SYNTHESIS OF THE CERAMICS WITH NEPHELINE FROM GEOPOLYMERIC PRECURSORS
SINTEZA CERAMICILOR CU NEFELIN DIN PRECURSORI GEOPOLIMERICI

A. MELINESCU, M. EFTIMIE *, A. NICOARĂ, R. TRUȘCĂ, M. PREDA
Universitatea Politehnica București, Str. G. Polizu nr. 1, cod 011061, București, România

Geopolymer technology can be used to obtain precursors for the synthesis of ceramic materials, being a much simpler alternative to conventional processes. In this paper we experimented the synthesis of nepheline-based material from calcined kaolin and NaOH solutions with 8M and 12M, respectively. To increase the SiO_2 concentration, the Govora fly ash was used. Chemical reactions that take place at low temperature and high temperature heat treatment are studied. It was found that by reaction at 800°C the sodium ortho-silicate was formed and at 800°C this compound was consumed for nepheline formation and, in the same time, $Na_2O{\cdot}SiO_2$ appeared. When introducing fly ash, the main crystalline phases are α-quartz, nepheline and the anorthite, the latter compound coming from the ash. Sodium metasilicate is no longer found in fly ash samples because it has reacted with the vitreous phase of ash leading to the formation of nepheline.

Tehnologia geopolimerică se poate folosi pentru obținerea de precursori la sinteza unor materiale ceramice, fiind o alternativă mult mai simplă comparativ cu procedeele clasice. În această lucrare s-a experimentat sinteza de material pe bază de nefelin pornind de la caolin calcinat și soluții de NaOH cu concentrația de 8M și, respectiv, 12 M. Pentru creșterea concentrației de SiO_2 s-a folosit cenușa zburătoare de Govora. S-au studiat reacțiile chimice care au loc la tratamentul termic de temperatură joasă și, respectiv, de temperatură ridicată. S-a constatat că, prin reacție la temperatura de 80°C se formează ortosilicatul de sodiu, iar la 800° C acesta se consumă în reacția de formare a nefelinului concomitent cu apariția $Na_2O{\cdot}SiO_2$. La introducerea cenușii zburătoare principalele faze cristaline sunt α-cuarțul, nefelinul și anortitul, acesta din urmă provenind din cenușă. Metasilicatul de sodiu nu se mai constată la probele cu cenușă pentru că a reacționat cu faza vitroasă din cenușă ducând la formarea nefelinului.

Keywords: *nepheline, geopolymer technology, XRD, SEM*

1. Introduction

Geopolymers are materials that are obtained through a chemical reaction between a component rich in alumina and silica and a strong alkaline solution that can be made up of alkaline hydroxides or a mixture of alkaline hydroxides and silicates [1,2].

The aluminosilicate sources can consist of kaolins, clays, slags and some rich alumina fly ashes. Kaolins and clays can be used in natural or calcined state. These have the kaolinite as the main mineralogical component, with the formula $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$. Its structure consists from packets of $[SiO_4]^{4-}$ tetrahedrons layers with the bases placed in the same plane and octahedrons layers of $[AlO_2(OH)_4]^{5-}$ linked by strong covalent bonds. Between these packets weak hydrogen bonds exist. By heat treatment at relatively low temperatures, between 450 and 800°C, the two molecules of water from the structure of the kaolinite are removed as vapors. This wide range of temperatures can be explained by the different particle sizes and degree of purity and crystallinity of the raw material used. By eliminating HO^- ions from the network, its equilibrium is destroyed and results a metastructure which contains many defects and therefore a high degree of reactivity.

The reaction between the two components at low temperature is a polycondensation process that leads to the formation of amorphous or semi-crystalline aluminosilicates, such as zeolites or feldspars [1-4].

