LIANŢI PENTRU TEMPERATURI RIDICATE, PE BAZĂ DE CENUŞĂ ZBURĂTOARE
HIGH-TEMPERATURE CONCRETE BINDERS BASED ON FLY ASH

ANJA TERZIĆ [1*], ZAGORKA RADOJEVIĆ[1], LILJANA MILIČIĆ[1], LJUBICA PAVLOVIĆ[2], JOVICA STOJANOVIĆ[2]

[1]*Institute for Material Testing, Vojvode Mišića Bl. 43, Belgrade, Serbia*
[2]*Institute for Technology of Nuclear and other Raw Mineral Materials,Franchet d'Esperey 86, Belgrade, Serbia*

High-temperature concrete binders in which fly ash, as environmentally harmful secondary raw material, is combined with masonry and refractory cement is a new option for reapplication of this coal combustion by-product. In this study, the design of the bonding agents was based on the fly ash from lignite coal combustion process and two types of cement: Portland cement and aluminate cement. Fly ash was applied without any further mechanical or thermal treatment. Mechanical properties of the binders were investigated and subsequently correlated with changes which occurred in the phase composition and microstructure of the agents. Scanning electron microscopy was used in investigation of microstructural changes caused by temperature. X-ray diffraction method was used in monitoring of the mineral phase changes also induced by increasing temperature. The investigations conducted on the bonding agents highlighted presence of good refractory properties and temperature-resistance, and also showed high values of compressive strength. The investigated bonding agents, thus, can be applied in refractory concretes, but also in various types of thermo-insulations.

Lianţii pentru betoane de temperaturi ridicate, în care cenuşa de termocentrală, ca materie primă secundară, dăunătoare pentru mediu, este asociată cu ciment pentru mortare de zidărie sau refractare, reprezintă o nouă opţiune pentru utilizarea acestui subprodus al arderii cărbunelui. In acest studiu, s-a urmărit proiectarea unor materiale de liere (lianţi) pe bază de cenuşă rezultată la arderea lignitului şi două tipuri de ciment: portland şi aluminos. Cenuşa a fost utilizată ca atare, fără un tratament mecanic sau termic.S-au determinat proprietăţile mecanice ale lianţilor micşti şi s-au corelat cu modificările care au avut loc prin aceste tratamente, în caracteristicile compoziţionale şi microstructurale. Modificările microstructurale, determinate de tratamentul termic au fost investigate prin microscopie electronică SEM. Analiza de difracţie cu raze X a fost utilizată pentru a se evidenţia modificările determinate de tratamentul termic în compoziţia minerală. Investigaţiile realizate pe lianţi au evidenţiat stabilitate termică bună, proprietăţi refractare, precum şi rezistenţe la compresiune ridicate. Deci, lianţii cercetaţi pot fi utilizaţi în betoane refractare sau pentru izolaţii termice.

Keywords: *Portland cement, refractory cement, fly ash, microstructure, compressive strength*

1. Introduction

Number of coal fired power plants has been increasing over the years due to the enhanced demand for the electric power generation. This resulted in perpetual increasing of the amount of the combusted waste in number of its forms: fly ash, bottom ash, slag. Worldwide annual production of fly ash is estimated to approximately 500 million tons or even more [1, 2]. The fly ash generation is a global problem with severe implications for the environment: leaching of toxic elements through soil, pollution of groundwater; air pollution, etc. At the other side, transport, disposal and storage costs are high, and have to be faced by plant operators and waste management companies.

Fly ash is defined as main waste by-product of coal combustion which is collected by electrostatic precipitators in a plant. Fly ash represents about 80 % of coal-ash produced by power plants, while bottom ash accounts for 10–15 % [3]. The coal from which fly ash originates and the combustion procedure, both determine its mechanical, chemical and microstrutural characteristics. What is common for all fly ashes is that its particles are spherical and fine sized (usually counted in microns); bulk density of fly ash is relatively low; while the surface area is high [4]. Most of fly ash is reused in the construction materials industry: in concrete or mortar production [5-8], in road construction [9], in cement clinker production [10, 11], for bricks and tiles [12, 13], as geopolymers [14-16]. The high recycling rates the fly ash achieved are mainly due to its pozzolanic behavior [17].

