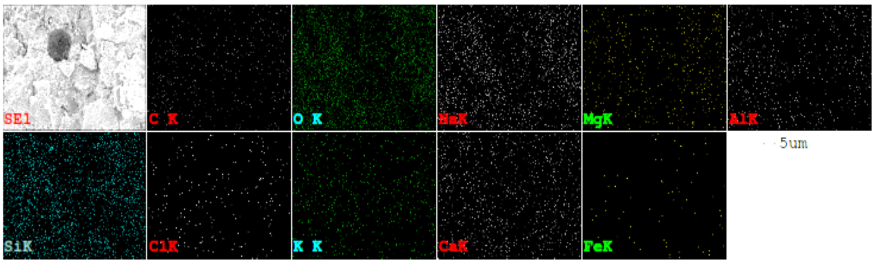


Figure 5.19 Chemical element distribution for the R70Na(c)28 after geopolymerisation

In the microstructure in figure 5.22 a matrix formed in the geopolymeric gel material in very large amounts can be observed, evenly distributed with a low amount of unreacted particles but with loads of microcavities and cracks which can be owed to an accelerated polycondensation or the tear after the compressive strength test.

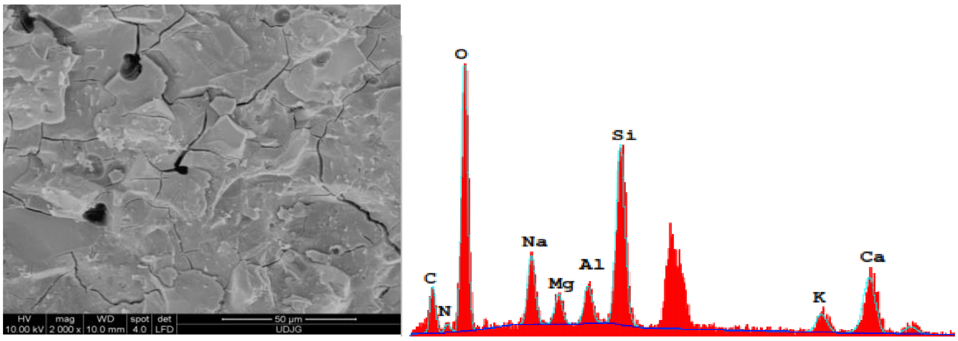


Figure 5.22 SEM image of sample R70Si(n)28 after geopolymerisation and EDAX spectrum for sample R70Si(n)28

The microcavities in the structure can be due to the air inserted after the blending of the material that underwent the geopolymerisation process or the space occupied by water before evaporation. As far as EDAX analysis goes, it can be observed that the Si/Al ratio is high, 5,69, and the Ca/Si ratio is 1,09, which, according to other studies [120] indicates the presence of N-A-S-H gel in the resulting material after geopolymerisation. The presence of such gel determines a better compressive strength

Figure 5.23 shows the map of element distribution corresponding to the sample R70Si(n)28, after geopolymerisation.

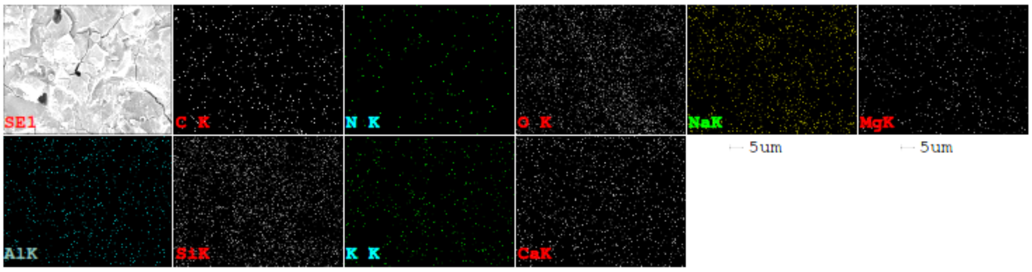


Figure 5.23 Chemical element distribution for R70Si(n)28 sample, after geopolymerisation

On the map of chemical element distribution in figure 5.23 it is observed that the elements present have a uniform and dense distribution, in accordance with other studies, in which it is stated that a homogenous and dense distribution of the elements is characteristic to the structure of geopolymers.[258]

Figure 5.26 represents the microstructure and the spectrum determined through EDAX analysis for the sample noted R70Si(28)

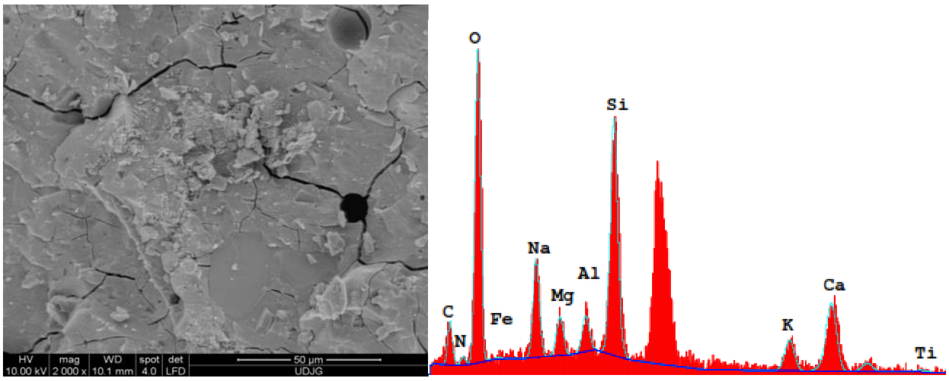


Figure 5.26 SEM image of sample R70Si(c)28 after geopolymerisation and EDAX spectrum for sample R70Si(c)28

The microstructure in figure 5.26 can be observed to have significant amounts of geopolymeric gel in its formed matrix, uniformely distributed with a low number of unreacted particles, but with loads of microcavities and crackes which could be due to an accelerated polycondensation or a tear resulted from the compressive strength test.