Geopolymers offer a new alternative of preparation of the ceramics in comparison to the classic methods currently used: mechanical homogenization, mechanical activation, co-precipitation, sol-gel method etc. This method is more accessible, uses cheaper raw materials and requires much lower heat treatment temperatures. Geopolymers can be transformed into ceramic materials by a suitable heat treatment with a well-defined phases composition and proper properties. For this reason, they can be used as precursors for construction ceramics, ceramic tiles, technical ceramics, matrices for composite materials, high temperature resistant products etc. [1,2,5-13]. To use them as ceramic materials, it is necessary to know the chemical reactions that occur when the geopolymers are subjected to thermal treatment, as well as their behavior at sintering, to obtain porous or dense products. Geopolymeric method allows the synthesis of some compounds that can be used as refractory materials, medical ceramic implants,

* Autor corespondent/*Corresponding author*,
E-mail: m.eftimie@gmail.com

Table 1

The recipes of the synthesized samples / *Rețeta probelor sintetizate*

Sample	%			Ratio
	calcined kaolin	NaOH	Govora fly ash	Al:Si
1	80	20	-	1:1
2	51.58	20	28.42	1:1.5
3	38.07	20	41,93	1:2

Table 2

Oxide and mineralogical compositions of Govora fly ash / *Compoziția oxidică și mineralogică a cenușii Govora*

Oxide composition, % weight / Compoziția oxidică, % gravimetrice					
SiO_2	Al_2O_3	FeO	CaO	MgO	R_2O
49.76	21.94	12.45	9.42	4.20	2.22
Phase composition, % weight / Compoziția fazală, % gravimetrice					
S	CAS_2	A_3S_2	CMS_2	NAS_2	F_2S
15.45	17.61	16.48	22.70	10.18	17.63

Note: C-CaO; A-Al_2O_3; M-MgO; N-Na_2O; S-SiO_2; F-FeO

matrices for the storage of radioactive waste etc. [14].

Although many experiments have been made, the reaction mechanisms that lead to the formation of mineralogical composition of the geopolymers are not well known. In this paper the chemical reactions that are taking place at the synthesis of the nepheline starting from metakaolin and sodium hydroxide solution with or without fly ashes were studied.

2.Experimental

The raw materials used for the synthesis were Bojidar kaolin and fly ash from the Govora thermal power plant. The calcined kaolin was obtained by thermal treatment of the kaolin at 750°C with two hours plateau at maximum temperature. The recipes of synthesized samples are given in Table 1, the ratio between Si and Al being 1:1.5 and 1:2.0 to facilitate the formation of a compound of the feldspar type. The proportion of NaOH was 20%, constant for all samples. The first of these samples was obtained only from calcined kaolin and sodium hydroxide solution. To increase the amount of silica, for the other two samples Govora fly ash was used. Sodium hydroxide was used as solution of 8M and 12M, respectively. The mixtures were mechanically homogenized for 15 minutes and a paste resulted. Cylindrical shape samples with a diameter of 20mm and a height of 40mm were obtained by molding in polyurethane shapes and, after 45 minutes, extracted from the forms. Samples were stored at room temperature for 24 hours and afterwards were dried at 80°C for 10 hours. After drying, the samples were heat treated at 800°C with two-hours plateau. The phase composition of the samples was examined by X-ray diffraction using a Shimadzu 6100 diffractometer and the microstructure by scanning electron microscopy (SEM Quanta FEG).

3. Experimental results

3.1. Phase composition of solid raw materials

The thermal treatment of kaolin at 750°C leads to the elimination of the two molecules of water from kaolinite network, its main mineralogical compound, in accordance with the reaction:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \rightarrow Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (1)$$

(kaolinite) (metakaolinite)

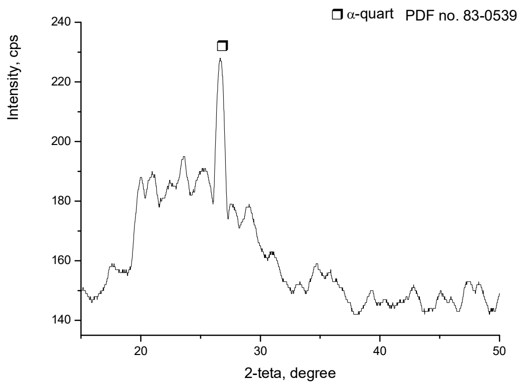


Fig.1 - X-ray diffraction pattern for calcined kaolin obtained by thermal treatment at 750°C / *Spectrul de difracție RX la caolinului calcinat la 750°C* .