The request for finding the new applications for the fly ash is pending hence produced amounts of this waste are continuously rising while the land-

* Autor corespondent/*Corresponding author*,
Tel.: 381112651842, e-mail: anja.terzic@institutims.rs

fielding is neither eco-friendly nor sustainable option. Some of the possible new solutions are the reapplication of combustion products in thermo-insulation materials, refractory concretes and high-temperature resistant building cement based composites. In order to satisfy mechanical and thermal requirements, fly ash has to show adequate behavior at elevated temperatures, no strength or other mechanical properties loss, high thermo-insulation, fire resistance and refractoriness [18]. The application of the fly ash in a composite could affect the material behavior or some of its properties when it is subjected to high temperature [19]. However, materials that could retain certain quantity of water are more desirable in such conditions because the part of the water evaporates and subsequently gets transported from the exterior surface to the unexposed side where the water cools and condenses again forming a liquid film as a certain fire protector. It is found that fly ash has similar chemical composition and microstructure, and subsequently properties, as commercial products used for passive fire protection in residential or industrial installations facilities [20-24].

The two types of fly ash based concrete binders were, in this investigation, subjected to thermal, mechanical and microstructural analyses in order to monitor their behavior under elevated temperature, mechanical properties and, finally, possibility of application under high-temperature conditions.

2. Description of Method of Work

Here investigated fly ash was originally collected directly from the filter system of the lignite coal-fired power plant “Kostolac” in Serbia. The fly ash was applied in its original form without any additional mechanical or thermal treatments, which are used in previous study [25]. Grain size distribution of the fly ash sample is given in Figure 1 [26]. Cyclo-sizer Warman International LTD, Australia was used in the grain size analysis of the original fly ash sample.

Standard Portland cement (PC 42.5R Lafarge) and refractory calcium-aluminate cement (HAC Secar 70/71, Lafarge) were used in the preparation of the testing samples. Grain size anlysis showed that 95.5 % particles of HAC and 97.5 % particles of PC were in range 0.00 - 0.63mm.

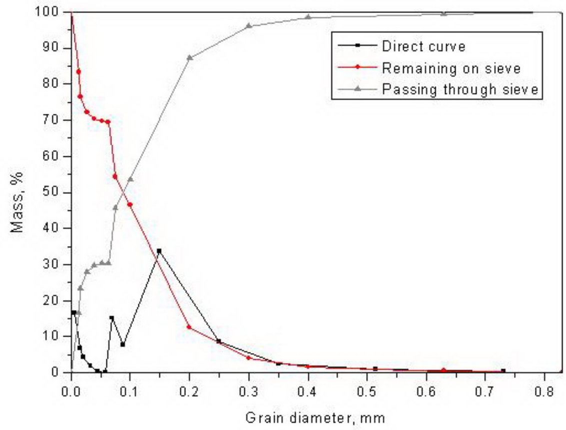

Fig. 1 - Distribution of fly ash grain fractions given in percentage of total mass / *Distribuția granulometrică a cenușii*.

The chemical analysis of the fly ash and cements was conducted by atomic spectroscopy technique (PinAAcle™ 900 AA Spectrometer, Perkin Elmer). Chemical compositions of fly ash, PC and HAC are given in Table 1.

The components for the mix design of the binders were in ratio 2:3 (40 % of fly ash and 60 % of cement). The sample BA1 was mixture of fly ash and Portland cement, and sample BA2 contained fly ash and refractory (HAC) cement. Further analyses were conducted in accordance with standards for cement quality: standard for PC cement quality SRPS EN 197-1:2010 (analogue to EN 197-1:2000/A3:2007) and standard for HAC cement quality SRPS EN 14647:2008/AC:2008 (analogue to EN 14647:2005/AC:2006). The binder components were mixed for 10 minutes in laboratory RILEM-cem mixer. After homogenization mixtures were shaped in 10 cm cubic molds. The molds spend following seven days in a climate chamber at 20 ºC and humidity 60 %. On the seventh day the samples were demolded and cured for another 21 days outside of climate chamber but under the same conditions as during previous curing session (Standard SRPS EN 12390-1:2012 / EN 12390-1:2000). The compressive strength of the samples was tested by means of the conventional laboratory hydraulic pressure device (Standard SRPS EN 12390-3:2010). Samples were tested at ambient temperature and after firing in laboratory electric furnace at 800, 900, 1100 and 1300 °C. The heating rate was 100 °C/h. The samples were exposed to each temperature during 4 hours.