Figure 5.27 presents the map of chemical element distribution in sample R60Si(c)28.

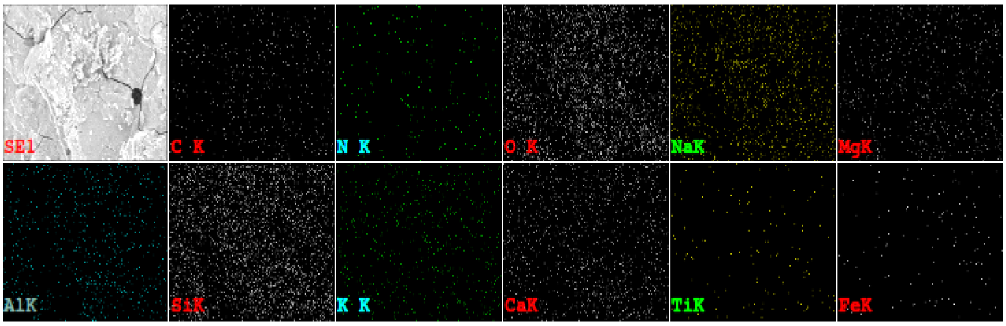


Figure 5.27 Chemical element distribution for sample R70Si(c)28, after geopolymerisation

As far as the EDAX analysis goes, table 5.5 presents the chemical compositions of the synthesised geopolymers. Thus, it was observed that for samples R70Na(c)7, R70Na(n)7, R70Si(c)7 and R70Si(n)7 the elements found in significant amounts are O_2, C and Na and the amount of Si and Al are smaller in comparison with the other samples. The explanation lies in the fact that little stable Si-O or Al-O bonds were created and more Na_2CO_3 unstable bonds were formed because the curing time was very short – only 7 days – which lead to low values of compressive strength.

Table 5.5 Chemical element composition determined through EDAX analysis of R70 samples after the process of geopolymerisation

Sample	Chemical composition (%)					
	Carbon	Oxigen	Sodiu	Siliciu	Aluminiu	Calciu
R70Na(n)7	13,66	40,60	6,27	13,39	2,35	14,69
R70Na(c)7	16,56	37,85	9,34	16,71	1,72	7,31
R70Si(n)7	13,92	35,39	5,83	17,78	2,57	1,13
R70Si(c)7	8,10	32,42	5,59	15,91	2,90	12,47
R70Na(n)28	16,69	38,63	8,92	12,75	2,39	10,99
R70Na(c)28	9,81	37,18	7,86	14,77	2,58	13,12
R70Si(n)28	11,35	33,42	5,46	17,17	3,23	18,52
R70Si(c)28	8,64	30,33	6,20	18,18	2,40	17,47

5.4.3. Determination of compressive strength

The resulting values after the compressive strength tests of the obtained geopolymers are given in figure 5.28 and are in accordance with the microstructures of the analysed samples in the study. The results of the testing have demonstrated that the sample of resulting material after the synthesis of geopolymer R70N(u)7 has had the lowest value, 24 MPa, and for the 28 day testing, the compressive strength reached a value of 28 MPa. The highest values were obtained by the sample noted R70Si(c)7, 68 MPa for the 7 day trial and 85 MPa for the 28 day testing. The sample noted R70Si(c)7 was obtained with 70% GGBFS, 25% WSA and 5%RM(c), and the blending was alkali activated with a solution obtained through mixing a sodium hydroxide soluttion with a sodium silicate solution in 50/50 equal portions, the sample being kept in laboratory conditions for a period of 28 days.

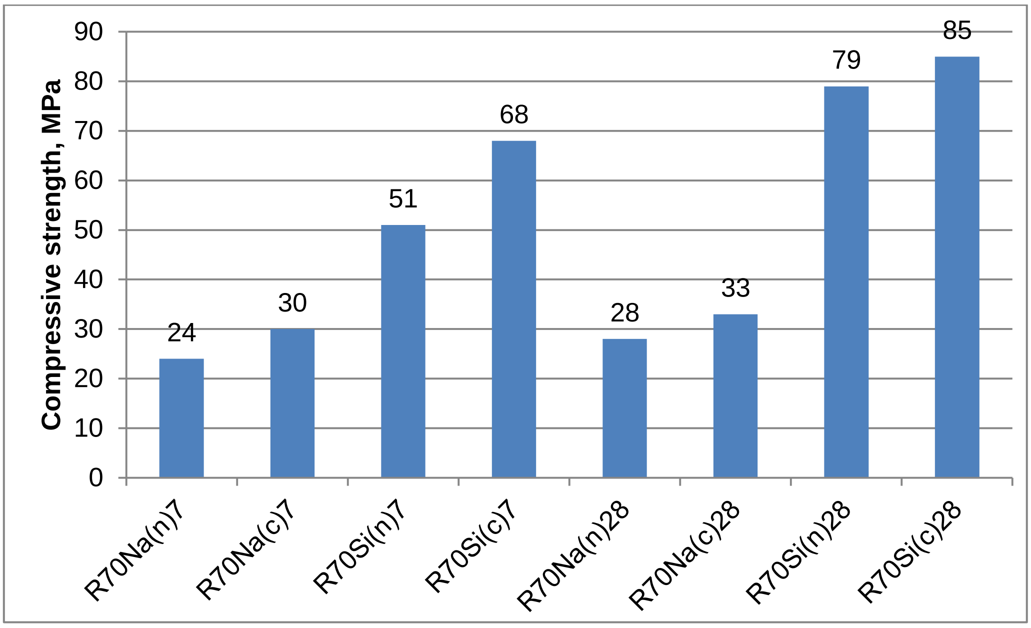


Figure 5.28 Compressive strength values for samples noted R70 after geopolymerisation