The obtained powder was examined by X-ray diffraction and its XRD spectrum is given in the Figure 1. This figure shows only specific lines for α-quartz, that is found as impurity in kaolin. Also, the deviation of baseline from linearity shows that the calcined kaolin contains amorphous material that comes from the structural transformation of the kaolinite.

The oxidic composition of fly ash, used in this paper, is presented in the Table 2. It is noticed that the sum of oxides of silicon, aluminum and calcium represents about 80% of the total composition and it can be noted the high content of aluminum oxide. In the same table the mineralogical composition at thermodynamic equilibrium is presented, calculated based on the phase diagram. We can note a composition with many phases accompanied by free silica, which indicates that the fly ash is acidic. Therefore, this can react with the NaOH introduced into the mixture. The XRD spectrum of fly ash is give in the Figure 2, where two crystalline phases were identified: the α-quartz and the anorthite which confirm the results obtained in the paper [15].

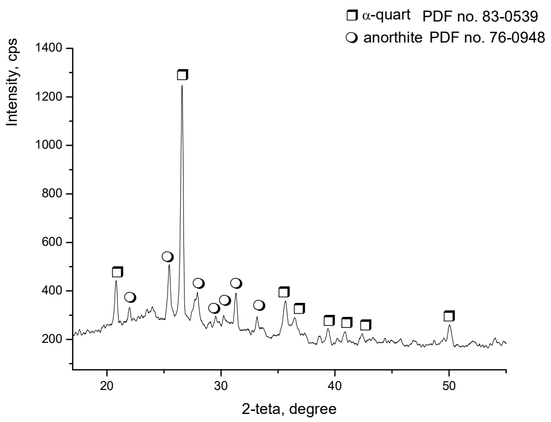


Fig.2 - X-ray diffraction pattern for the Govora fly ash / *Spectrul de difracție RX al cenușii Govora.*

The rest of the compounds calculated at the thermodynamic equilibrium are found in the vitreous phase.

3.2. *Phase composition of the synthesized samples*

The XRD spectrum for the sample 1, dried at 80°C, is given in Figure 3. Thus, for both solutions of 8M and 12M NaOH two crystalline compounds were identified, namely, α-quartz and sodium orthosilicate [$2Na_2O\cdot SiO_2$]. The thermal treatment of these samples at 800°C (Figure 4) shows that the well-crystallized major phase is nepheline [$Na_2O\cdot Al_2O_3\cdot 2SiO_2$]. Together with this, one can see the lines of the α-quartz and sodium metasilicate [$Na_2O\cdot SiO_2$]. The presence of vitreous phase can be seen for sample 1 even at 800° C. The phase composition obtained for sample 1 is not favorable for a nepheline ceramic because sodium metasilicate has a low melting temperature that influences refractoriness and is also soluble in water.

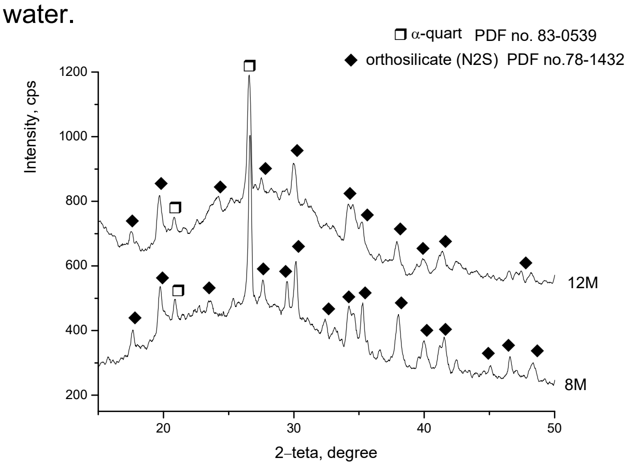


Fig.3 - X-ray diffraction pattern for sample 1 after drying for 10 h (80°C) / Spectrul de difracție RX al probei 1 după uscare 10h (80°C)