Table 1

Chemical analysis of fly ash and cements / *Analize chimice ale cenuşii şi cimenturilor*

Oxides, *Oxizi* %	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	P_2O_5	SO_3	Na_2O	K_2O	MnO	CO_2
FA	54.25	20.45	7.12	0.52	7.23	2.79	0.02	0.71	0.44	1.21	0.03	0.22
PC	19.45	6.21	2.56	0.08	58.96	1.70	-	-	0.02	0.03	-	-
HAC	0.15	71.25	0.04	0.01	26.95	0.06	-	-	0.25	0.05	-	-

Temperature dependant mineral phase changes of the milled and homogenized samples were analyzed by means of the X-ray powder diffraction (XRD). The XRD diffractograms were obtained on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. All the XRD measurements were performed at room temperature in a stationary sample holder.

The microstructure of the samples was investigated characterized by scanning electron microscopy method (SEM) using a JEOL JSM-6390 Lv microscope. Composite samples were crushed, and parts of original samples were used in SEM investigation.

3. Results, interpretation and discussion

The chemical analyses of the binder components - fly ash and cements (given in Table 1) indicate that main oxides appearing in the composition of binders are also silica, alumina, calcium and iron oxides. Due to the differences in the chemical composition of applied cements, binder BA1 has higher CaO content than BA2, while BA2 contains higher amount of Al_2O_3 in its composition [25]. The investigated fly ash belongs to the class of alumino-slicate ashes, which means that the fly ash is attributed with excellent pozzolanic characteristics, which is of importance when fly ash is applied as partial substitution of cement in a concrete.

Increasing of the compressive strength of BA1 and BA2 samples during first 28 days and the comparison with standard PC and HAC samples is given in Figure 2. One of the main characteristics of the refractory cement is its rapid gain of strength, which is not drastically changed by addition of the fly ash. Situation is similar in the case of Portland based binder: compressive strength of BA1 measured at each point in time is only 2-3 MPa lower than in case of PC.

The compressive strength of the bonding agent samples at ambient temperature and its change with increasing temperature is given in Figure 3. As it can be seen from Figure 3, the lowest peak on both diagrams was noticed at 800 °C, due to the breaking of existing chemical bonds and formation of "ceramic" bond in the agent. The "ceramic" bond is characteristic for refractory cements. Formation of the "ceramic" bond induces small but noticeable strength increasing in case of the BA2. BA1 shows almost "horizontal" line on the diagram up to 1100 °C when compressive strength starts increasing. Strength gain which follows increasing temperature is clear evidence of the certain micro-structural changes, i.e. densification, and the initiation of sintering process. Both bonding agents BA1 and BA2 retained the compressive strength at critical temperatures (800 °C) and showed relative strength increasing (above 1100 °C) despite the addition of the fly ash and the fact that Portland cement is not normally used at elevated temperatures. Portland cement based binder showed improved crystallinity towards higher temperatures (1300 °C) as can be seen later in Figures 7 and 8, which certainly influences the strength increasing.

The mineralogical analysis of the Portland cement and the refractory cement, conducted by XRD technology, is given in Figures 4 and 5. XRD diffractogram of the investigated fly ash is presented in Figure 6 [27].

Phase compositions of PC and HAC are different due to the differences in the cement manufacturing procedure. Identified crystalline major phases present in the Portland cement sample were: alite - tricalcium silicate (Ca_3SiO_5), belite - dicalcium silicate (Ca_2SiO_4), ferrite - calcium aluminoferrite/brown-millerite ($Ca_2(Al,Fe)_2O_5$) and gypsum – (Ca_2SiO_4 $(H_2O)_2$). The main defined peaks on diffractograms relate to alite and belite. In case of HAC the main defined peaks correspond to monocalcium aluminate

