EFECTUL COMPOZIȚIEI ŞI A CONDIȚIILOR DE ÎNTĂRIRE ASUPRA UNOR PROPRIETĂȚI ALE GEOPOLIMERILOR PE BAZĂ DE DEŞEURI DE STICLĂ DE LA TUBURILE CINESCOP ŞI CENUŞĂ DE TERMOCENTRALĂ

EFFECT OF COMPOSITION AND CURING REGIME ON SOME PROPERTIES OF GEOPOLYMERS BASED ON CATHODE RAY TUBES GLASS WASTE AND FLY ASH

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In this study was assessed the possibility of geopolymers synthesis by alkaline activation of cathode ray tube (CRT) glass waste with/without fly ash addition. The nature of solid component and alkali activator (sodium or potassium hydroxide solution) combined with the curing conditions (initial curing at 60°C for different times – 1 up to 7 days) exert an important influence on the fresh mortars workability, microstructure and consequently on mechanical properties. The higher values of the compressive strength were obtained for geopolymers based on CRT glass waste activated with KOH solution cured the first 4 days at 60°C. The substitution of CRT glass waste with fly ash decreases the workability of fresh mortars and consequently the compressive strength values. The durability of this type of geopolymer is affected by water conservation but the substitution of CRT glass waste with 25% fly ash improves to a certain extent this property.

În această lucrare se prezintă date referitoare la sinteza unor geopolimeri prin activarea alcalină a deşeurilor de sticlă provenite din tuburile cinescop (CRT) cu/fără adaosuri de cenuşă de termocentrală. Tipul componentului solid şi a soluției activatoare (soluție de hidroxid de sodiu sau potasiu) în corelare şi cu condițiile de întărire (păstrare inițială la 60°C timp de 1 până la 7 zile) exercită o influență importantă asupra lucrabilității mortarelor în stare proaspătă şi implicit asupra valorilor rezistenței la compresiune. Cele mai mari valori ale rezistenței la compresiune s-au obținut pentru compozițiile de geopolimer pe bază de deşeu de sticlă CRT activată cu soluție de KOH şi păstrată primele 4 zile la 60°C. Substituirea deşeului de sticlă CRT cu cenuşă de termocentrală determină o scădere a lucrabilității mortarelor şi în consecință o scădere a valorilor rezistenței la compresiune. Durabilitatea acestui tip de geopolimeri este redusă în cazul păstrării în apă, dar substituirea sticlei CRT cu 25% cenuşă de termocentrală poate îmbunătăți într-o anumită măsură această proprietate.

Keywords: *Geopolymer, Cathode ray tube glass waste, Fly ash, Properties, Water stability*

1. Introduction

Geopolymers, first defined by Davidovits [1], are mineral polymers with three-dimensional aluminate-silicate network. These materials are produced by the alkaline activation of an aluminosilicate source (metakaolinite, fly ash, slag, natural puzzolana etc.). As alkali activator sodium or potassium hydroxide solutions with/without sodium or potassium silicate solutions (waterglass) are generally used.

Recently was reported the use of different waste as precursors for geopolymer preparation such as glass cullet [2], mixtures of glass waste and blast furnace slag [3], mixtures of metakaolinite and thin film transistor liquid crystal display waste glass [4], ceramic waste (red clay brick and porcelain stoneware)[5], as well as hazardous waste i.e. air pollution control residues treated with DC plasma [6,7].

Geopolymers with good mechanical performances (around 50 MPa) can be produced by alkaline activation of cullet soda-glass with sodium or potassium hydroxide solutions and curing at 40-60°C for minimum 7 days [2]; nevertheless, the high value of Si/Al ratio (around 20) determines also a high sensitivity of these materials when cured in water [2].

Cathode ray tubes (CRT) glass is a waste resulted from the discarded computer monitors and TV sets; this material contains a large amount of lead (mainly as lead oxide) as well as other heavy metals such as barium and strontium. Several recycling options were studied including treatments for the recovery of lead or reutilization of CRT glass in synthesis of other products [8].

CRT glass waste can also be processed by crushing, acid washing and water rinsing, in order to remove Pb and the treated material can be used to replace fine aggregate in portland cement

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mortars [9-11]. The main drawback of this recycling option is generation of wastewaters with high concentration of heavy metals (mainly Pb). In addition, the use of treated CRT glass waste in portland cement mortars, for partial or total substitution of fine aggregate, modifies some properties including workability, compressive strength, alkali-silica reaction expansion or water absorption; for an optimum dosage of CRT glass waste these properties remains at satisfactory levels [10,11]. However, due to lead leaching, the upper limit for the replacement ratio of the CRT glass waste, suggested by Ling and Poon, is 25% [11].

Portland cement has the ability to immobilize heavy metals including Pb [12, 13]. Our previous results showed that CRT glass waste (non treated) can be also immobilized in alkali activated binders (geopolymers), based on slag or fly ash, activated with a mixture of sodium silicate and sodium hydroxide solutions [13].

To our best knowledge, the synthesis of geopolymers by alkali activation of non-treated CRT glass waste was not reported yet in literature; therefore in this paper is assessed the possibility of synthesis of geopolymers by alkaline activation of a mixture of CRT glass waste (non-treated) and fly ash; these formulation have a lower values of Si/Al ratio as compared with those specific for the alkali activated CRT glass waste. The influence of processing parameters, such as nature and dosage of solid and liquid components and initial thermal treatment time, are presented in this paper. The main drawback of the geopolymer materials based on glass waste is their high water solubility [2, 13]; therefore in this study their durability (assessed by immersion in demineralized water) was also studied.

2. Material and methods

2.1. Liquid and solid components

As alkali activators were used KOH and NaOH solutions (5M).

As solid components were used:

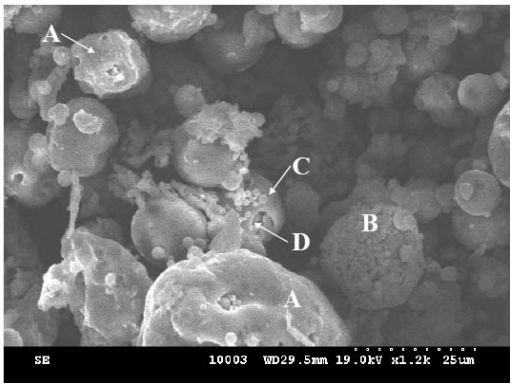
- cathode ray tubes (CRT) glass, resulted from the discarded computer monitors and TV sets (colour and black-white) mainly from the neck and panel parts; the mixed waste was crushed and ground up to a fineness corresponding to 3158 cm^2/g Blaine specific surface area; the main elements, assessed by X Ray Fluorescence (XRF), are: Si (33.99%), Pb (15.45%), Na (10.97%), Ba (8.84%), K (8.24%), Al (2.58%) and Sr (1.71%);
- fly ash, generated by coal combustion in power station, with the oxide and mineralogical composition presented in Table 1. The Blaine specific surface area of fly ash was 2639 cm^2/g.