5.5. Factors which influence the compression strength of sample materials resulted from geopolymer synthesis

5.5.1 Influence of drying time and alkali activator on compressive strength

As demonstrated, samples noted R70 and R50 from materials which contain geopolymers resulted from the alkali activation of industrial waste, are materials whose compressive strength is influenced by a number of factors such as: level and value of the geopolymerisation of the source material, chemical composition (e.g. Si/Al ratio), geopolymeric binder, filler material, filler material characteristics (e.g. impurities: Ca,Mg, Fe).

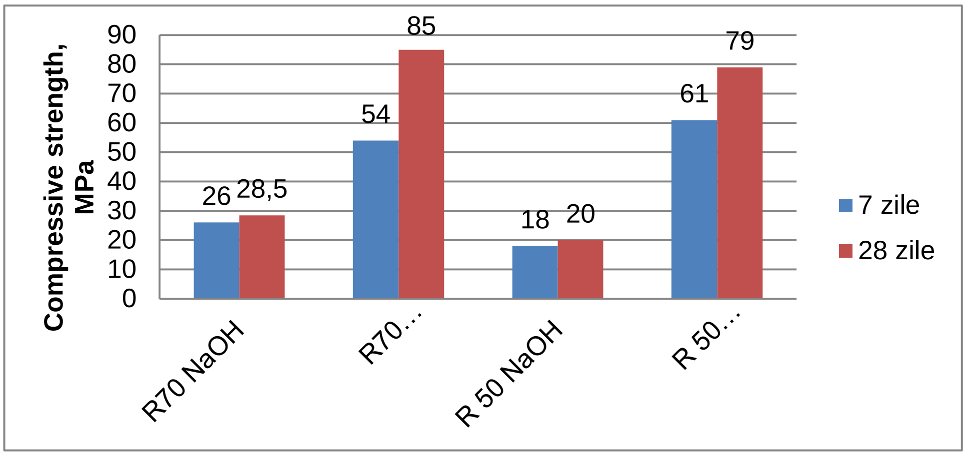


Figure 5.29 Influence of drying time and alkali activator on compressive strength

5.5.2 Influence of the type and concentration of the alkali activator

In the case of the activation of industrial waste that contains aluminosilicates (red mud, granulated blast furnace slag, ash or others), an important part is determining the structural and mechanical properties is the type and concentration of the alkali activator as well as the physical and chemical nature of the solid silico-aluminious precursor used in the synthesis of the geopolymer.

Some specific research has proved that for the obtaining of the top characteristics, based on the activator, the following factors should be taken into account: type of activator, physical state of activator (solution or in solid state) and the amount added in the recipe of the geopolymer. In this case different NaOH solutions with different concentrations were used and the compressive strength values according to the molarity values are given in figure 5.30.

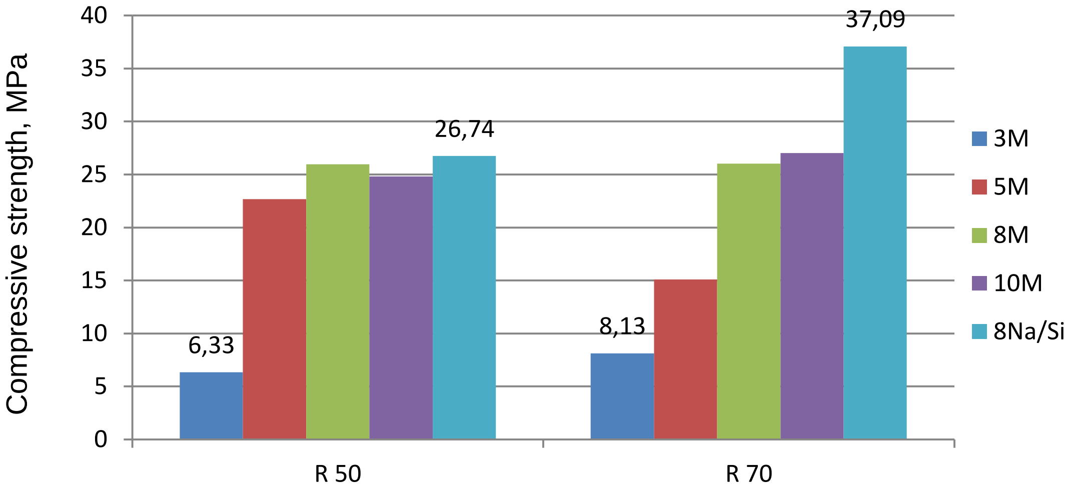


Figure 5.30 Influence of nature and concentration of the alkali solution on the compressive strength of samples R50 and R70 resulted in the process of geopolymerisation

5.6. Partial conclusions

1) Experimental research has focused on the obtaining of a geopolymeric material by mixing the three industrial wastes suggested in the research plan, in different combinations, according to the correspondent sample recipes noted R50 and R70, which were alkali activated with two types of activators (NaOH solution at different concentrations and a solution obtained through the mixing of a sodium hydroxide solution at 8M and a sodium silicate solution).

2) Recipes using both calcined and uncalcined red mud were made to observe the influence of the calcination on the chemical and structural composition as well as the compressive strength of the resulted material.