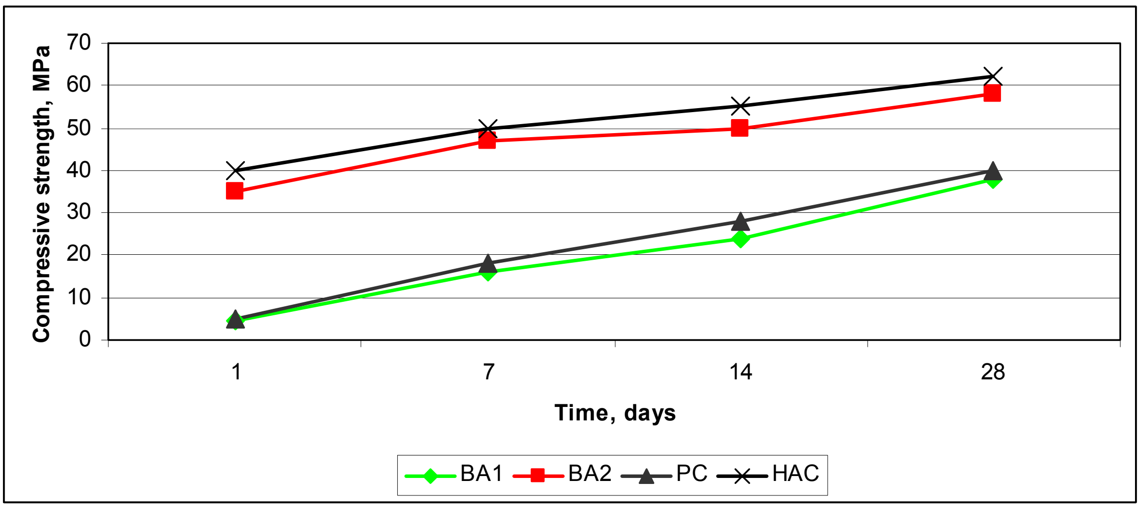

Fig. 2 - Increasing of the compressive strength of investigated bonding agents during period of 28 days / *Creşterea rezistenței la compresiune a lianților cercetați, în decursul a 28 zile.*

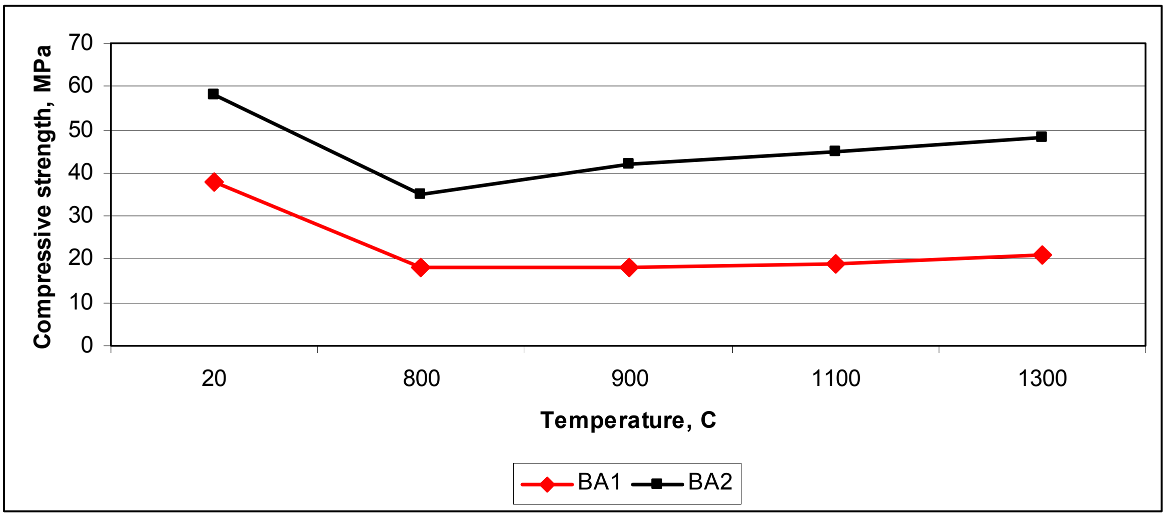

Fig. 3 - The change of compressive strength of investigated bonding agents with increasing temperature / *Modificarea rezistenței la compresiune a lianților micşti, la creşterea temperaturii.*