Table 1

Oxide and mineralogical composition of fly ash
Compoziția oxidică şi mineralogică a cenuşii de termocentrală

Compound/*Compus*	Content/*Conținut*
SiO_2 (%)	48.93
Al_2O_3 (%)	21.72
Fe_2O_3 (%)	10.01
CaO (%)	10.7
MgO (%)	2.6
SO_3 (%)	1.21
Other compounds (%) Alti compusi	0.93
Loss on Ignition (%)/*Pierdere la calcinare*	3.9
Mineralogical composition assessed by X Ray Diffraction/*Compoziția mineralogică determinată prin difracție de raze X*	Al_2SiO_5, SiO_2, $CaAl_2Si_2O_8$

The SEM micrograph of fly ash (Fig.1a) shows the presence of hollow cenospheres (C) partially filled with small plerospheres (D); also, carbon grains (A) with high porosity and average size of 20-40 μm, along with crystalline phase (B) are identified.



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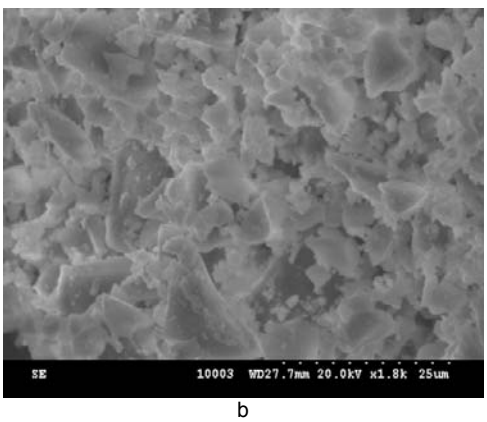


b

Fig.1 - SEM micrographs of fly ash (a) and CRT glass powder (b)/ *Imagini SEM ale cenuşii de termocentrală (a) şi sticlă CRTmăcinată (b).*

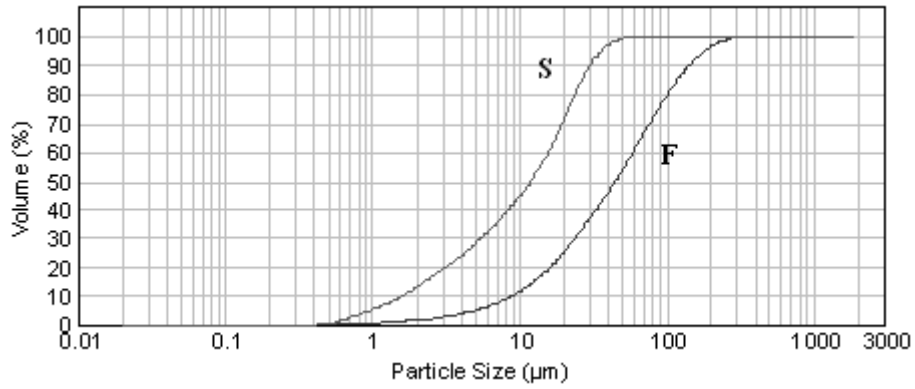


Fig.2 - Particle size distributions of CRT glass waste (S) and fly ash (F)/*Distribuția granulometrică a deşeului de sticlă CRT măcinat (S), respectiv cenuşă de termocentrală (F).*

The SEM micrograph of CRT glass powder (Fig.1b) shows the presence of angular glass particles with average sizes between 0.4 to 20 μm.

The particle size distribution, determined by laser granulometry, presented in Figure. 2, confirms the higher fineness of CRT glass powder (S), assessed by SEM, as compared with fly ash (F).

2.2. Preparation of geopolymers

Geopolymers mortars were prepared with the binder compositions presented in table 2 and siliceous sand (as aggregate). The binder to sand ratio was 0.5. The siliceous sand fulfilled the requirements of European and corresponding Romanian norm (SR EN 196-1, 2006) [14].

The mortar specimens were prepared by mixing the solid component (CRT glass powder with/without fly ash) with sand and alkali activator solution; the resulting material was cast in rectangular molds (15x15x60mm) and vibrated for 2 minutes. The specimens were cured in the mold (covered with cling film) at 60°C the first 24 h, then de-molded and cured at 60°C in humid atmosphere (R.H.85%) different periods of time – 1 up to 7 days. After that the specimens were stored in air (R.H.65%) at 20 ±2°C.

2.3. Test methods

Chemical composition of CRT glass waste was assessed by X ray fluorescence spectrometry (S8 Tiger Bruker) and of the fly ash (Table 1) with standard method described in European and corresponding Romanian Norm SR EN 196-2, 2006 [15]. The Blaine specific surface area was assessed with the method described in SR EN 196-6, 2010 [16].

The mineralogical composition of fly ash was assessed by X ray diffraction (XRD) analysis using a Shimadzu XRD 6000 diffractometer. The XRD spectrum was obtained using a monochromatic CuKα radiation (λ= 1.054 Å) and range 2θ from 5 to 60 degree.

The particle size distribution of fly ash and CRT glass powder were assessed with a Malvern Mastersizer 2000 laser particle seizer.

Compressive strength was assessed, using a Tonitech machine, on mortar specimens

Table 2

Compositions of geopolymers/*Compoziția geopolimerilor*

Composition/*Compoziție*	Solid component (%) *Component solid*		Alkali activator solution/*Soluție activator alcalin*	Liquid/solid (l/s)/*Raport lichid/solid*	Si/Al*	Si/M**
	CRT glass (S)/*Sticlă CRT*	Fly ash (F)/*Cenuşă de termocentrală*				
S_N	100	0	NaOH, 5M	0.4	13.2	9.8
				0.5	13.2	7.9
F25S75_N	75	25	NaOH, 5M	0.4	9.3	9.0
				0.5	9.3	7.2
F50S50_N	50	50	NaOH, 5M	0.4	6.9	8.2
				0.5	6.9	6.6
F75S25_N	25	75	NaOH, 5M	0.5	5.2	5.9
F_N	0	100	NaOH, 5M	0.5	3.4	5.3
S_K	100	0	KOH, 5M	0.4	13.2	5.9
F25S75_K	75	25	KOH, 5M	0.4	9.3	5.4

*Calculated based on chemical composition of raw materials/ *Calculat pe baza compoziției mineralogice a materiilor prime*

** M=Na or K

prepared and cured as presented in section 2.2. The compressive strength value is the average of at least three strength values assessed on specimens cured in similar conditions.

