

SYNTHESIS AND CHARACTERIZATION OF GEOPOLYMER BINDERS FROM FLY ASH

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Valorificarea unor deșeuri rezultate din activități industriale sau de minerit, a devenit un domeniu important în cercetare. O categorie de materiale în care aceste deșeuri pot fi valorificate, sunt lianții geopolimeri.

Lucrarea prezentă aduce unele date privind sinteza și caracterizarea unor mase liante geopolimere din cenușă de termocentrală și soluție de NaOH. S-au folosit cenuși cu caracteristici compoziționale și disperzionale diferite, dozaje diferite de NaOH, dar și condiții diferite de sinteză.

Procesele de formare și proprietățile liante au fost studiate în corelare cu factori compozitionali și de procesare. Pentru investigarea acestora, s-au utilizat metode de caracterizare fizico-mecanică și metode fizice de investigare, precum spectroscopia IR, difracția de raze X, microscopia electronică.

Valorization of wastes from industrial or mining activities has become an important area on research. A category of materials in which these wastes can be recovered, are geopolymers binders.

The present paper brings some data on the synthesis and characterization of geopolymers binder masses of fly ash and NaOH solution. Fly ashes with different compositional and disperitional characteristics and different dosages of NaOH were used as well as different conditions of synthesis.

The formation processes and binder properties have been studied in correlation with compositional and processing factors. In order to investigate these, compressive strength tests and physical methods of investigation, as FTIR spectroscopy, X-ray diffraction were used.

Keywords: Fly ash, Geopolymer binders, Compressive strength

1. Introduction

In the last years, more several experimental researches have as their object efficient valorization, with low cost, of fly ashes, which result in large quantities, by burning coal in the power stations and storage which has negative implications on the environment.

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Besides using fly ash as the admixture in the blended cements - limited in some countries (including our country too), it can be considered as material aluminosilicate that, by alkaline activation, leads to obtaining of the binders that are different from those considered classics, namely geopolymers type binders. Geopolymers are poorly crystalline materials (almost amorphous), similar from the point of view of composition to the zeolites, and are formed by the polymerization processes of silicate and aluminite groups favored, in general, by higher temperature [1-5].

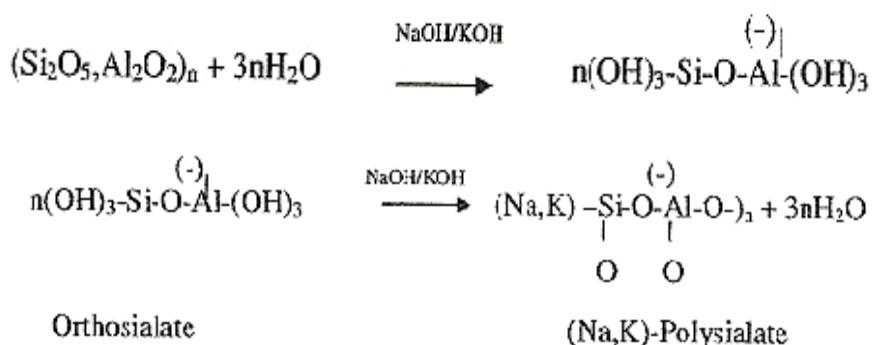
Their synthesis from aluminosilicate materials, as fly ash or metakaolin, take place by the so-called geopolymization process, which involves polycondensation phenomena of aluminate and silicate groups with formation of - Si-O-Al- type bonds.

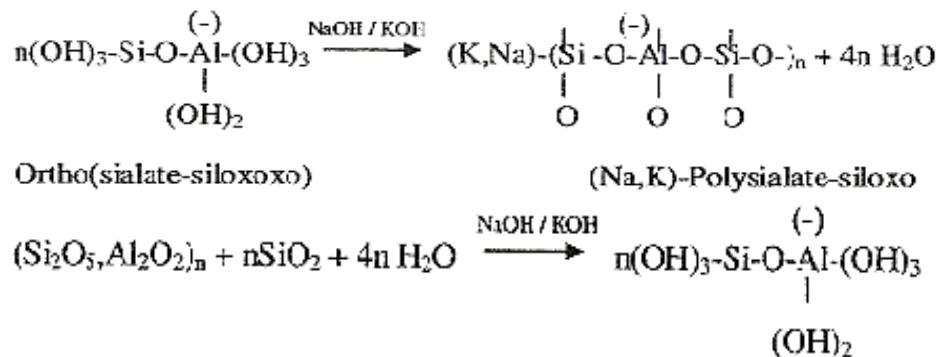
Geopolymerization mechanism consists, by different authors [4-7], in the following main stages:

- dissolution of aluminosilicate material in alkaline medium, with the destruction of the surface links, in highly alkaline pH conditions, with movement in solution of hydrated silicate and aluminate ions:

- polycondensation of silicate and aluminates ions, with the participation of alkali ions and formation of a gelic product, type sialate;

- evolution of sialate groups into more organized structural formations, type of poly (sialate-siloxo) [4]; the gel formation is passing, in time at semi-crystalline compounds





The alkalis compounds are necessary for the dissolution of silica and alumina from initial solid component and favor the polycondensation process. Alkaline cations and Ca^{2+} cations is assumed to be embedded in the reaction products, so physical, in structural cavities, and chemical, bound by $\text{Al}-\text{O}$ and $\text{Si}-\text{O}$ bonds[4].

Silico-aluminate materials used in geopolymers performing can be: fly ash, granulated blast furnace slag, calcined clay (metakaolin), together eventually, with some admixtures as: cement kiln dust, lime etc. Commonly used alkaline activators are: NaOH , Na_2CO_3 , K_2CO_3 , K_2SO_4 [1-13]. The nature of these influences the geopolymerisation process and the properties of the obtained product. Usually, geopolymerisation processes involves initial thermal treatment of reactants mixture [1-13] that enhance these processes. Less used is the curing at room temperature, when the geopolymerisation processes are slower [14].

The present paper brings some data regarding synthesis and properties of some geopolymers type binders from Romanian fly ashes, having specific compositional and dispersional characteristics, activated with NaOH. For synthesis were considered the initial hydrothermal treatment at different temperatures (60 – 100°C). Geopolymerisation processes and reaction products formation, in correlation with initial hydrothermal treatment and subsequent storage in air, were investigated by X-ray diffractions and FTIR spectroscopy.

The binding properties were appreciated by the mechanical strengths determination, for the same conditions.

2. Experimental

Two types of fly ash from Romanian power stations were considered. Their chemical composition is shown in the Table 1. Some compositional differences can be mentioned:

- amount ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$): 80.66% - fly ash T and 84.11% - fly ash D

- the ratio $\text{SiO}_2 / \text{Al}_2\text{O}_3$: 2.25 - fly ash T and 2.17 –fly ash D;
- CaO content: 10.01% - fly ash T and 6.69% –fly ash D;
- LOI: 1.10% - fly ash T and 2.69% - fly ash D.

Table 1

Chemical compositions of the fly ashes

Fly ash type	Composition (%)								
	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
T	1.10	48.93	21.72	10.01	10.70	2.61	1.21	—	—
D	2.69	51.5	23.68	8.93	6.69	1.99	1.10	0.50	2.18

The ashes were ground at corresponding specific surface areas of $5900\text{cm}^2/\text{g}$ approximately. The alkaline activator was NaOH – as solutions 8M and 12M. The liquid/solid ratio of binding pastes was 0.39, for all compositions (table 2).

Table 2

Geopolymer type binder's indicatives and curing conditions

Fly ash type	Sa (cm^2/g)	NaOH concentration	Curing conditions	Liquid/solution ratio	Indicative of cured samples in air, for:		
					24 hours	7 days	28 days
T19	5952	12M	24 hours $\rightarrow 60^\circ\text{C}$	0.39	T19.3	T19.4	T19.5
T20			24 hours $\rightarrow 80^\circ\text{C}$		T20.3	T20.4	T20.5
T21			24 hours $\rightarrow 100^\circ\text{C}$		T21.3	T21.4	T21.5
T22			atm		T22.3	T22.4	T22.5
T23		8M	24 hours $\rightarrow 60^\circ\text{C}$		T23.3	T23.4	T23.5
T24			24 hours $\rightarrow 80^\circ\text{C}$		T24.3	T24.4	T24.5
D36	5908	12M	24 hours $\rightarrow 60^\circ\text{C}$		D36.3	D36.4	D36.5
D37			24 hours $\rightarrow 80^\circ\text{C}$		D37.3	D37.4	D37.5
D38			24 hours $\rightarrow 100^\circ\text{C}$		D38.3	D38.4	D38.5
D39			atm		D39.3	D39.4	D39.5
D40		8M	24 hours $\rightarrow 60^\circ\text{C}$		D40.3	D40.4	D40.5
D41			24 hours $\rightarrow 80^\circ\text{C}$		D41.3	D41.4	D40.5