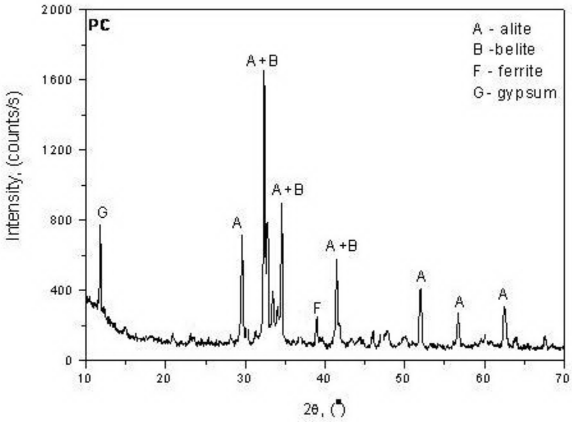

Fig. 4 - XRD diffractogram of Portland cement / *Difractogramă a cimentului portland (PC).*

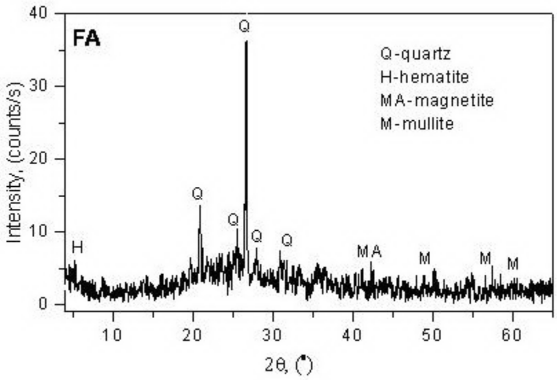

Fig. 6 - XRD diffractogram of fly ash / *Difractogramă a cenuşii.*

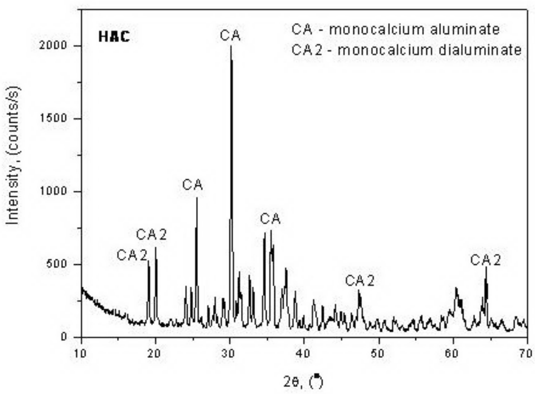

Fig. 5. - XRD diffractograms of HAC / *Difractogramă a cimentului superaluminos (HAC).*

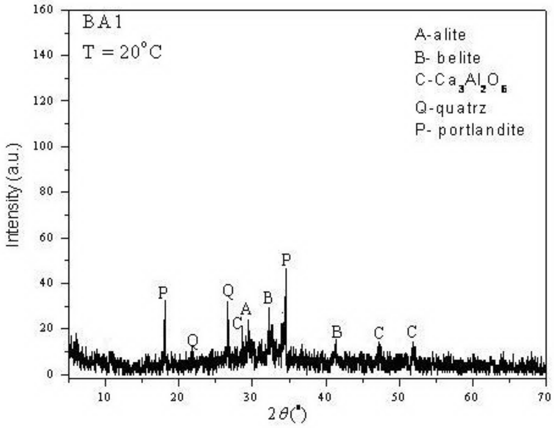

Fig. 7 - Diffractogram of BA1 at ambient temperature *Difractogramă a liantului BA1,întărit la temperatură normală.*

$CaO{\cdot}Al_2O_3$ and monocalcium dialuminate $CaO{\cdot}2Al_2O_3$ which were only two crystalline phases found in the sample.

Identified crystalline major phases present in fly ash sample are aluminosilicate glass, quartz and mullite. The main defined peaks on diffractograms relate to quartz. High amount of amorphous matter was present within all investigated fly ash sample. The background hump between 10 and 40° in the X-ray spectrum provided additional evidence of the presence of an amorphous phase. Magnetite, hematite, fluorite and anhydrite were noted in relatively negligible amounts [27].

Mineral phases found in BA1 sample at ambient temperature and 1300 °C are given in Figures 7 and 8. Changes of mineral phases induced by temperature were monitored by XRD method.