For the samples 2 and 3 Govora fly ash was used as a raw material. The XRD spectrum for sample 2 which contains calcined kaolin along with

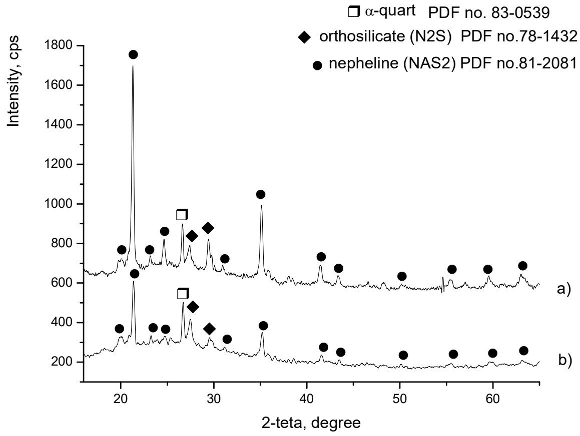


Fig. 4 - X-ray diffraction pattern for sample 1 heat treated at 800°C with 2h plateau a) obtained with NaOH 8M solution b) obtained with NaOH 12M solution / *Spectrul de difracție RX al probei 1 tratată termic la 800°C cu palier 2h a) cu soluție 8M NaOH b) cu soluție 12M NaOH*

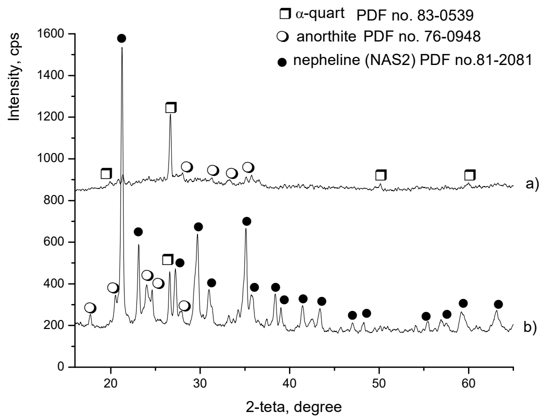


Fig.5 - X-ray diffraction pattern for sample 2 heat treated at 800°C with 2h plateau a) with NaOH 8M solution b)with NaOH 12M solution / *Spectrul de difracție RX al probei 2 tratată termic la 800°C cu palier 2h a) cu soluție 8M NaOH b) cu soluție 12M NaOH.*

fly ash, thermally treated at 800°C, is given in Figure 5. For the sample synthesized with 8M NaOH solution, there are three crystalline phases: α-quartz, anorthite and weak peaks characteristic of nepheline. On the opposite, when the 12M NaOH concentration solution is used, although the same three phases are found by X-ray diffraction, the major phase is the nepheline. This can be explained by the much better homogenization conditions for the 12M solution. The anorthite phase comes from fly ash, where it is found as a crystalline phase. The XRD spectrum for sample 3 is given in Figure 6 and, regardless of the concentration of NaOH solution used, the crystallinity of the samples is high, and the crystalline phases highlighted are the same as mentioned before. This sample has the highest fly ash content and it is possible that, at elevated temperature, some of the components, such as nepheline, crystallize from the vitreous phase.