The cylindrical samples with $d=h=20$ mm were prepared by pressing, and cured for geopolymersation and hardening in the next conditions: 24 hours – hydrothermal treatment at 60°C , 80°C and 100°C (in the tight closed box, with relative humidity approximately 100%) + n days (till 28) in the air ($T=20\pm 2^\circ\text{C}$ and $\text{RH}=55-60\%$).

On the hardened samples were determined compressive strengths, after thermal treatment at different periods of time, and respectively, after subsequent storage in the air.

Information on the geopolymers formation and reaction products formation was obtained by X-ray diffraction analysis and FTIR spectroscopy on the geopolymers samples, after different curing periods of time.

3. Experimental results

Mechanical strengths of the geopolymers type binders, synthesized in different conditions, are presented in Figs. 1 and 2.

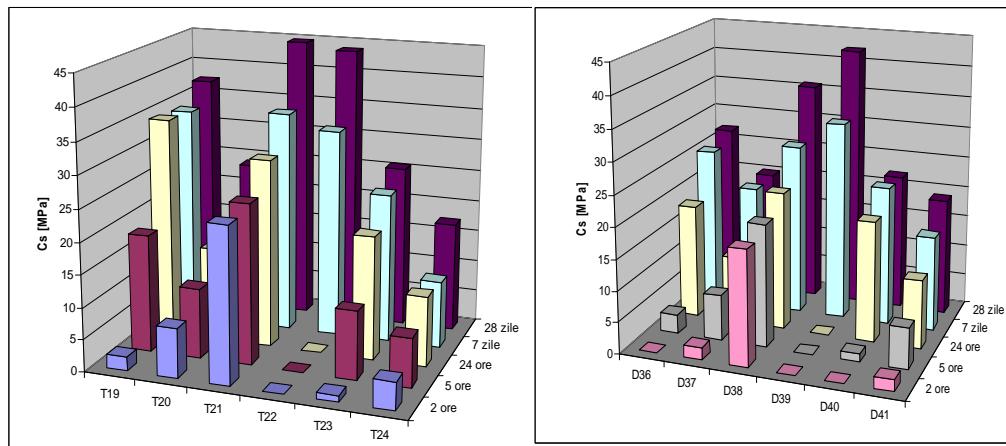


Fig. 1. Compressive strengths of the geopolymers binders resulted from fly ash T and 12M / 8M NaOH solution: $S_a = 5952 \text{ cm}^2/\text{g}$;

Fig. 2. Compressive strengths of the geopolymers binders resulted from fly ash D and 12M, 8M NaOH solution: $S_a = 5908 \text{ cm}^2/\text{g}$;

Higher compressive strengths are achieved for geopolymers compositions made from fly ash T, compared with those of type D masses.

The main *compositional characteristics* of T fly ash, which contribute to the better binding properties of the derived geopolymers, are:

- a greater CaO content (10.7% value is very close to the limit of the fly ashes type C and respectively of type F);
- a smaller loss on ignition, suggesting a lower carbon content, a high carbon content which could negatively influences the fly ash reactivity

The *initial thermal treatment*, of precursor mixtures, at temperatures up to 100°C, favors the development of compressive strengths, even after short periods of time (the first hours), better under conditions of high temperatures (100°C), in good correlation with literature data [1, 4]. Otherwise, for both categories of the masses, the best mechanical strengths were developed by the compositions T21 and D38, initial treated at 100°C (see Figs. 1 and 2). The continuous curing up to 7 days (28 days), in air, leads to further increases of strengths, for all compositions,

explained by the structuring processes of reaction products, which continues in these conditions.

Curing the samples at normal temperature ($20\pm2^\circ\text{C}$) determines a slow development of compressive strengths. Theirs values, determined for 7 and 28 days, are closely to those of the samples initial treated, at 100°C . This also confirms the accelerator effect of thermal treatment of these mixtures, on compressive strengths development, in correlation with the geopolymserisation process.

Concentration of NaOH solution influences the mechanical strength development. A higher NaOH concentration (12 M) favors the development of better mechanical strength, as can see in Fig. 3.