Mineral phases found in BA1 sample analyzed at 20 °C are: alite, belite, tricalcium aluminate, quartz, portlandite ($Ca(OH)_2$). All indicated phases showed very poor crystallinity degree. Gehlenite ($Ca_2Al_2SiO_7$) and quartz (SiO_2) are expected to appear towards higher temperature. Gehlenite normally induces increasing in degree of sample crystallinity. Towards 1100 °C gehlenite and rankinite ($Ca_3Si_2O_7$) are becoming only minerals which appear in the composition, accompanied only by low amount of quartz [25]. At 1300 °C, only rankinite and gehlenite are present while crystallinity degree is notably higher in comparison to starting. i.e. ambient temperature.

Mineral phases found in BA2 samples at ambient temperature and 1300 °C are given in Figures 9 and 10.

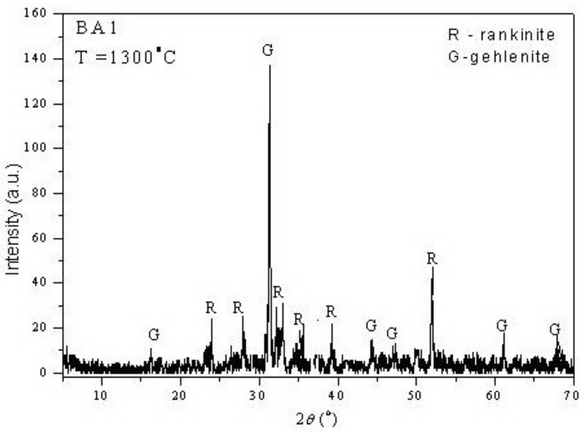

Fig. 8 - Diffractogram of BA1 at 1300 °C / *Difractogramă a liantului BA1, tratat termic la 1300°C.*

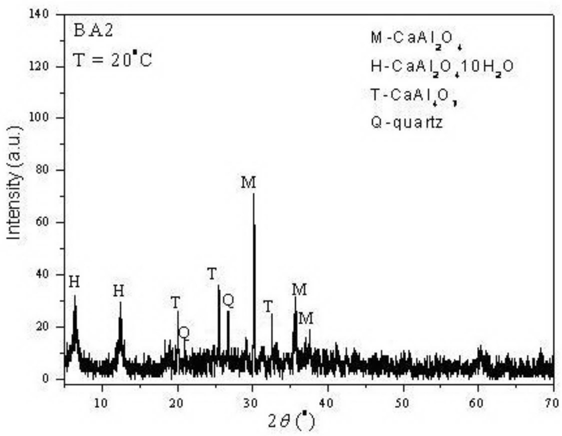

Fig. 9 - Diffractogram of BA2 at ambient temperature / *Difractogramă a liantuluiu BA2, întărit la temperatură normală.*

Analyzed BA2 sample gave following composition at 20 °C: $CaAl_2O_4$, $CaAl_4O_7$, $CaAl_2O_4 \cdot 10H_2O$, and quartz. $CaAl_2O_4$ was the most abundant, while $CaAl_4O_7$ is less present and $CaAl_2O_4 \cdot 10H_2O$ and quartz are present in the smallest amounts. All present phases showed very low crystallinity degree. Towards 900 °C the composition slightly shifts making $CaAl_2O_4$, $CaAl_4O_7$, gehlenite, anorthite ($Ca_2Al_2Si_2O_8$) and quartz more abundant. However, the crystallinity degree of all listed present phases is still low at this temperature. The stage above 1000 °C is characterized by initiation of gehlenite and anorthite crystallization [25]. At highest analyzed temperature (1300 °C) gehlenite, corundum (Al_2O_3), $CaAl_4O_7$, anorthite and cristobalite (SiO_2) were detectable mineral phases. Ghelenite appeared to be the most abundant phase is gehlenite, while anorthite, corundum and $CaAl_4O_7$ were less present phases. There is also possibility of presence of cristobalite but in very small amounts. Crystallinity degree is the significantly higher in comparison with ambient temperature.

The XRD analysis of the both investigated binders pointed out to the certain thermally induced phase changes. Namely, with the increase of the temperature more complex aluminosilicates were formed, especially in HAC based samples (BA2). In BA1 sample, the number of the minerals was being reduced with increasing temperature since the simple minerals were gradually incorporated into the complex aluminosilicates during thermal treatment of the samples. Thermal treatment reduced the amount of glassy phase and quartz originating from the fly ash and promoted formation of anorthite, mullite, and cristobalite. The formation of rankinite, gehlenite, anorthite and cristobalite is highly important because they have high melting point, which contributes to their refractory characteristics and also makes them thermally stable. Therefore, formation of these mineral phases contributes to the refractoriness and thermal stability of the bonding agents.