3) In this case, the chemical analysis by inductively coupled plasma spectroscopy was carried out on samples of the industrial waste blends in powder state, without being alkali activated to observe the influence of the concentration of the alkali activator on the level of solubilisation of Al and Si.

4) After the analysis, it was found that the ash has a silica content of 53,13% and in view of the fact that in the sample corresponding to the recipe R50 ash content is 30% and in sample R70 25%, this may explain the higher amount of solubilised Si for the sample denoted R50. It can be considered that the solubilization Al and Si is influenced by the concentration of the alkali activator and the amount of Al and Si existing in the solid materials of the recipe.

5) In the microstructure characteristics of the sample denoted R50Na alkali activated with NaOH solution of a concentration of 10M, the reaction products have formed a dense gelic structure, a matrix in which the unsolubilised particles of the alkali activator were embedded. The sample shows pores in the structure of the fractured geopolymeric material.

6) In terms of the alkali activation of the material corresponding to the recipe noted R70Na with the solution of NaOH of a concentration of 10M, it is observed that the microstructure is more homogeneous, characteristic of an effective solubilisation of the Si and Al elements of raw materials in the NaOH solution with a concentration of 3M, in which the unreacted particles are embedded in the geopolymeric gel.

7) It has been observed that there is a tendency of the compressive strength to increase in the materials corresponding to the samples denoted R50 and R70, depending on: the chemical composition of the materials in the recipe, the concentration of the activation solution used and the duration of curing of the samples. For the recipe R70, the compressive strength is higher than that corresponding to the samples denoted R50 regardless of the concentration of the alkaline solution and the duration of hardening. This is due to the amount of slag in the system, namely 70% for the recipe R70 and only 50% for the recipe denoted R50, to the quantity of solubilised silico-aluminates in the activation solution and which form the structure hardened geopolymer.

8) It was observed that for samples of the materials resulted after the geopolymerisation process, denoted R70, the compressive strength value for the sample alkaline activated with a solution of NaOH 3M, is 25,9 MPa, and for the activation with NaOH 10M, the value is 39,03 MPa.

9) FT-IR spectrum for the samples analyzed was achieved and there were exhibited differences in what regards the position of the band of absorption of the vibrations of chemical bonds specific to geopolymers, depending on: the chemical composition of industrial wastes, the nature of the alkali activator as well as of the maintenance period of the of the final materials containing a geopolymer matrix.

10) By comparing the two geopolymeric samples denoted R50Na and R50Si following the alkali activation with two different solutions (NaOH 8M, and solution obtained by mixing the solution of NaOH with sodium silicate solution in equal proportions) it was observed that in the geopolymer sample R50Si a displacement of the peaks towards higher values of wave numbers occurs. The explanation for this movement is that a different activation solution that brings a greater amount of reactive Si and which determines a higher degree of geopolymerisation, which has had a positive impact on the compressive strength.

11) The comparison of the geopolymeric samples denoted R70Na and R70Si following the alkali activation with two different solutions (NaOH, 8M, and solution obtained by mixing the solution of NaOH with sodium silicate solution in equal proportions) the following aspects have been observed: the geopolymer sample denoted R70Si also experiences a displacement of the peaks towards higher values of wave numbers. The explanation for this displacement and in this case is the use of the activation solution that contains reactive Si and which favors the reactions of polycondensation, so a greater degree

of geopolymerisation with a positive impact on the compressive strength.

12) In terms of the behaviour of materials corresponding to the samples denoted by the R70 the trend is similar, the sole difference being that in this case the amount of slag in the mixture has a positive influence in accelerating the reactions of polycondensation and obtaining geopolymers with a much better compressive strength than in the samples denoted R50.

13) The microstructure achieved for the sample denoted R70Na(n)28 highlighted an inhomogeneous aspect and the characteristic gel which has embedded in its structure unreacted particles. This fact may be due to incomplete geopolymerisation of solid materials from the geopolymeric mixture or an insufficient amount of silica and alumina. The Si/Al ratio determined by the EDAX analysis is less than 5,44, and the ratio Ca/Si is 0,82, which resulted in a good compressive strength.

14) The sample denoted R70Na(c)28 present in the microstructure of the reaction products formed following the activation of the alkaline materials with a high content of Si and Al, which formed a dense structure, with a good homogeneity but with pores and cracks. In this case, the Si/Al ratio is 5,74, the Na/Si ratio is 0,05, and the Ca/Si ratio is 0,88, which justifies the presence of compounds of the type C-A-S-H (hydrated silico-aluminate of calcium) in the analysed system.

15) The microstructure of the sample material denoted R70Si(n)28 highlights a matrix of the geopolymeric gel which is uniformly distributed, with a reduced number of unreacted particles, but with many micro-cavities and cracks which can be due to an accelerated polycindensation or breakage after applying the compressive strength test, because the analysis of the microstructure was achieved after the determination of the compressive strength.

16) In the microstructure of the sample denoted R70Si(c)28 it has been observed that the matrix formed from the geopolymeric gel was in very large amount, evenly distributed, with a reduced number of unreacted, but with many micro-cavities and cracks which can be due to an accelerated polycondensation or breakage after applying the compressive strength test. Micro-cavities in the structure may be due to air introduced after the mixing of the material subjected to the process of geopolymerisation or of the space occupied by the water before evaporation.

17) For the samples of the materials resulted in geopolymerisation, corresponding to samples denoted R70 and R50 it was found that the compressive strength is influenced by a variety of factors such as: the degree of geopolymerisation the source of the material, the chemical composition (ex. the Si/Al ratio) of the geopolymeric binder, and the particle size, the shape, their density and the elements considered impurities.