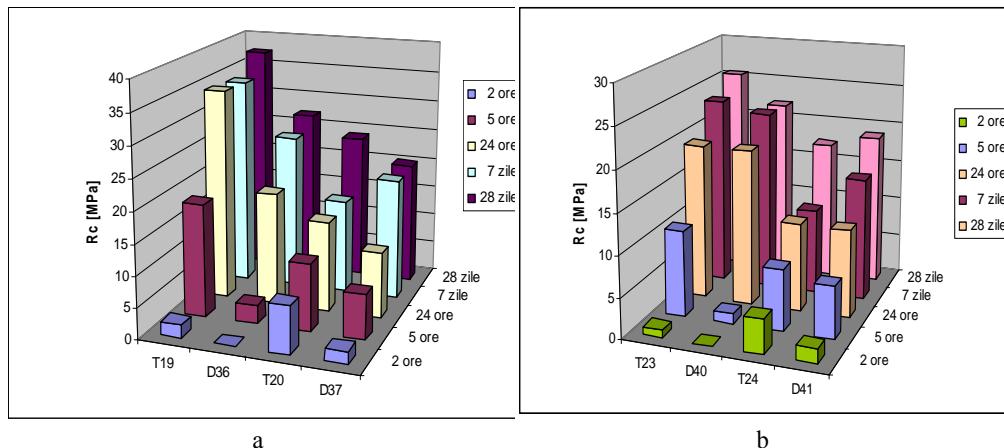


Fig. 3. Compressive strengths of some geopolymers from T fly ash and D fly ash, with: a- NaOH 12 M; b- NaOH 8 M; curing conditions: $24\text{h} \rightarrow 27^\circ\text{C} + 24\text{h} \rightarrow 60^\circ\text{C} + n$ days in air, and $24\text{h} \rightarrow 27^\circ\text{C} + 24\text{h} \rightarrow 80^\circ\text{C} + n$ days in air (for binders indicatives, see Table 2)

This influence is in correlated with a higher solubility of alumino-silicates compounds in concentrated alkaline solutions [4], the geopolymserisation process being also, favored.

Information on the **geopolymserisation processes evolution and reaction products formation** that ensure the mechanical strengths development, are obtained of FTIR spectroscopy and X-ray diffraction analysis.

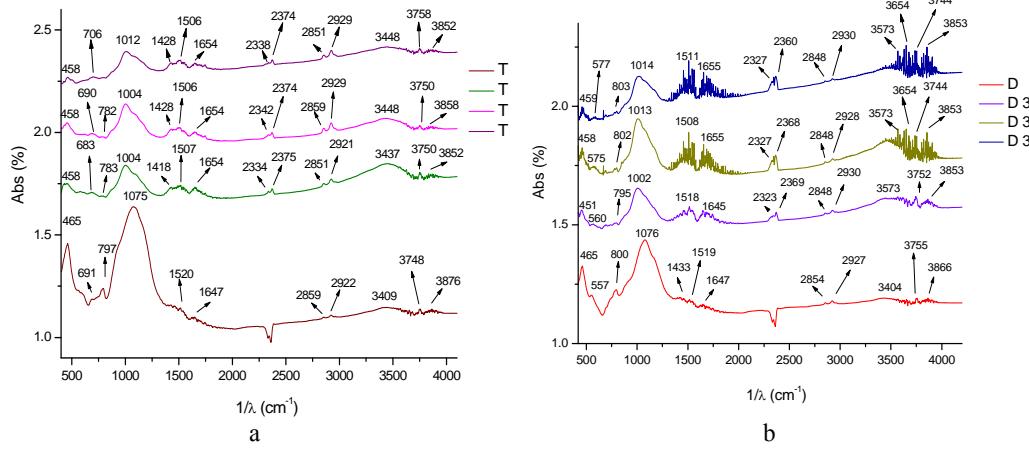


Fig. 4. FTIR spectra of fly ashes T and D and geopolymers prepared from these ashes and NaOH 12M, after thermal treatment at 60°C for 24 hours, and subsequent storage in air for 6 days respectively 27 days: a- fly ash T; b- fly ash D

FTIR spectra of the fly ashes show the following absorption bands (Fig. 4):

- 1075 cm⁻¹ - attributed to the asymmetric vibrations of bonds Si-O and Al-O [1];
- 465 cm⁻¹ - attributed to the deformation vibrations of Si-O bonds;
- 797 cm⁻¹ - attributed to Al-O bonds vibration.