The durability of studied compositions was assessed by the immersion of mortar specimens in demineralized water [2]. The mortar specimens cured for 7 days (4 days at 60°C and 3 days at room temperature - 20±2°C) were immersed in demineralized water (water to solid ratio was 1.3). The immersion solutions were renewed daily in the first 4 days and then weekly up to 28 days.

Mass variation of specimen was calculated with the formula:

$$\Delta m = (m_t - m_i)/m_i \ (\%) \qquad (2.1)$$

were m_t = specimen mass after "t" days of immersions in water; m_i = specimen mass before immersion in water.

Compressive strength (Cs) variation after 28 days of immersion in water was calculated with the formula (2.2):

$$\Delta Cs = (Cs_w - Cs_i)/Cs_i \ (\%) \qquad (2.2)$$

were Cs_w = compressive strength of specimens immersed in water for 28 days; Cs_i = compressive strength before immersion in water.

The values of mass variation are the average of at least three individual values assessed on specimens cured in similar conditions.

SEM analyses were performed on selected mortar specimens (before and after immersion in demineralised water) coated with Ag, using a HITACHI S2600N microscope with accelerating voltage 25 kV.

3. Results and discussions

3.1. Effect of curing time on compressive strength

The compressive strengths developed by the geopolymers prepared from CRT glass waste with NaOH 5M solution as alkali activator, after different times of curing at 60°C, are presented in Figure 3. As it can be seen, the compressive strength of the specimens cured at 60°C increases with the increase of curing time up to 4 days. Prolonged curing at 60°C, up to 7 days, decreases the compressive strength value, opposite to the specimens cured from the 4th day up to 7th day in air at room temperature (20 ±2°C), for which the compressive strength continues to increase (hachure column). A possible explanation can be the decrease of water content in the specimens, which plays an important role in the raw materials dissolution, hydrolysis and polycondensation processes [1, 17]. Based on these data one can conclude that the optimum curing conditions, for this research program, are: 4 days at 60°C followed by air curing at room temperature (20±2°C).

3.2. Effect of solid component composition and liquid to solid ratio on compressive strength

The compressive strengths recorded for specimens prepared with different solid components and liquid to solid (l/s) ratios of 0.5 and 0.4 are presented in Figure. 4.

As it can be seen (Fig. 4a) the mortar specimens based on fly ash prepared with l/s=0.5 (F_N_0.5) do not develop recordable compressive strengths up to 28 days; this is mainly the consequence of low workability of fresh mortar, due to the partial absorption of the liquid component by the porous carbon grains present in the fly ash [18]. The increase of CRT glass waste content in the solid component increases also the fresh mortar workability and consequently higher values are achieved for the compressive strengths.

The reduction of l/s ratio from 0.5 to 0.4

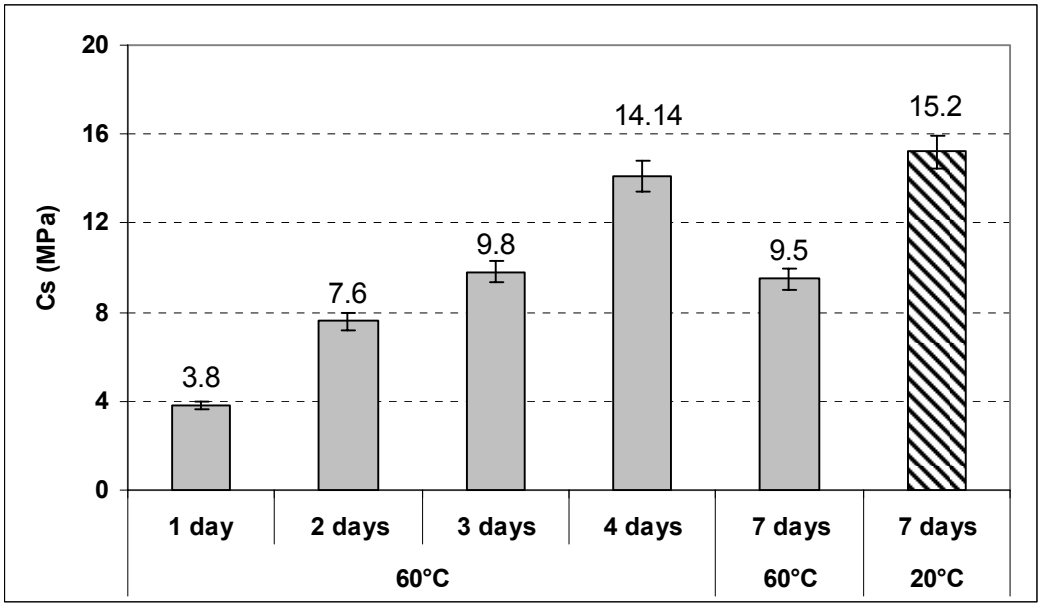


Fig.3 - Compressive strengths vs. curing time at 60°C/20°C of S_N mortars/ *Variația rezistenței la compresiune în funcție de timpul de păstrare la 60°C/20°C a probelor de mortar S_N.*