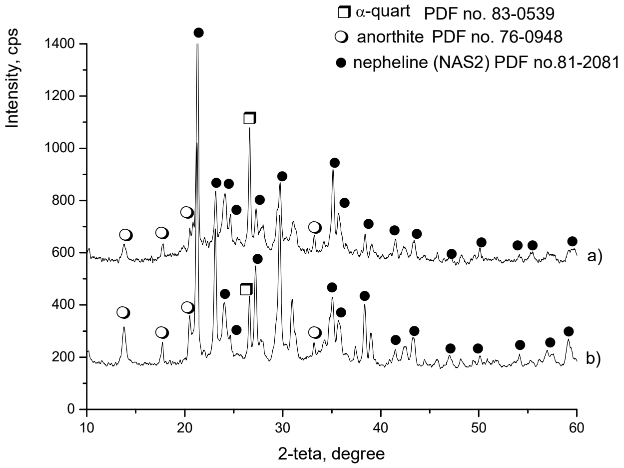


Fig.6 - X-ray diffraction pattern for sample 3 heat treated at 800°C with 2h plateau a)with NaOH 8M solution b)with NaOH 12M solution / *Spectrul de difracție RX al probei 3 tratată termic la 800°C cu palier 2h a) cu soluție 8M NaOH b) cu soluție 12M NaOH.*

3.3. Microstructure of the samples

The microstructure and the size of the grains for the synthesized samples were studied by scanning electron microscopy. Figure 7a shows the electron microscopy images of the sample 1 dried at 80°C. This figure indicates the presence of some grains still having the kaolinite microstructure, although this raw material was thermally treated at 750°C. This confirms the results of the paper [2]. Figure 7b shows that the sample is made up of agglomerated nanometric grains. In the Figure 8 is presented the electron microscopy image of sample 3, that contains the fly ash from Govora thermal power plant. The presence of spherical hollows from ash (Figure 8a) is observed and the space between these contains elongated nepheline grains which are resulted from the chemical reaction between the components (Figure 8b). Figure 8c shows that the sizes of the grains after heat treatment at 800°C increase to submicronic values.

3.4. The chemical reactions

Based on the determination of the phase composition, the reaction mechanisms for the synthesized samples were elaborated. Thus, for sample 1, resulting from calcined kaolin and NaOH solution, the formation of the compounds depends on the temperature. At 80°C, sodium hydroxide reacts with silicon dioxide, which leads to the formation of $2Na_2O\cdot SiO_2$ simultaneously with the elimination of two molecules of water in accordance with the reaction:

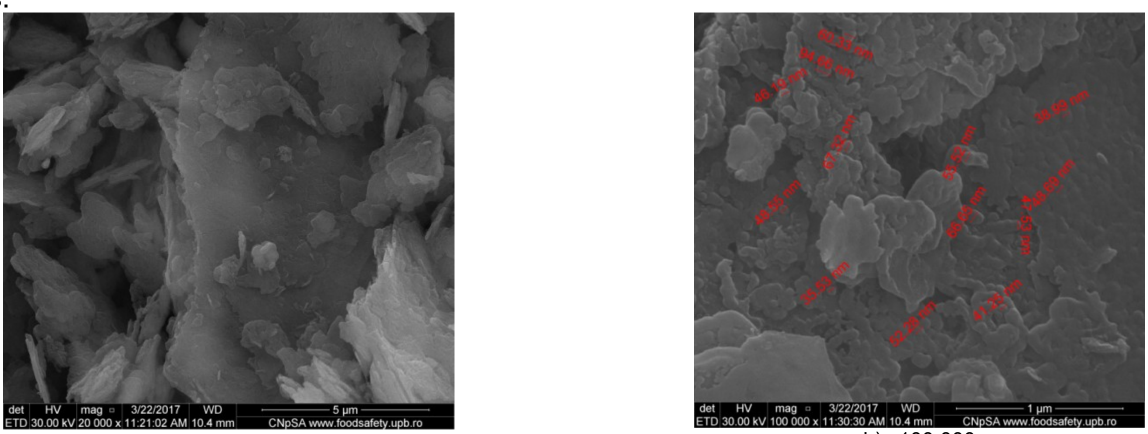
$$4NaOH + SiO_2 \rightarrow 2Na_2O\cdot SiO_2 + 2H_2O \quad (2)$$

The same sample thermally treated at 800°C contains two crystalline phases, namely nepheline and sodium metasilicate, which shows that sodium orthosilicate was consumed in the reaction:

$$Al_2O_3\cdot 2SiO_2 + 2Na_2O\cdot SiO_2 \rightarrow Na_2O\cdot Al_2O_3\cdot 2SiO_2 + Na_2O\cdot SiO_2 \quad (3)$$