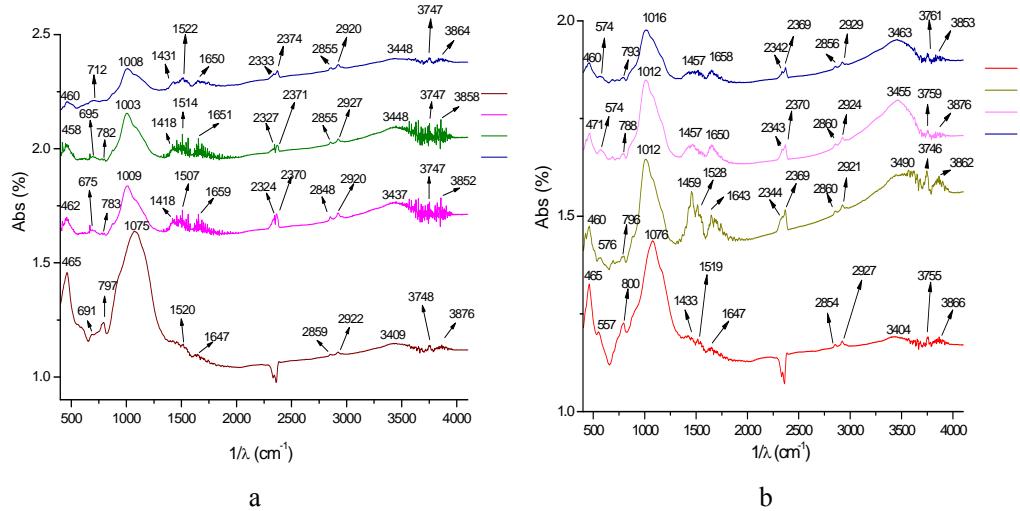


Fig. 5. FTIR spectra of fly ashes and geopolymers prepared from these, by activation with NaOH 12M, after thermal treatment at 80°C for 24 hours, and subsequent storage in air for 6 days respectively 27 days: a- fly ash T, b- fly ash D

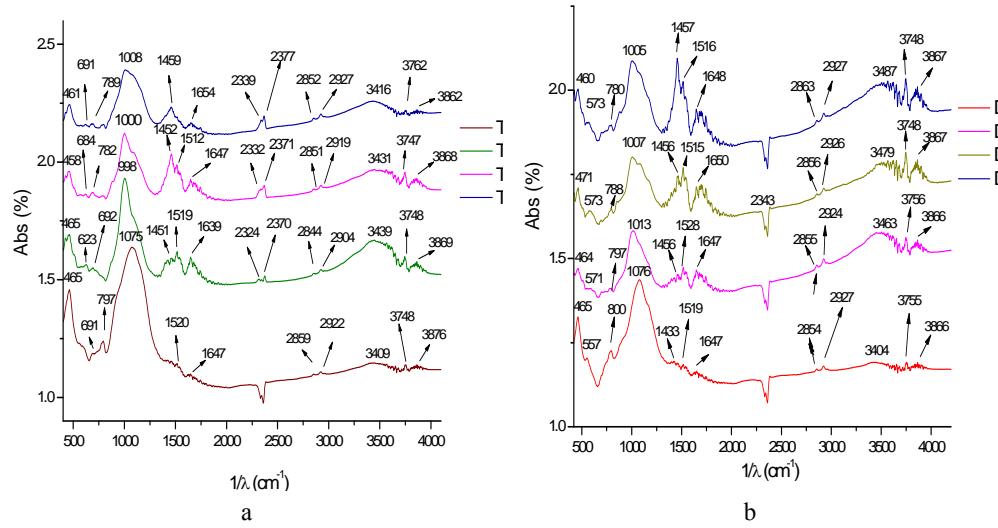


Fig. 6. FTIR spectra of fly ash and geopolymer binder prepared from fly ash and NaOH 12M, after thermal treatment at 100°C for 24 hours, and then kept in air for 6 days respectively 27 days; a- fly ash T, b- fly ash D

The main changes that are recorded on the geopolymer IR spectra, after hydrothermal treatment and subsequent storage in air (Fig. 4-6 T_{21.1}-T_{21.3}), consist in:

- the shifting of the main band (1075cm⁻¹) to smaller wave numbers (1003-998cm⁻¹), in parallel with the decrease of the its amplitude, which suggests the silica solubilisation and polycondensation processes, with partial substitution of SiO₄⁴⁻ with AlO₄⁵⁻ groups, in the newly formed network [3]; the valences compensation is achieved by Na⁺ ions; the shift is significantly for the thermal treated samples and practically does not change, for the storage in air;
- the disappearance of the band at 797 cm⁻¹, what point out the consumption of tetrahedral coordinated Al [3];
- the appearance of a two new bands, at about 3450 and 1650cm⁻¹, which belonging to the vibration bonds H-O and H-OH from aluminate-silicates hydrates, formed as reaction products;
- a well outlined band, at about 1459-1500 cm⁻¹, is attributed to C-O bond from alkaline carbonates formed by atmospheric CO₂ action.

X-ray diffraction analysis, performed on a geopolymer binders from fly ashes T and D, hydrothermal synthesized at 60°C, 80°C and 100°C - 24 hours and then kept in the laboratory atmosphere (air), up to 7 and 28 days respectively, are presented in Figs. 7 and 8.

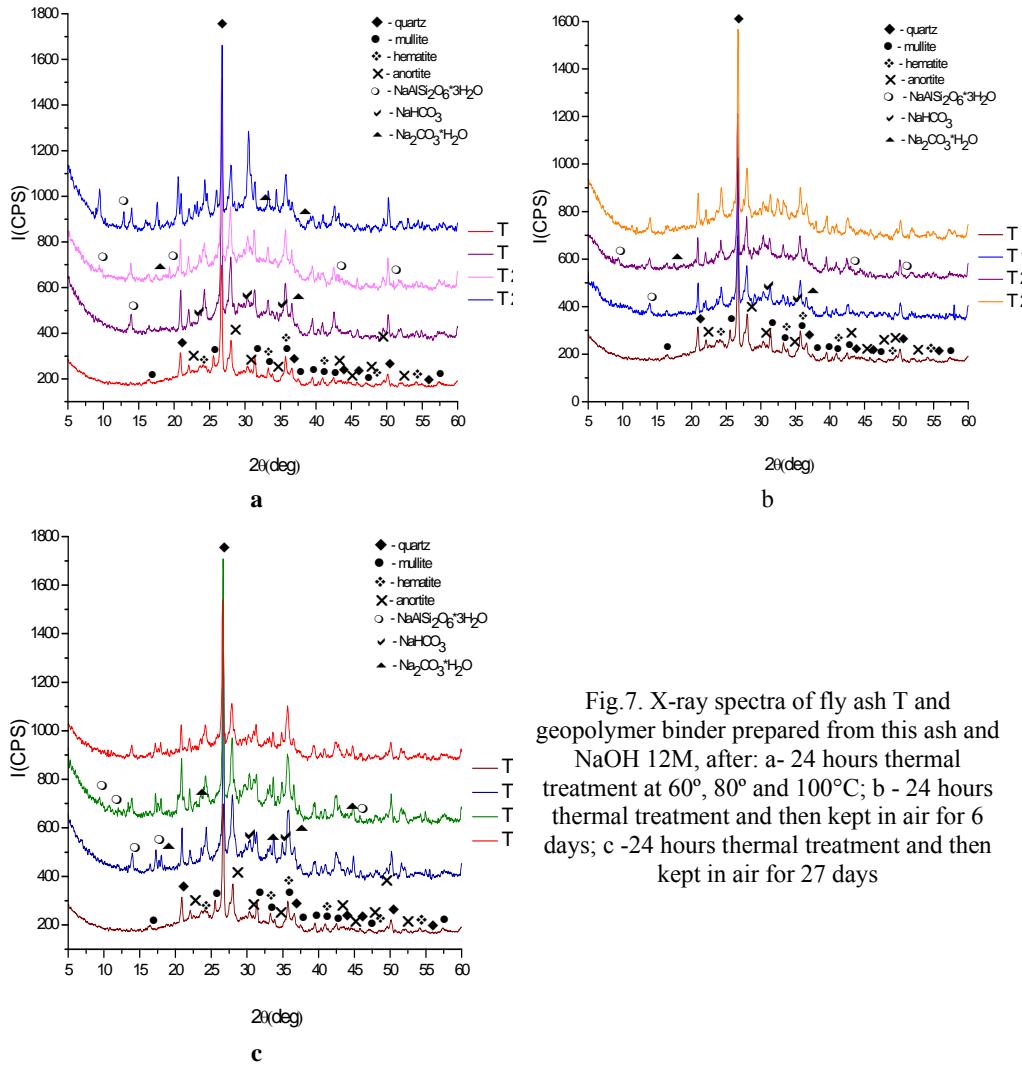


Fig. 7. X-ray spectra of fly ash T and geopolymers prepared from this ash and NaOH 12M, after: a - 24 hours thermal treatment at 60° , 80° and 100°C ; b - 24 hours thermal treatment and then kept in air for 6 days; c - 24 hours thermal treatment and then kept in air for 27 days

On the X-ray spectra of the geopolymers a small halo is present, in the range of $2\theta=20^\circ$ - 40° , which suggests the presence of poorly crystalline phases (nano-sized) - geopolymeric gel. As crystalline compounds are found in the fly ash main components - quartz, mullite, hematite, and some reaction products, these compounds, of zeolites type (hershelit ($\text{NaAlSi}_2\text{O}_6\cdot 3\text{H}_2\text{O}$) [11], phylipsit $\{\text{KCa}(\text{Si}_5\text{Al}_3)\text{O}_{16}\cdot 6\text{H}_2\text{O}\}$) have a certain crystallization degree. Their formation is favored by hydrothermal treatment [13]. Beside these products, the X-ray spectra suggest the presence of alkali carbonates too, in good correlation with IR spectra [16].