18) The best values of compressive strength were obtained for the materials corresponding to the samples denoted R70 in comparison with the samples denoted R50. The explanation lies in the fact that slag has an appreciable amount of CaO (42,61%), SiO_2 (36,91%), Al_2O_3 (8,27%) which alkali activated with a solution of $NaOH/Na_2SiO_2$ enters into the geopolymerisation reactions and helps in the formation of the geopolymeric matrix.

CHAPTER 6. GENERAL CONCLUSIONS. ORIGINAL CONTRIBUTIONS AND NEW RESEARCH OPPORTUNITIES

6.1. General conclusions

1) The solid materials used in the process of geopolymerisation for the obtaining of construction materials which contain in their structure geopolymers, are different and can be represented by industrial waste such as: granulated furnace slag, red mud, fly ash, powders.

2) Geopolymers are new materials, have chemical compositions similar to silico-aluminious zeolitesm different properties which are, in fact, amorphous polymers.

3) Many research studies regarding the obtaining and the characterisation of alkali activated industrial waste geopolymers were carried out. The main wastes used in this paper were granulated furnace slag, red mud in different concentrations and combinations than those presented in specialised literature. As far as using wheat straw ash as an addition to the solid materials later to be alkali activated and obtain a geopolymer, that was a personal contribution.

4) Factors that influence the chemical, physical and mechanical properties of geopolymers are: particle dimensions, Si/Al ratio, calcium quantity, type and concentration of the alkali activator, curing time and synthesis temperature.

5) The technology used in obtaining these industrial waste construction materials through the process of geopolymerisation is in full ascension and can be proved to be a highly impacting one in the world of construction, both in the way of protecting the environment but also from an economic standpoint and the production of materials with special properties that can be used in a multitude of fields among which we can name the field of energy.

6) The methods, investigation or analysis procedures that laid the foundation for this research have imposed the use of machinery and appliances of the “Dunarea de Jos” University laboratories, as well as the laboratories from the Catholic University in Leuven, The National Institute of Research-Development and Environment Protection Bucharest and the ECOMET laboratories from the Polytechnic University in Bucharest.

7) The powder materials used in the synthesis of geopolymers were: granulated furnace slag, red mud and wheat straw ash. The ash obtained from the controlled burning of organic waste was used as an addition in creating the binder materials for cementic geopolymers, because of their significant amounts of Si, element which favourises the formation of stable structures in the geopolymeric matrix.

8) The alkaline solutions used in the study were the NaOH solution with different concentrations or the blending of the NaOH solution with a Na_2SiO_3 solution at a 1:1 ratio.

9) The obtaining of geopolymers imposes a series of material preparatory operations such as decreasing the size of the particles through grinding, followed by sieving, and calcination in the case of red mud.

10) The solid materials in the suggested recipes for the geopolymer synthesis have been physically chracterised, namely the determination of the density, the average particle diameter and the specific surface of the materials used.

11) The chemical analysis by inductively coupled plasma spectroscopy is chemical element determination technique by solubilising said element in different reactive environments depending on the concentration of the alkali activator used.

12) The amount of solubilised Al in red mud was 39,5% in the NaOH solution with a 8M concentration, granulated furnace slag 6,18%, while in the case of the ash, the amount

of Al was quasi-invisibile (0,37%) which is in accordance with the values registered for the amount of aluminium oxide determined through the XRF analysis.

13) Silica has solubilised in higher quantities compared to aluminium, out of all the wastes used. Also, it was observed that it solubilised at approximately 55% Si from granulated furnace slag at a concentration of the NaOH solution of 8M. For more concentrated soltuions, 10M, the Si amount solubilised is significantly lower which means that the NaOH 8M solution is ideal for solving the Si in slag mass.

14) FT-IR analyses have followed the chemical structure of the studied materials at the same time as the EDX.

15) Through the thermogravimetric analysis it was found that the change in mass of the samples depends on the drying temperature, the nature of the sample and the retention period. The mass variation due to chemical reactions of oxidation and decomposition was analysed.

16) By analyzing the DSC calorimetric differential scanning curves with the help of which the thermal effects corresponding to transformations and changes of mass due to transformations of the physical and chemical characteristics of the compounds which enter into the structure of the red mud were determined

17) The microstructures determined by analyzing the SEM and the EDAX spectrum corresponding to the sample of uncalcined red mud point out that the constituent particles have varied shapes and sizes, from submicron to larger sizes of 20 µm, and the EDAX spectrum shows that the element in the highest concentration is oxygen followed by aluminum and silica, and other elements such s iron, calcium, sodium and carbon are in small quantities, even negligible, as is the case with titanium.

18) In the case of the sample of calcined red mud at a temperature of 600°C it was observed that the particle sizes are much smaller than 20 µm, evenly distributed and have varied forms.

19) The Vicat test has been carried out in compliance with the working method imposed by the standards, and the results obtained fall into the category of the specific values for cements with rapid hardening, because the difference between the period of the beginning of the outlet and the final outlet was less than 30 minutes.

20) One of the most important determinations on the mechanical properties of a building material that contains geopolymer formed in the process of geopolymerisation, is the compressive strength. The test assumes that the sample for analysis to be carried out according to the standard in force, the EN 196-1. The recorded values represented the average of three samples.

21) The influence of the concentration of the alkali activator on the properties of the material obtained from industrial waste used in the study (blast furnace slag, uncalcined red mud and wheat straw ash) which has been subjected to the action of the solution of NaOH at different concentrations.