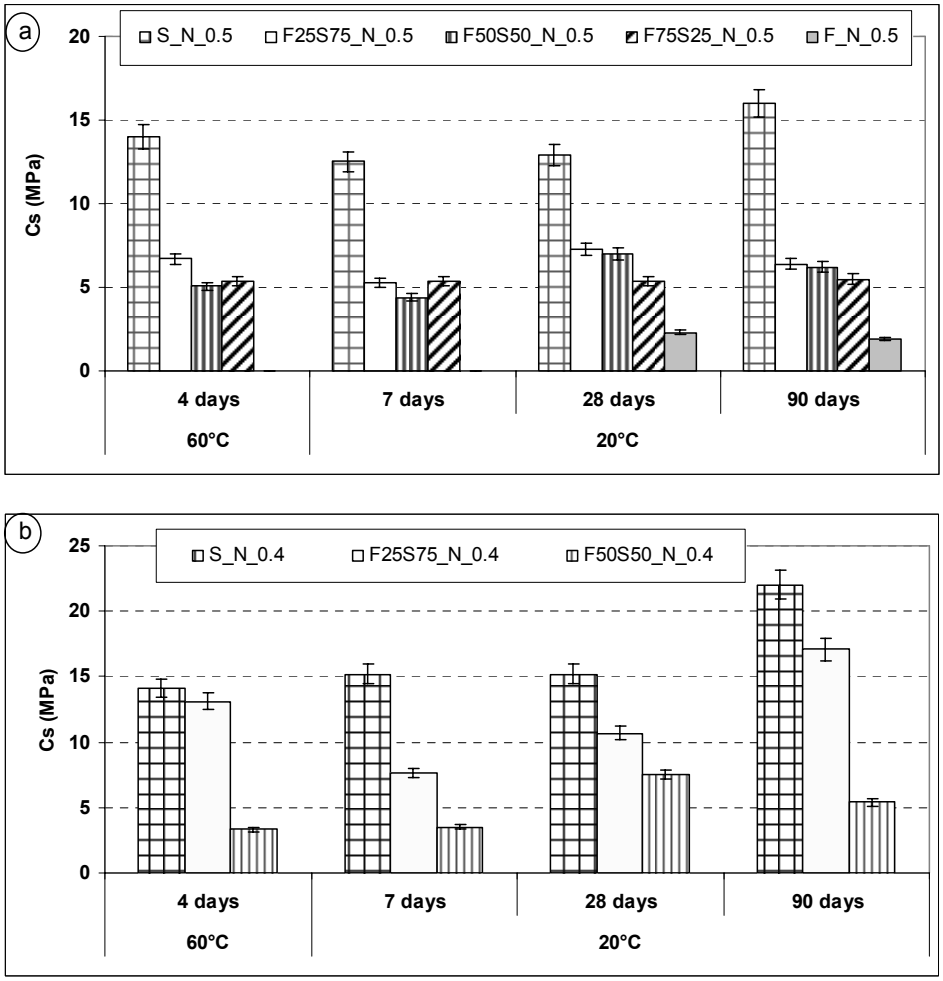


Fig.4 - Compressive strengths recorded for mortars prepared with liquid/solid ratio of 0.5 (a) and 0.4 (b)/*Rezistențe la compresiune determinate pe probe de mortar preparate cu raport lichid/solid de 0,5 a) şi 0,4 (b).*

(Fig. 4b), increases the compressive strengths of geopolymers with high CRT glass content (S_N and F25S75_N). This increase, observed also in other studies [2, 18], is explained by the reduction of hardened mortar porosity when the amount of liquid component (and consequently water) decreases.

3.3. Effect of alkali activator type on the mechanical strengths

The compressive strengths developed by the mortars based on CRT glass powder activated with KOH (S_K) are, in general, higher as compared with those activated with NaOH (S_N) – Figure. 5. According to literature data [19, 20],

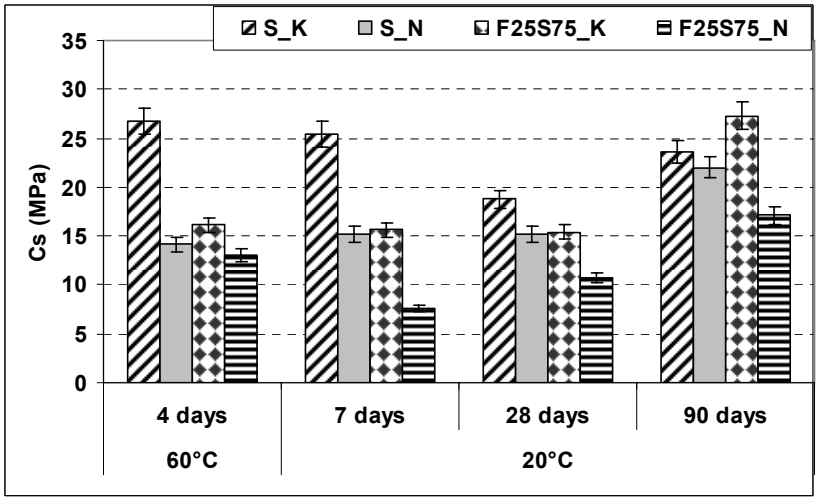


Fig.5 - Compressive strengths of geopolymer mortars based on CRT glass waste with/without fly ash activated with KOH and NaOH solutions/*Rezistențe la compresiune ale mortarelor de geopolimer pe bază de deşeu de sticlă CRT cu/fără cenuşă de termocentală.*

cations with small sizes, such as Na^+, react preferentially with silicate anions with low connectivity degree (monomers, dimers); larger K ions favour the stabilization of silicate oligomers and extend the geopolymerisation process, increasing accordingly the compressive strength values. This explains the lower compressive strength values recoded for the S_N as compared with S_K composition.

The substitution of CRT glass with 25% fly ash decreases the compressive strength values mainly due to the decrease of fresh mortar workability; this decrease is correlated with the liquid absorption on fly ash, due to it's content in porous carbon grains [18].

3.4. Water solubility

Mass changes of mortar specimens, cured in air the first 7 days and then immersed in demineralized water up to 28 days, are presented in Figure. 6.

As it can be seen, for the specimen based on CRT glass (S_K and S_N), mass losses are recorded even from the first day of immersion in water, confirming the high solubility of these materials. According to Tongovi et all. [21], large cations, such as potassium, tend to reconstitute rapidly their hydration shell and consequently are easily solubilised. This could explain the higher values of mass loss recorded for S_K as compared with S_ N.

On the contrary, the specimens with fly ash (F25S75_K and F25S75_N) show a mass increase after the first day of immersion due to water absorption in the porous material. After longer immersion periods, mass loss is also recorded for these materials but the values are smaller as compared with the mass loss recorded for the mortar based on alkali activated CRT glass waste (see Fig. 6).

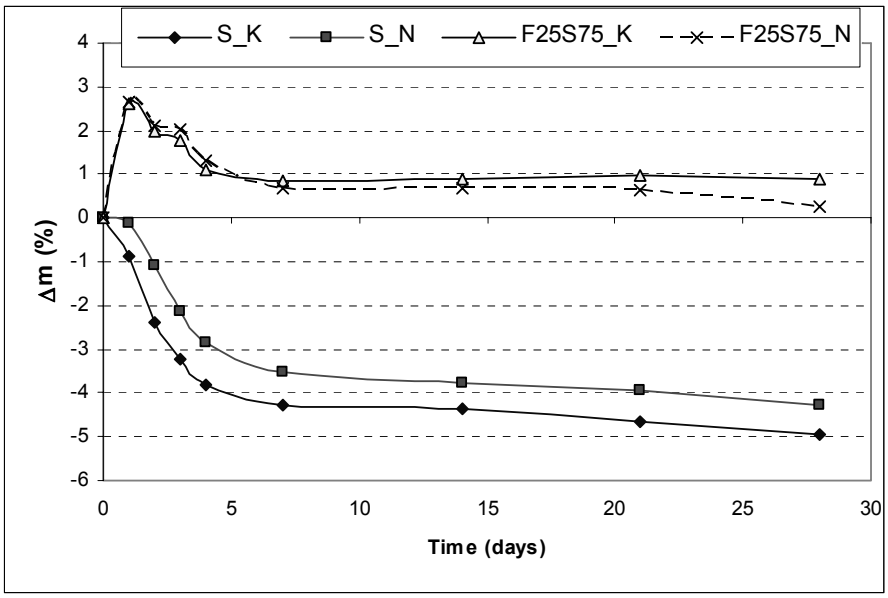


Fig.6 - Mass changes of mortar prisms (previously cured 7 days in air) immersed in demineralized water/*Variații de masă ale prismelor de mortar (păstrate în prealabil 7 zile în aer) imersate în apă distilată.*