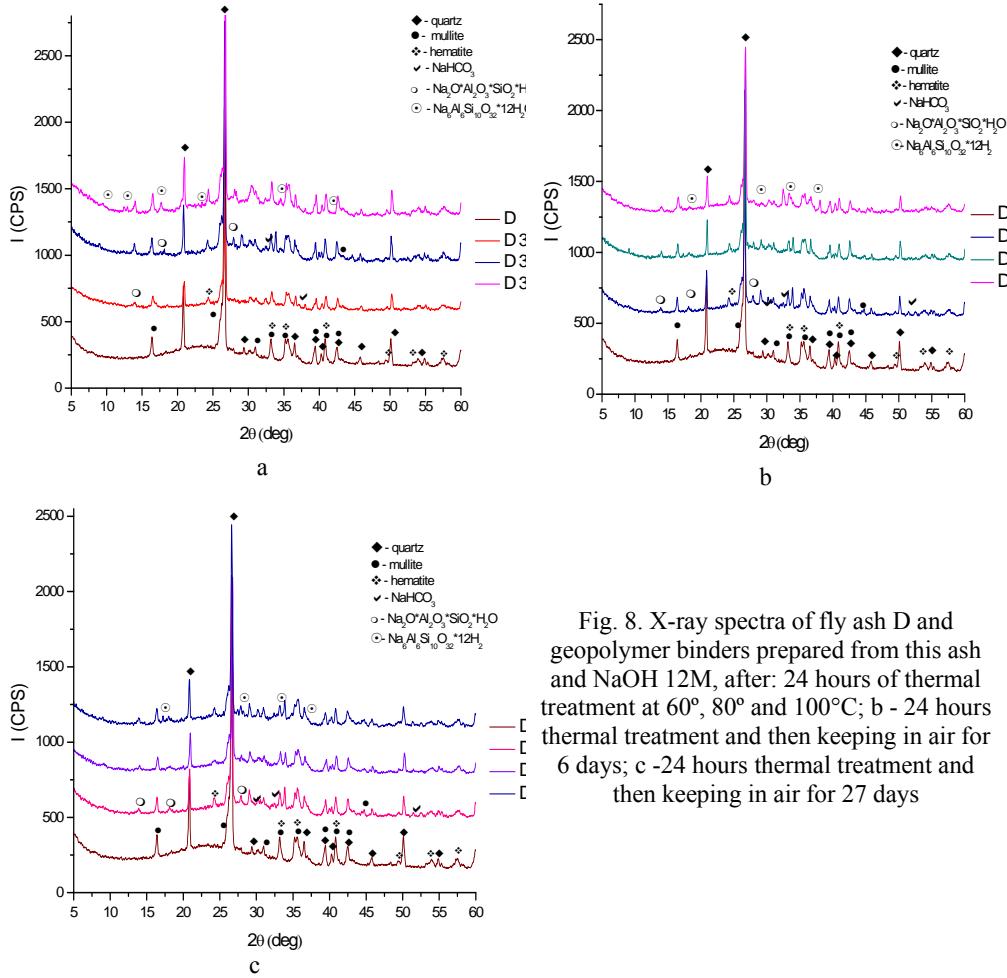


Fig. 8. X-ray spectra of fly ash D and geopolymers prepared from this ash and NaOH 12M, after: 24 hours of thermal treatment at 60°, 80° and 100°C; b - 24 hours thermal treatment and then keeping in air for 6 days; c - 24 hours thermal treatment and then keeping in air for 27 days

4. Conclusions

- The geopolymers type binders prepared by alkaline activation of the fly ashes with NaOH solution can develop good mechanical strengths, that are influenced by the compositional features and the processing conditions too.
- A great CaO and vitreous phase content, as well as small quartz content in fly ash T, exert a favourable influence on geopolymersation and mechanical strengths development.
- A higher concentration of NaOH solution favours the geopolymersation process and higher mechanical strengths development.

- The initial thermal treatment of the fly ash + NaOH solution mixtures, at temperatures up to 100°C, favours the geopolymersation process and the development of mechanical strengths, even after short periods of curing (2 hours).

- The curing at normal temperature (20±2°C) determine a slow development of mechanical strengths, as consequence of a very slow geopolymersation process.

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R E F E R E N C E S

1. *A. Palomo, M.W. Grutzeck, M.T. Blanco* – Alkali activated fly ashes. A cement for the future – Cem. Concr. Res. 29 (1999), 1323-1329
2. *M. Criado, A. Palomo, A. Fernandez-Jimenez* – Alkali activated of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products – Fuel 84 (2005), 2048-2054
3. *M. Stevenson, K. Sagoë-Crentsil* – Relationships between composition, structure and strength of inorganic polymers. Part2 Fly ash-derived inorganic polymers – J. Mater. Sci. 40 (2005) 4247-4259
4. *D. Khale and R. Chaudhary* – Mechanism of geopolymersation and factors influencing its development: a review, J. Mater. Sci 42 (2007), 720-740