22) To highlight the effect of the concentration of the activation agent used the chemical analysis by optical spectroscopy of electrons inductively coupled plasma was performed. The results obtained, in percentage, determine the amount of solubilised Si and Al in the solution of sodium hodroxide at different molarities. It was found that the percentage of solubilised chemical element differ depending on the amount of pre-existing Al and Si in the material analysed as well as the concentration of the activating solution.

23) In the case of silica solubilisation in solutions of NaOH at different molarities the drawn conclusion is that the percentage of solubilised silica is about 20% higher in the case of blast furnace slag in comparison with the values obtained for solubilised aluminum from

the slag, for the same molarities, which is explained by the fact that the dioxide of silicon, SiO_2, free or bound is in much greater amount than the content of Al_2O_3 in the chemical composition of the slag, and for that it is present in large amount in amorphous phase.

24) In the FTIR spectra of the samples of blast granulated furnace slag, wheat straw ash and red mud alkaline activated, each of these, with the solution of NaOH of a concentration of 3M and 10M it was found that the absorption bands appeared extensively to vibrations due to the deformation of the ties of oxygen in the based ties of Si-O and appearing at 915 cm^{-1}. In the FTIR spectrum for the alkaline activated ash or red mud with a solution of NaOH 3M, the absorption band corresponding to the wave number of 802 cm^{-1} , which corresponds to ash and the absorption band corresponding to the wave number 1435 cm^{-1} is associated with calcium carbonate, $CaCO_3$. The intensity of the peak in this area is increased and may be due to the presence of calcium carbonate ($CaCO_3$) resulting from the alkaline activation.The wave number at 3410cm^{-1} is owed to the formation of composites with H-O bonds in the resulting products.

25) For the alkali activated slag with solution of NaOH 10M the microstructure presents small unreacted particles, micro-cavities and cracks. At a lower concentration of the solution of NaOH (3M) alkali activator it has been observed that the microstructure contains more pores than the one formed from the sample of granulated blast furnace slag activated with a solution of 10M. This difference in microstructure is due to the concentration of the alkaline solution which favored the formation of a gel on the basis of the compound C-S-H (hydrated calcium silicate) which after curing has an amorphous structure.

26) The compressive strength test of the samples made from industrial waste shows that the compressive strength differs from a very good value of 41,18 MPa in the case of blast granulated furnace slag to unsolidified samples even after 7 days as is the case with red mud alkali activated with a solution of sodium hydroxide 10M.

32) Since the alkaline activation of a single industrial waste was found to not have the appropriate chemical reactivity of the material source (granulated blast-furnace slag, ash from straw of wheat and red mud), the combination of two materials was taken into account.

37) FTIR spectrum of the construction sample with geopolymer, denoted ZG95/NR(5) 60, observed that the specific absorption band vibration corresponding to the wave number of about 3279 cm-1 is due to the vibration of the deformation of covalent water molecule links corresponding to H-O-H bonds. With regard to the broad absorption band located at around 954 cm-1, it is characteristic of geopolimeric gel, which confirms the results of the analysis as well as the highest compression strength.

27) For the samples of construction materials that contain a geopolymer consisting of blast furnace slag granulated (85%) and wheat straw ash (15%), the sample denoted ZG85/CPG15, at a temperature of 20°C and 60°C, the thermogravimetric curves have the peaks corresponding to temperatures of approximately 69°C and 71°C which are attributed to the loss of bound water in the physical structure of the material subjected to analysis. In terms of the peaks corresponding to temperatures of about 362°C and 388°C, they are attributed to the formation of sodium carbonate, Na2CO3 due to the interaction between NaOH and CO2. For the peaks formed at temperatures of about 687°C and 692°C, they are attributed to the loss of hydroxyl group properties of Si-OH.

28) In the sample denoted ZG85/CPG15, at 20°C, the gel matrix of the geopolymer is rough and it was highlighted that some of the particles that have been reacted partially with the alkaline solution resulting in the formation of the geopolymer presenting some cracks and pores. The spectrum of EDAX specific to this evidence has highlighted the fact that, in the structure of the gel matrix oxygen is abundant, followed by sodium and carbon, and in

smaller amounts of aluminium and silica. This was due to the presence of sodium carbonate, revealed from the XRD analysis and the thermogravimetric analysis. Sodium carbonate was probably formed in the presence of CO2 in the atmosphere, during the period of hardening, although the values of compressive strength are not low.

29) In the microstructure of the sample geopolymer material denoted ZG85/CPG15, at 60°C,it reveal particles remaining uncontested and trapped in the geopolymeric matrix that contains the reaction products resulting from the alkaline activation. Also, it is observed that it formed a continuous gel, cracks and microcavities are present, created probably by water that evaporated during the heat treatment.

30) In the sample denoted ZG95/CPG(5)20 the distribution of the components is not homogeneous, the gel products have not been compacted in the process of alkaline activation which explains the poor compressive strength.

31) For the sample of the geopolymer material, denoted ZG95/NR5, at 60°C, it was observed that the matrix is not compact, but rather fractured due to tensions created in the result of the test of compressive strength, or vacuum due to the sample preparation for SEM, and even due to heat treatment. The structure reveals a large amount of geopolymer and a very small amount of unreacted particles. The EDAX spectrum observed that the major element is oxygen followed by silica, sodium and aluminium, elements which are directly involved in the formation of the structure of the geopolymer.

32) In the microstructure of the sample of construction geopolymer material, ZG85/NR15 synthesized at a temperature of 20°C,a gel matrix with small unreacted particles and needle-shaped particles was observed which could be due to the carbonate content present in the structure or the presence of re-crystallised NaOH . In the EDAX spectrum the amount of sodium is very high, a situation also found in the sample of slag with ash (to the same amount of ash, 15% and the same temperature of synthesis 20°C). The presence of the phase of the carbonate has not adversely affected the compressive strength of the samples.