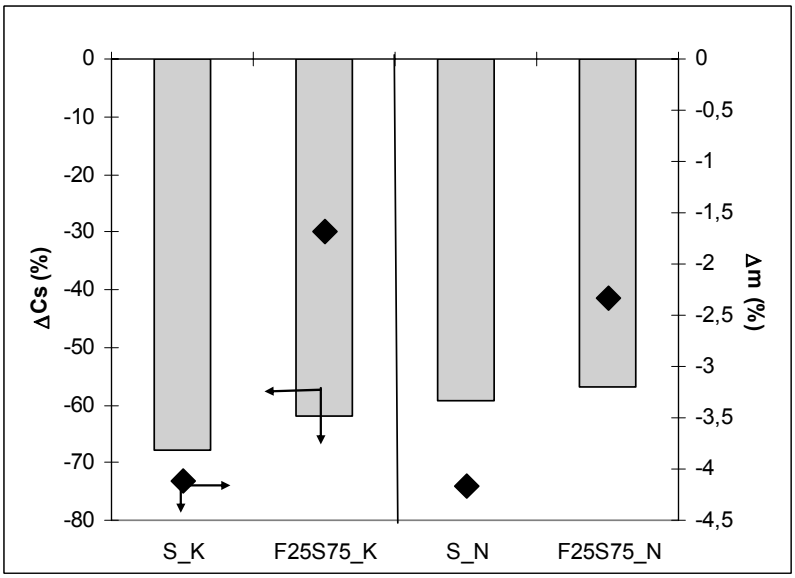


Fig.7 - Compressive strength (columns) and mass (dots) losses after 28 days of immersion of mortar prisms in demineralized water/ *Pierderea de rezistență la compresiune (coloane) şi pierderea de greutate (puncte) înregistrate după 28 de zile de imersare în apă demineralizată a probelor de mortar.*

The compressive strength values of specimens immersed in water for 28 days decrease for all studied compositions – Figure 7. The compressive strength loss (calculated formula 2.1) were smaller for the specimens with fly ash content (F25S75_K and F25S75_N) as compared with the ones recorded for S_K and S_N, in good correlation with the lower values of mass loss (calculated with reference to the specimen mass after 1 day of immersion).

Nevertheless the strength losses are high (over 50%) for all studied compositions therefore further researches are necessary to improve the hydrolytic stability of these materials. According to Cyr at all. [2], strength loss, recorded for geopolymer mortars based on glass cullet when stored in water, is influenced both by fineness of glass powders and initial curing temperature. An increase of fineness of CRT glass powder (or/and fly ash) could improve the water stability of studied compositions.

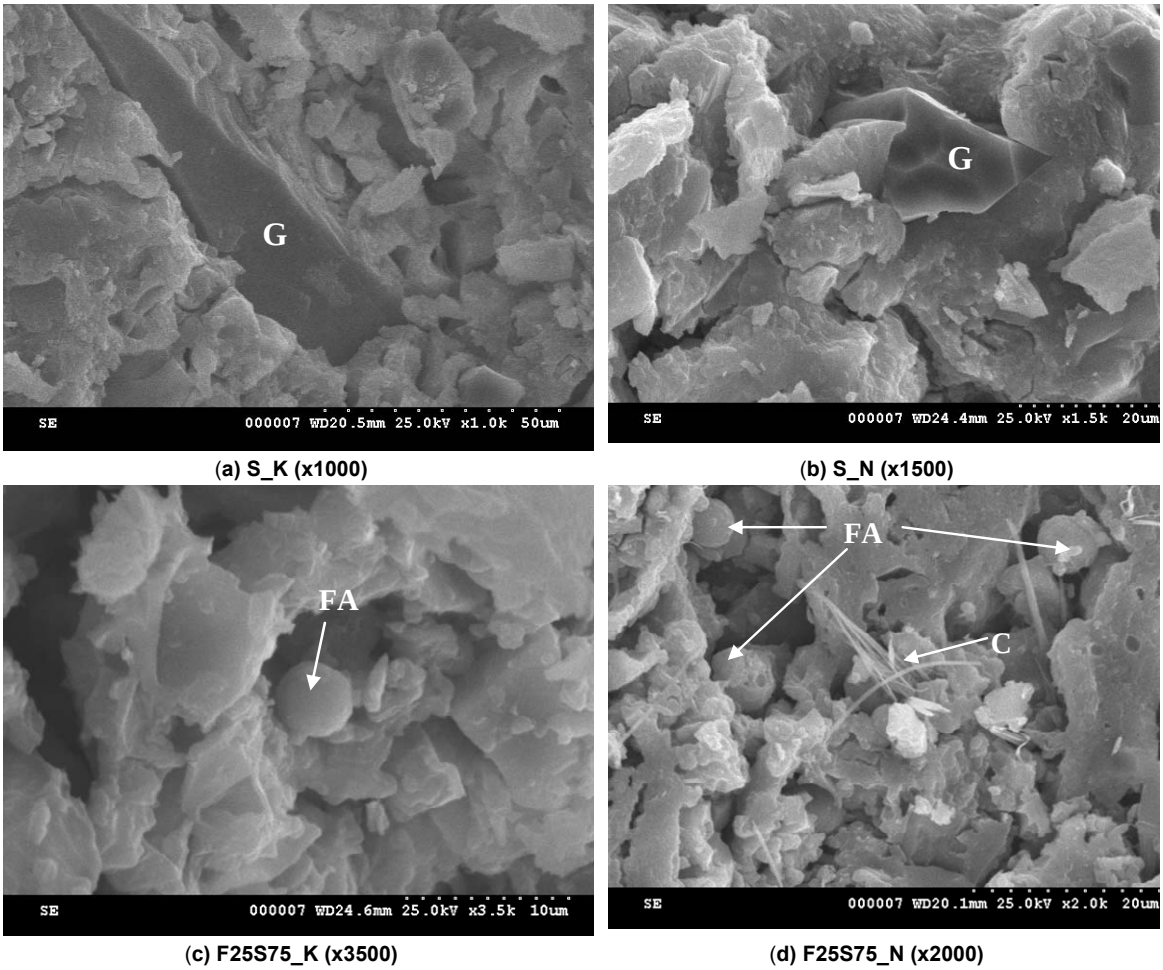
3.5. Microstructure

The SEM micrographs show the microstructure of alkali activated CRT glass waste (Fig. 8a,b) and CRT glass waste and fly ash (Fig. 8c,d) after 28 days of curing (4 days at 60°C and 24 days at room temperature – 20±2°C).