5. *J. Davidovits* – Geopolymer. Chemistry and applications, Institute Geopolymere, 2008
6. *S. Kumar, R. Kumar, T.C. Alex, A. Bandopadhyay and S.P. Mehrotra* – Influence of reactivity of fly ash on geopolymersation – Advances in Applied Ceramics (2007), v. 106, n.3
7. *F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali* – Alkali activated binders: A review. Part 2. About materials and binders manufacture - Construction and Building Materials xxx (2007)
8. *Sang-Sook Park and Hwa-Young Kang* – Strength and microscopic characteristics of alkali-activated fly ash-cement – Korean J. Chem. Eng. 23 (3), 367-373 (2006)
9. *K. Dombrowski, A. Buchwald, M. Weil* – The influence of calcium content on the structure and thermal performance of fly ash based geopolymers – J. Mater. Sci. 42 (2007), 3033-3043
10. *Fr. Skvara, L. Kopecky, J. Nemecek, Z. Bittnar* – Microstructure of geopolymer materials based on fly ash – Ceramics – Silikaty 40(2006), 208-215
11. *F. Pacheco-Torgal, J. Castro-Gomes, S. Jalali* – Alkali activated binders: A review Part 1. Historical background, terminology, reaction mechanism and hydration products – Construction and Building Materials xxx (2007)
12. *S. Kumar, R. Kumar, S.P. Mehrotra* – Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymers – J. Mater. Sci., published online, 15 oct. 2009
13. *D. Ravikumar, S. Peethamparan, N. Neithalath* – Structure and strength of NaOH activated concretes containing fly ash or GGBFS – Cem. Concr. Comp. xxx (2010)

14. *D. Kalousek, J. Brus, M. Urbanova, J. Andertova, V. Hulinsky, J. Vorel* – Preparation, structure and hydrothermal stability of alternative (sodium silicate free) geopolymers, *J. Mater. Sci.* 42 (2007), 9267-9275
15. *M. Georgescu, I. Cătănescu, G. Voicu* – Fly ash based geopolymer binders. Influence of some compositional characteristics, *Romanian Chemistry Journal* 62 (2011), 872-877.