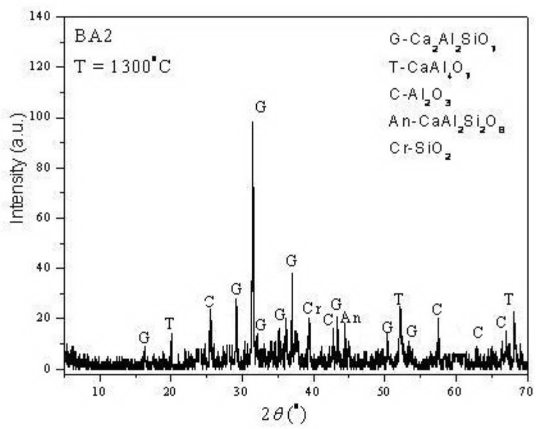

Fig. 10 - Diffractogram of BA2 at 1300 °C / *Difractogramă a liantului BA2, tratat termic la 1300°C.*

In the Figure 11, SEM microphotograph at 1000x magnification of a fly ash particle is given. It can be seen that majority of fly ash particles are rather small and highly porous. Also fly ash particles usually contain smaller sized spheres within huge hollow particles. Beside that, fly ash particles are spherical with galssy appearance on its surface. One of the benefits of high porosity of the particle is that fly ash based material has higher water absorption and, thus, it can retain certain quantity of previously absorbed water. As such it can serve as temperature or even fire-proof layer. Spherical shape of fly ash particles helps in dense “packing” of the binder structure.

The SEM microphotographs of samples BA1 and BA2 recorded after firing at 1300 °C at 650x magnification, are given in Figures 12 and 13, respectively.

Spherical fly ash particles of different sizes can be seen incorporated in cement matrix. As it has been previously said, spherical fly ash particles can help better “packing” of the microstructure which subsequently promotes increasing of the mechanical strength. The bond between fly ash and cement particles in both samples – BA1 and BA2 seems to be quite strong which indicates that these two materials are thermally compatible. At 1300 °C there are no visible signs on melting or formation of glassy phases on samples BA1 and BA2.

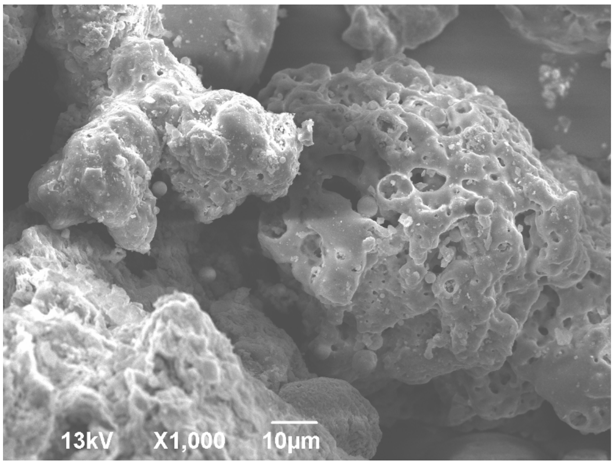

Fig. 11 - The SEM microphotograph of fly ash particles. *Micrografie SEM a particulelor de cenuşă*

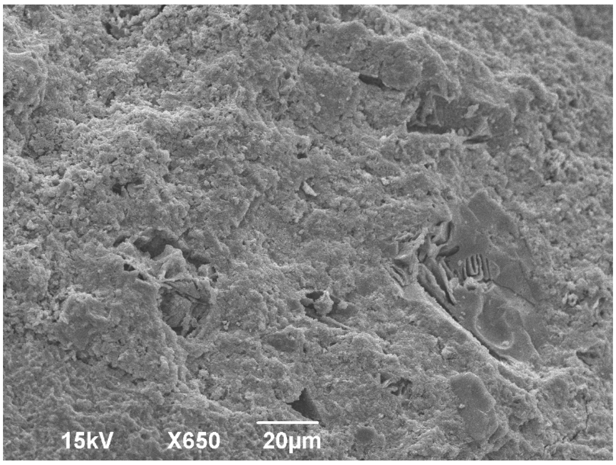

Fig. 12 - The SEM microphotographs of BA1 after thermal treatment at 1300 °C / *Micrografie SEM a liantului BA1, după tratament termic la 1300°C.*