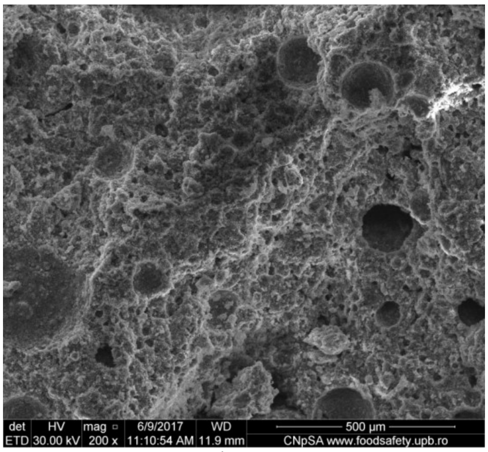
This indicates that the chemical reactions take place in stages and that, at 800°C, the thermal equilibrium has not been achieved.

For samples 2 and 3, the fly ash was used as the raw material, which leads to the modification of the composition of phases. Thus, the appearance of a crystalline compound, anorthite, coming from the ash, is observed. Next to this there are α-quartz and nepheline. The disappearance of sodium metasilicate is observed, which means that it reacted with the vitreous phase of the ash, thus contributing to the increase in the proportion of nepheline. This last compound could also come from the crystallization of ash, because it is a compound that can crystallize at thermodynamic equilibrium.

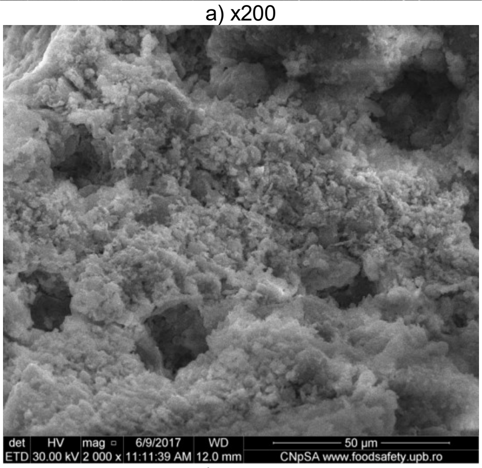


a) x20.000 b) x100.000

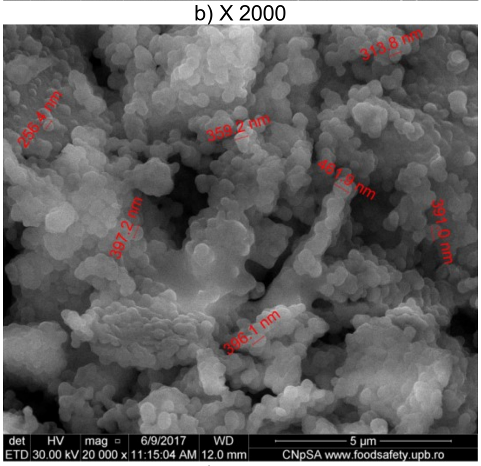
Fig.7 - Electron microscopy images for sample 1, obtained with NaOH 12M solution, after drying at 80°C/ *Imagini de microscopie electronică pentru proba 1, obținută cu soluție 12M NaOH, după uscare la 80°C.*



a) x200



b) X 2000



c) 20.000

Fig. 8 - Electron microscopy images for sample 3 heat treated at 800°C / *Imagini de microscopie electronică pentru proba 3 tratată termic la 800°C.*

4.Conclusions

Three compositions were synthesized by geopolymer technology using calcined kaolin, fly ash from power plants and sodium hydroxide solutions of 8M and 12M, respectively. X-ray diffraction studies showed in all samples the existence of the quartz which originates from the raw materials used. The chemical reactions take place in stages with the initial formation of some more basic compounds, which are then consumed to form nepheline. Compositions containing fly ash have a more complex phase composition, compared with those obtained from calcined kaolin. Some of the phases come from ash either due to chemical reactions with the vitreous phase or because of its crystallization.

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