The microstructure of S_N and S_K specimens consists mainly from angular glass particles (G) covered with reaction products, most probably potassium/sodium silicates [2, 22]. In the microstructure of in the geopolymer with fly ash content, developed after 28 days of curing, can be assessed also spherical fly ash particles (FA). In the specimen F25S75_N (Fig. 8d) can be also identified fibrous crystals (C) which can be attributed to Na_2CO_3 formed by NaOH carbonation [23].

The SEM micrographs of geopolymers immersed in water for 28 days are presented in Figures 9-12.

On the surface of specimen S_K (Figs. 9c,d) the thickness of binding layer is much smaller and as compared with the one assessed in the inner zone (Figs. 9a,b); moreover, at the surface of glass grains from the outer layer, a gel like phase (see arrow) can be assessed (Fig. 9d); this phase is most probably formed by the solubilisation of the binding matrix.



(**a) S_K (x1000)** (**b) S_N (x1500)**

(**c) F25S75_K (x3500)** (**d) F25S75_N (x2000)**

Fig. 8 - SEM micrographs of geopolymers based on CRT glass (a, b) and on CRT glass + fly ash mixture (c, d) activated with alkali hydroxide solutions /*Imagini SEM ale geopolimerilor pe bază de sticlă CRT (a,b) şi amestecuri de stilcă CRT şi cenuşă de termocentrală (c,d) activate cu soluții de hidroxid de potasiu şi sodiu.*

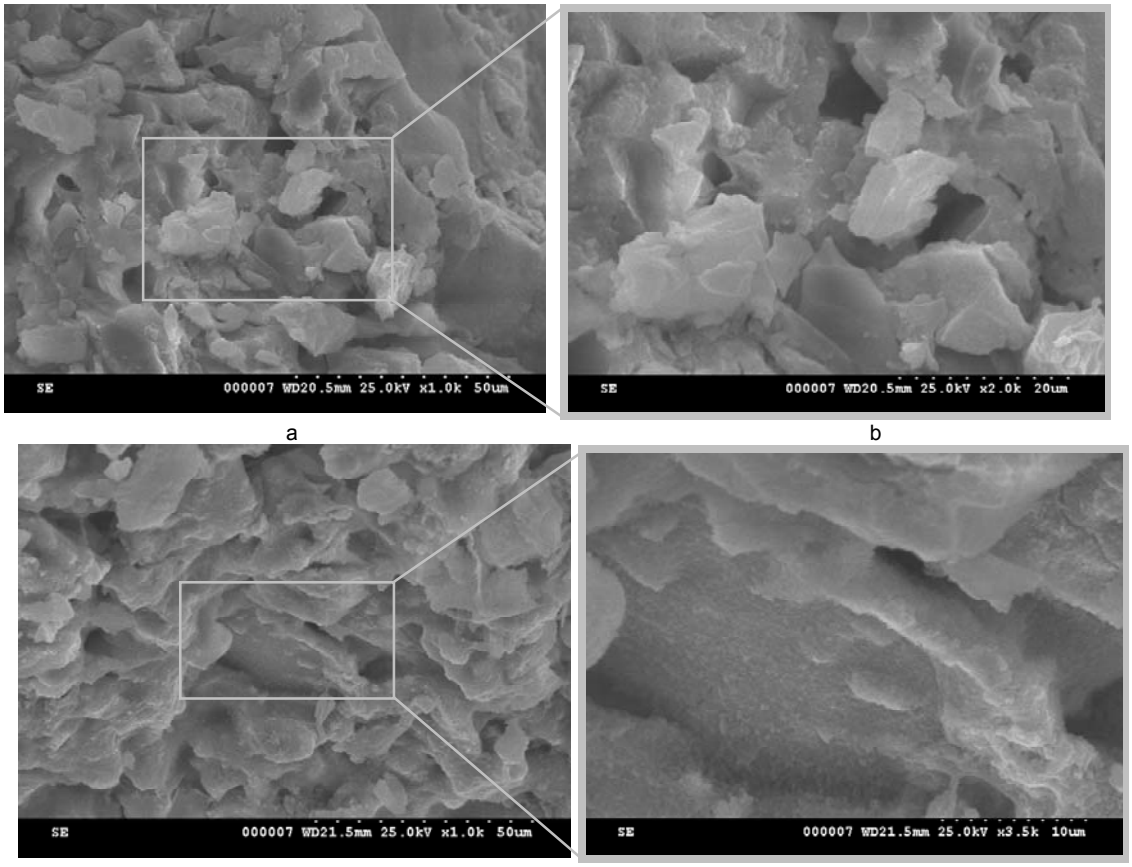


Fig. 9 - SEM micrographs of S_K specimen immersed for 28 days in demiterialized water: a and b - interior; c and d – surface/*Imagimi SEM ale probei S_K imersată timp de 28 zile în apă demineralizată.*