33) In the microstructure of the sample geopolymer material, denoted ZG85/NR15 subjected to heat treatment at 60°C, it was observed that the matrix is compact, with small unreacted particles and cracks. Also, in the EDAX spectrum, the matrix shows a rich content in the oxygen, as well as in other elements such as sodium and silica.

34) The highest value of the compression strength was obtained for the sample of the geopolymer material, denoted ZG95/NR(5)60 124,33 MPa and it is observed that there is a difference of approximately 54% compared to the sample ZG95/CPG(5)60 to 68 MPa. In this case the low value may be due to a large Si/Al ratio , which causes a relatively low compression strength, or the temperature that caused an intensification of the reactions resulting in the compound that are specific to bonds of the type Al-O, which inhibited the formation of stable ties of the type Si-O-Si or Si-O-Al.

35) The experimental investigations were focused on obtaining a geopolymeric material formed by mixing the three industrial waste proposed in the research plan, in different combinations (R50 and R70) and alkali activated with two types of activators (NaOH solution at different concentrations and the solution made of the mixture of sodium hydroxide 8M and a solution of sodium silicate) material that has the properties recommended to be used in construction.

36) Recipes with uncalcined red mud and calcined red mud were made to observe the influence of calcination on the chemical composition, structure and compressive strength of the material resulting geopolymeric material.

37) In the appearance of the XRD corresponding to sample denoted R70 alkali activated with solution of NaOH 10M there is a halo between 45-50° 2θ, which indicates the presence of phases such as silica and alumina in amorphous phases. In view of the chemical composition, alumina is present in large amount in the form of amorphous phase, as it was not identified on the XRD pattern, while the silica may be present in both phases, both crystalline (quartz) and amorphous. It can be seen from the appearance of the XRD that phases such as quartz did not change appearance when phases such as melilite and akermanite were diminished following geopolymerisation, especially in the strongly alkaline solution (10M). The products resulting from the solubilisation of aluminatesand silicates from the system, can form geopolymers by polycondensation that are amorphous at room temperature.

38) It has been observed that there is an increasing trend of compressive strength of the material corresponding to the recipes noted R50 and R70, depending on the chemical composition of the materials in the recipe, the concentration of the solution of activation used and the duration of curing of the samples. For the recipe noted R70, the compressve strength is higher than the compressive strength of the formed geopolymeric material in the recipe denoted R50 regardless of the concentration of the alkaline solution and the duration of hardening. This fact may be due to the amount of slag in the system, 70% for the recipe denoted R70 and only 50% for the recipe denoted R50, of the quantity of silico-aluminates solubilised in the solution of activation and which form the structure of the hardening of the resulting geopolymer.

39) In the FT-IR spectra for samples of the materials resulting from alkali activation, it was observed that they differ in terms of the position of the band of absorption of the vibrations of chemical bonds specific to geopolymers depending on: the chemical composition of the industrial wastes in the recipe for the synthesis of geopolymers, the nature of the activator alkaline as well as the period of keeping them in for drying.

40) By comparing the two samples of materials containing geopolymers following the alkali activation with two different solutions (NaOH, 8M, and solution obtained by mixing the solution of NaOH with sodium silicate solution in equal proportions) noted R50Na and R50Si it was observed that sample denoted R50Si with geopolymer a displacement of the peaks towards higher values of wave numbers occurs. The explanation for this displacement is the fact that a different activating solution that brings a greater amount of reactive Si in the solution, thus determining a higher degree of geopolymerisation, which has had a positive impact on compressive strength.

41) The microstructure of the sample material with geopolymer, denoted R70Na(n)7 has a gel matrix which includes particles of unreacted slag. It has been observed that the particles with the smaller ones have formed the gel in which the larger particles are trapped. The high concentration of Si had as an effect the acceleration of the reactions, with the formation of a structure based mainly on compounds of the type C-A-S-H.

42) The created microstructure for the obtained sample after the geopolymerisation process of the blending corresponding to the noted recipe R70Na(n)28 has highlighted that the microstructure is porous, with a heterogenous aspect and the characteristic gel has unreacted particles in its structure. This fact can be owed to incomplete geopolymerisation of solid materials from the geopolymeric mix or an insufficient amount of amorphous silica and alumina solubilised in the matrix. The Si/Al ratio determined through the EDAX analysis is lower than 5,44 and the Ca/Si ratio is 0,82, which has determined a good compressive strength.

43) The noted R70Na(c)28 sample presents in its microstructure reaction products

formed through alkali activation of materials with a high content of Si and Al, which have formed a dense structure with good homogenity but porous and cracked. In this case the Si/Al ratio is 5,74, the Na/Si ratio is 0,05% and the Ca/Si ratio is 0,88% which justifies the presence of C-A-S-H type composites in the analysed system.

44) A uniform chemical element distribution in the R70Si(c)28, which consist of silica oxygen, sodium and aluminium which correspond to the sodium alumino-silicate hydrate gel, type N-A-S-H. In this trial, the obtained gel has a high content Si and a Si/Al rapport of 7,57%, which although excessively high, it has proven the best compressive strength values.
61) For all compressive strength values the best results were obtained for the sample denoted R70 in comparison with the sample denoted R50. The explanation for this phenomenon is that the slag has an appreciable amount of CaO (42,61%), SiO_2 (36,91%), Al_2O_3 (8,27%), and when alkali activated with a solution of $NaOH/Na_2SiO_3$, it enters into the geopolymerisation reactions and helps in the formation of the geopolymeric matrix.