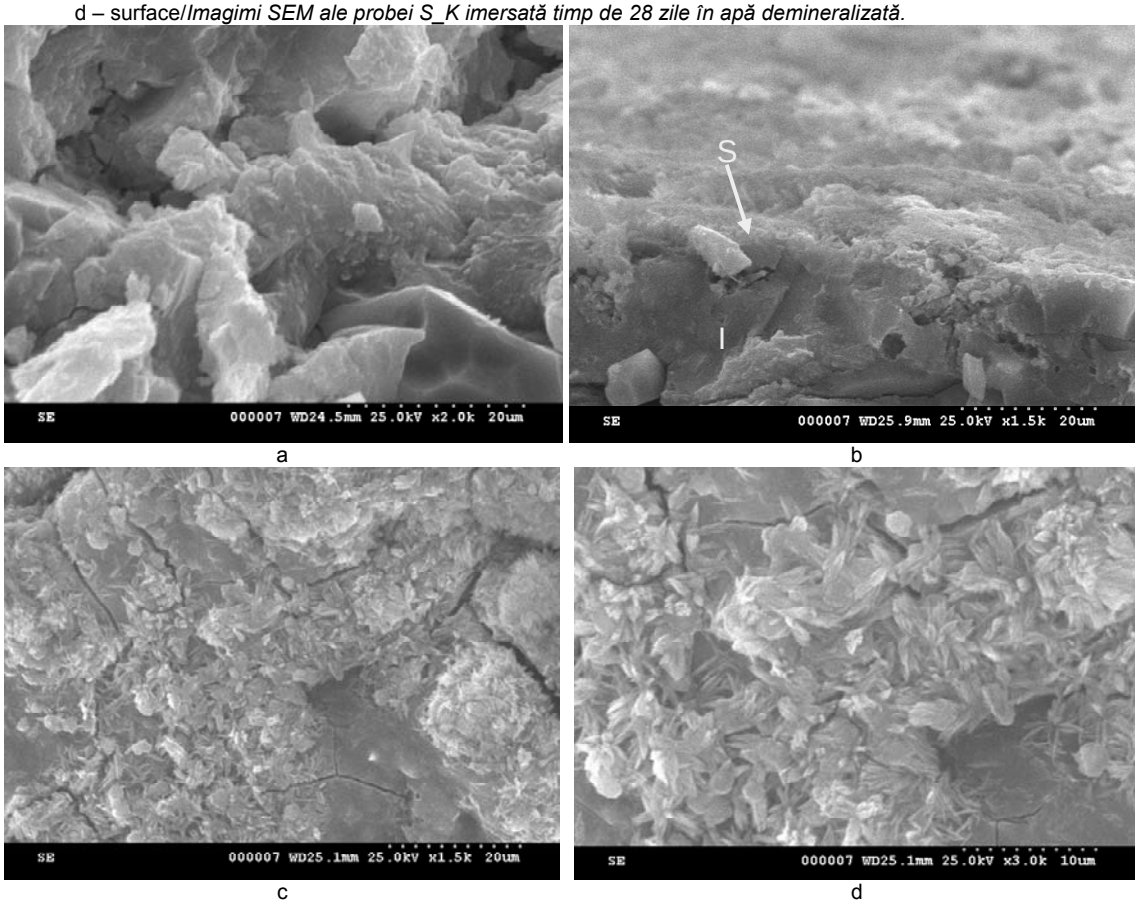


Fig. 10 - SEM micrographs of S_N specimen immersed for 28 days in demineralised water: a - interior (I); b - interface; c and d - surface (S)/*Imagini SEM ale probei S_N imersate timp de 28 zile în apă demineralizată: a - interior (I); b - interfață; c şi d - suprafață (S).*

The SEM micrographs of mortar specimen, based on CRT glass waste activated with NaOH solution (S_N), are presented in Figure 10. In the section of mortar specimen (Fig.10b) which shows the inner (I) and the surface (S) zones, one can notice a lower density of surface layer, as compared with the inner zone. On the specimen surface (Figs. 10c,d) one can also assess rod like crystals generally associated with zeolite phases [24]. The presence of zeolites in this material is connected with the higher zeolitization capability of sodium cations in gel forming systems [25].

On the SEM images of specimen with fly ash (F25S75_K), presented in Figure 11, can be assessed also spherical gel aggregates (see dotted circle), generally associated with the development of zeolite nuclei [24]. As it can be seen in Figures 11 e,f at the surface of the mortar specimen, the binding layer is thinner (as compared with the one assessed in the inner zone) and fly ash and glass grains (see arrows Fig. 11f) have fewer interactions with the binding layer (matrix).

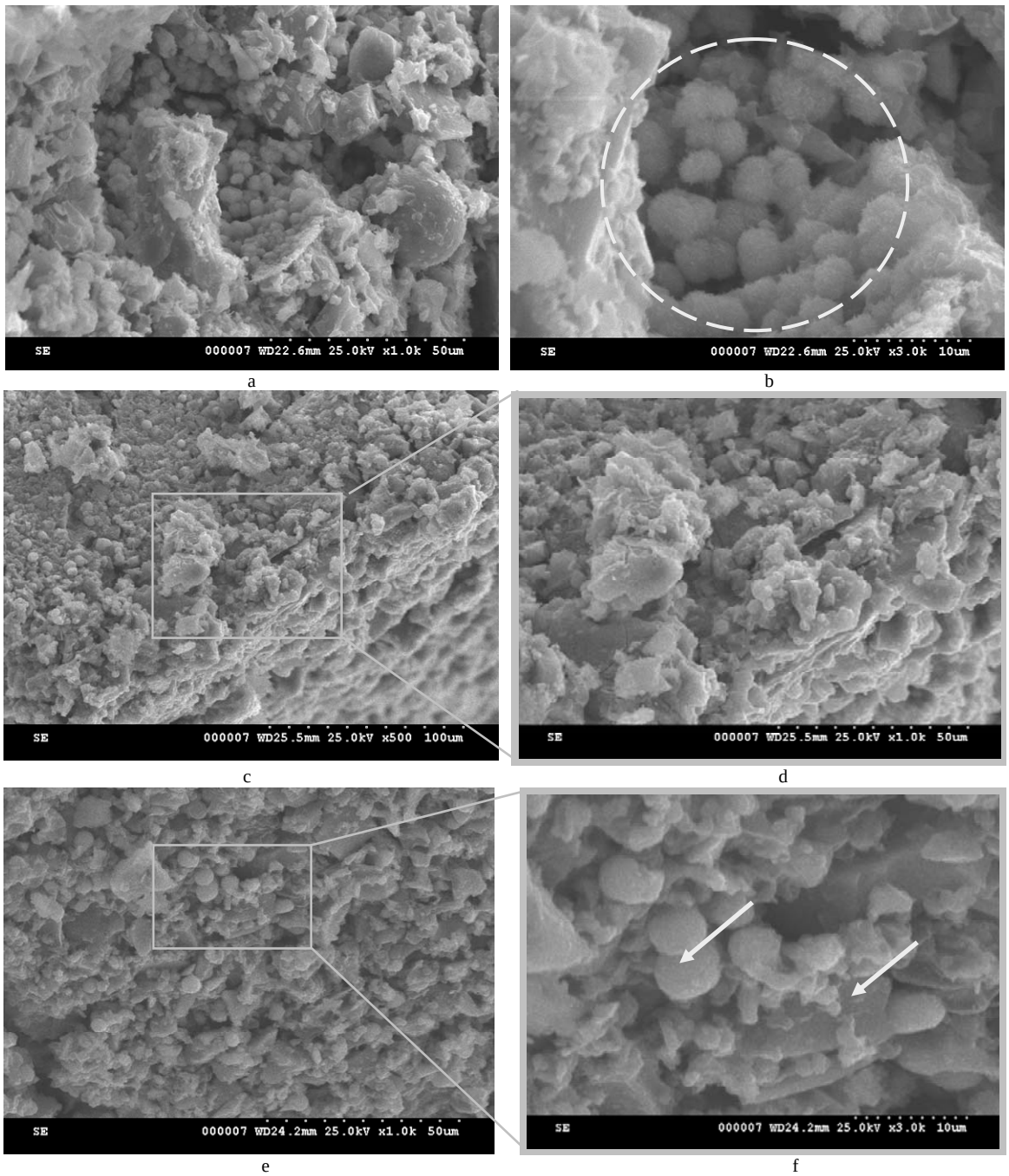


Fig. 11 - SEM micrographs of F25S75_K specimen immersed for 28 days in demineralized water: a and b - interior; c and d - interface; e and f – surface/*Imagini SEM ale probelor F25S75_K imersate timp de 28 zile în apă demineralizată: a şi b- interior; c şi d - interfață; e şi f – suprafață.*