6.2. Original Contributions

The theme approached by the author of the thesis can be registered in a wide direction of research in what regards the diminishing of air pollution, of water and soil pollution by recyclng the industrial wastes which have in their chemical composition alumino-silicates, in view of obtaining new materials such as geopolymers or construction materials that contain geopolymers and which are known to be non-polluting materials(green).

The author's contributions can be cuantified as such:

1. Carrying out a bibliographic study based on the data in specialised literature regarding the obtaining and characterisation of geopolymers and materials that contain the resulted geopolymer through alkali activation of industrial waste that contain aluminosilicates and/or silicates;
2. The solid materials from the study that were taken through the geopolymerisation process through alkali activation are industrial wastes (GGBFS, RM, WSA) which pose many issues of depositing and valuing. By recycling these with the purpose of obtaining geopolymers or construction materials which contain synthesised geopolymers, it's a means of waste elimination which determins a positive impact on the environment and some economic and financial advantages as well;
3. In the experimental research carried out in this paper, granulated furnace slag, red mud and wheat straw ash, so that the proportions of these materials in solid state and their combinations differ from the ones studies so far by other researchers.The use of ash obtained by the burning of wheat straw ash, mixed with granulated furnace slag, with red mud or both, to be alkalia activated, is researched for the first time and it has contributed to the rise of the necessary silica content for the geopolymerisation process as well as the aluminium content brought in larger amounts by red mud;
4. To emphasise the effect of the concentration of the activating agent used, ICP-OES analysis was carried out. After this determination was made, the Si and Al solubilised quantities in the sodium hydroxide at different molarities was found in percentage. It was found that the chemical element percentage solubilised differs depending on the pre-existent quantity of Al and Si in the analysed material as well as the concentration of the activation solution.
5. In the case of solubilising silica in the NaOH solutions at different molarities (3M, 5M, 8M, 10M) the drawn conclusion was that the percentage of solubilised silica is

approximately 20% higher in the case of granulated furnace slag in comparison with the values obtained for the solubilised slag aluminum for the same molarities which is explained by the fact that SiO_2 loose or bound is in much larger quantity than the content of Al_2O_3 from the chemical composition of slag and because it is present in large amounts in an amorphous phase;

6. To evaluate the influence of the nature of the industrial waste, the combination between these for certain specific conditions to the process of geopolymerisation, certain research regarding the obtaining and characterisation of geopolymers and construction materials that resemble cement were done using the wastes: granulated furnace slag, red mud and wheat straw ash, alkali activated, combined in twos or threes and alkali activated with a NaOH solution with different molarities and a solution of Na_2SiO_3, in a 50/50 ratio. After the research, it was found that the best results were obtained for the samples R70Si(c)7, for which the compressive strength was 68 MPa at 7 days curing and 85 Mpa at 28 days.

7. FT-IR spectrums were interpreted for the samples of the resulted materials after the alkaline activation of industrial wastes and it was noticed that these present differences in what concernes the vibration absorption bands corresponding to specific chemical bonds between geopolymers, depending on the chemical composition of the industrial waste, their set recipes in the research program, the nature of the alkali activator as well as the drying time period;

8. The necessary installation was made to test water absorption of the samples of the resulted materials after the geopolymerisation process;

9. The researched materials which have in their composition synthesised geopolymers through the alkali activation of different blends with different contents of granulated furnace slag, red mud and ash which care comparable from their phyical, chemical, structural, thermic and compressive strength properties point of view.

10. The change in mineral phases after the 60°C thermic treatment was investaged, so that the XRD analyses justify the crystallisaton and the hardening of the polymeric gel.

11. Research regarding the obtaining and characterisation of geopolymers and resulting materials with a higher or lower geopolymer, depending on the proportions and the number of industrial waste from the blends created with a recipe basis, as well as depending on the concentrations of the alkali activators and the synthesis conditions, they focused on the determination the physico-chemical, structural, thermic and mechanical properties of the solid materials through modern investigation methods such as analysis based ones: SEM, EDAX, XRF, ICP-OES, XRD, DSC, TGA, DTA. Specific tests and analyses were carried out on the construction material such as: stability test, Le Chatelier, determination of the type of bond, Vicat test and the ones regarding sustainability through compressive strength and water absorption test.

12. Taking into account the chemical, structural, thermic and construction material specific properties, it is considered that the materials obtained through the alkali activation with solutions created through the blending of NaOH 8M with a Na_2SiO_3 in equal proportions, of the blending of two industrial wastes (granulated furnace slag, red mud in 95%/5% ratios) or the mixing of three materials (granulated furnace slag, red mud and wheat straw ash) in a GGBFS 70% + WSA 25% and RM 5%(c) ratio, and which present in their structure the different geopolymeric contents but also unreacted or partially reacted particles, they can easily replace the classic cements made with sand, bigger aggregates and cement in certain types of constructions where fireproofing, corrosion, thermic and sound isolation as well as high compressive strength is needed.

6.3. Future research directions

Taking into account the vast domain of use and versatility in obtaining materials through geopolymerisation, the following future search directions can be outlined:

1. Use of the industrial waste that have aluminosilicates in their chemical composition for the obtaining of cements with geopolymers or gross aggregates so that these can have performances comparable to those obtained from natural source materials;
2. Obtaining of reinforced geopolymers and their characterisation from the point of view of structural and mechanical properties and their structural, mecanical and strength characterisation for chemical attacks in corrosive environments;
3. Usage of other types of slag or industrial by-products for the obtaining of geopolymers or construction materials through additives for the improvement of geopolymer properties such as high fire resistance;
4. The obtaining of porous gopolymers, lightweight which can be both sound and heat proof through the alkali activation of some mixes of industrial wastes.

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