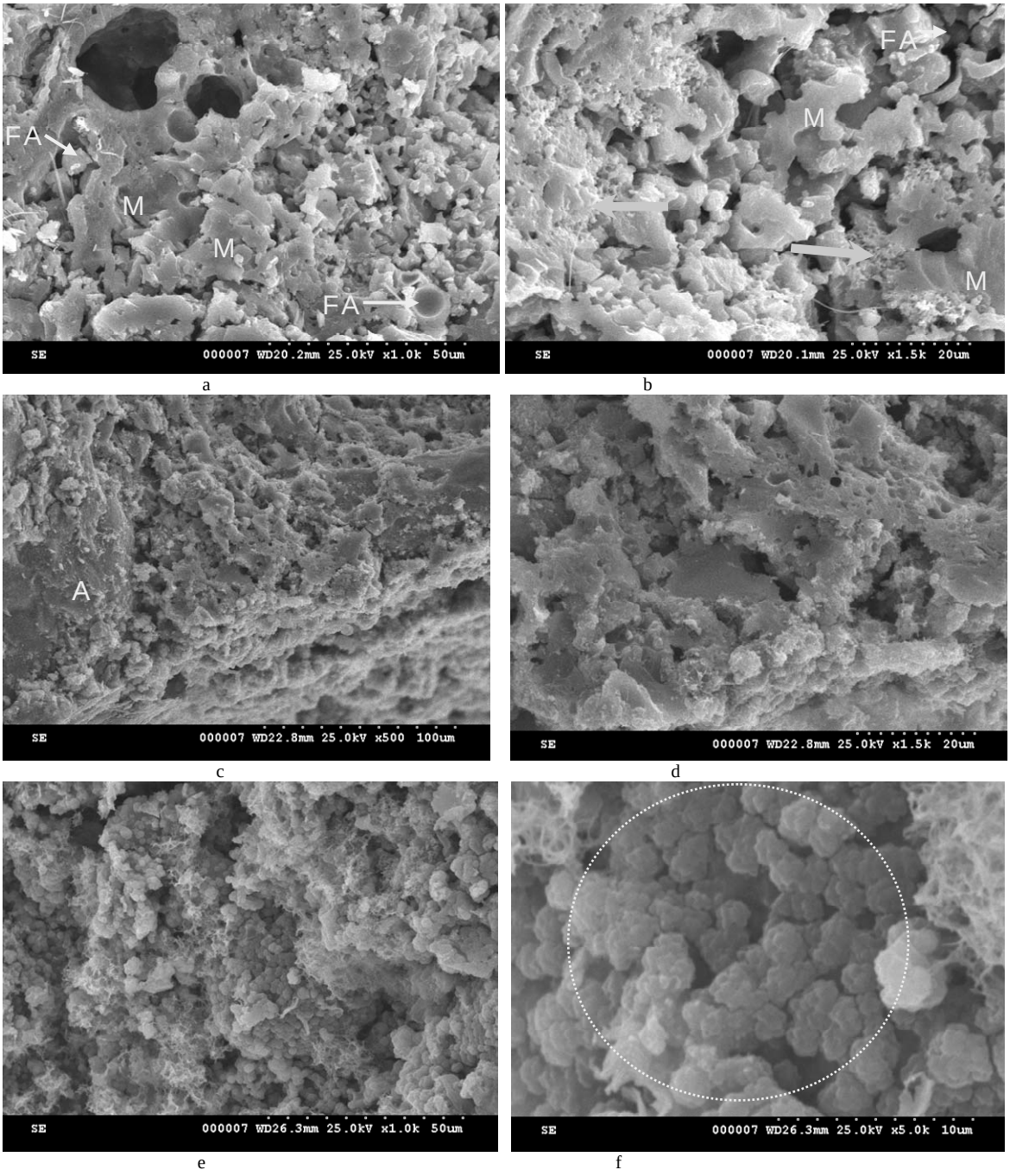


Fig. 12 - SEM micrographs of F25S75_N specimen immersed for 28 days in demineralized water: a and b - interior; c and d - interface; e and f - surface (FA- fly ash; A - aggregate; M - matrix)/ Imagini SEM ale probelor F25S75_N imersate timp de 28 zile în apă demineralizată: a şi b - interior; c şi d - interfață; e şi f - suprafață (FA- cenuşă de termocentrală; A- agregat; M - matrice).

In the inner zone of the mortar specimen activated with NaOH (F25S75_N - Figs. 12a,b) can be assessed spherical fly ash (FA) particles embedded in an amorphous matrix (M); also, one can observe “islands” of white phase (see arrows in Fig. 12b), generally attributed to carbonate species [23]. The matrix, although discontinuous and with high porosity, seems to adhere well at the surface of sand particles used as aggregate (A) – Fig. 12c. At the surface of mortar specimen (Fig. 12e,f) this matrix is no longer visible but two phases are present - octahedral crystals aggregated in spherical structures (dotted circle), attributed to zeolites, and an amorphous phase which can be attributed to aluminosilicate gel [24].

4. Conclusions

The results obtained in this study confirm that geopolymer materials can be obtained by the alkali activation of CRT glass waste with/without fly ash additions.

The nature of solid component (CRT glass waste with/without fly ash) as well as of the liquid

component (sodium/potassium hydroxide solutions) plays an important role in the hardening processes, resulted microstructure and consequently on mechanical strength values. The higher values of the compressive strength were obtained for geopolymers based on CRT glass waste activated with KOH solution cured the first 4 days at 60°C. The substitution of CRT glass waste with fly ash decreases the workability of fresh mortars, most probably due to partial absorption of liquid component (alkaline hydroxide solutions) on the porous carbon grains present in fly ash.

The mass losses of mortar specimens, immersed in demineralized water up to 28 days, were higher for the materials obtained by alkali activation of CRT glass, as compared with those based on CRT glass and fly ash mixture. These data, correlated with the values of compressive strength loss, suggests a better stability in water of specimens with 25% fly ash addition. It has to be noticed also that the durability of these materials is influenced both by material's solubility in water and the initial porosity of mortar specimen (before water immersion). Nevertheless, long term durability test are need, as well as optimization of composition and processing parameters of these materials.

The microstructure of inner zone of mortar specimens, based on CRT glass waste activated with NaOH or KOH solutions, consists mainly in angular glass grains embedded in an amorphous matrix. When fly ash is present in the system, one can also assessed spherical fly ash particles partially covered with an amorphous phase. The surface layer of mortar specimens, immersed in demineralised water for 28 days, is less dense as compared with the inner zone, supporting the idea of a partial solubilisation. At the surface of mortar specimens were also assessed octahedral crystals aggregated in spherical structures as well as rod like crystals, phases generally associated with zeolites.

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