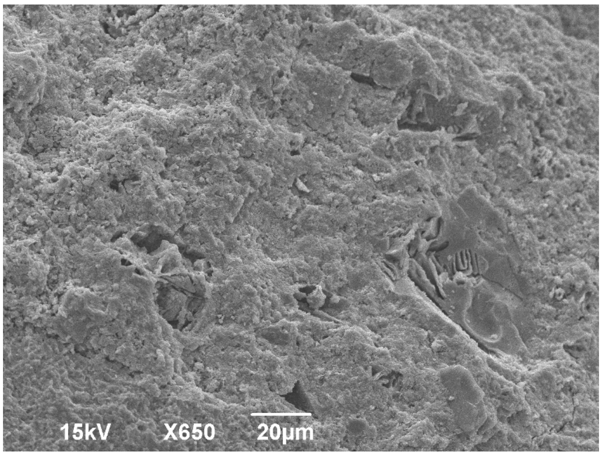

Fig. 13 - The SEM microphotographs of BA2 after thermal treatment at 1300 °C / *Micrografie SEM a liantului BA2, după tratament termic la 1300°C.*

4. Conclusion

The conducted investigation showed that the fly ash based binders showed no signs of melting even at the highest experimental temperature (1300 °C). The previous highlights the binders satisfactory thermal behavior and also enables their application in either refractory composites or termo-insulatiors. The spherical shape as well as the smooth texture of the fly ash particles improve ”packing” of cement grains making the binder structure significantly denser which in addition promotes strength increasing and also distinguishes difference in compressive strength between standard Portland cement and investigated binder BA1, i.e refractory cement and binder BA2. Increased porosity of the fly ash particles enables higher water absorption, which allows that binders retain certain quantity of previously absorbed water. Retained water creates fire protection fil in the structure of the material. XRD method detected thermally induced increasing of the crystallinity of both binders BA1 and BA2. Also, it detected formation of certain mineral phases - rankinite, gehlenite, anorthite and cristobalite in the BA1 and BA2 samples which is important because these minerals are thermally stable and therefore they contribute to the thermal stability of the bonding agents and additionally to good refractoriness. The investigated binders based on Portland cement or refractory cement, and addition of fly ash are promising temperature resistant material. As such, these bonding agents might be applied in thermo-insulation concrete layers and even in refractory concretes or mortars.

Acknowlegements

This investigation was supported by Serbian Ministry of Education, Science and Technological Development and it was conducted under following projects: 172057 and 45008.

REFERENCES

1. R. Thakur and S. Ghosh, Effect of mix composition on compressive strength and microstructure of fly ash based geopolymer composites, Journal of Engineering and Applied Sciences 2009, **4**, 65.
2. H. Feuerborn, Coal ash utilisation over the world and in Europe, Workshop on Environmental and Health Aspects of Coal Ash Utilization (2005) Tel-Aviv, Israel
3. S. Wang, L. Baxter, and F. Fonseca, Biomass fly ash in concrete: SEM, EDX and ESEM analysis, Fuel, 2008, **87**, 372.
4. C. Munteanu, M. Georgescu and A. Moncea, The influence of fly ash additions associated with polycarboxylate superplasticizer on the main properties of Portland cement pastes and mortars, Romanian Journal of Materials, 2012, **42** (4) 350.
5. H. Lee, H. Kim and E. Hwang, Utilization of power plant bottom ash as aggregates in fiber-reinforced cellular concrete. Waste Management, 2010, **30**, 274.
6. G. Li, A new way to increase the long-term bond strength of new-to-old concrete by the use of fly ash, Cement and Concrete Research, 2003, **33**, 799.
7. N. Kockal, and T. Ozturan, Effects of lightweight fly ash aggregate properties on the behavior of lightweight concretes, Journal of Hazardous Materials 2010, **179**, 954.
8. M. Cinquepalmi, T. Mangialardi, L. Panei, A. Paolini, and L. Piga, Reuse of cement-solidified municipal incinerator fly ash in cement mortars: Physico-mechanical and leaching characteristics, Journal of Hazardous Materials, 2008, **151**, 585.
9. E. Mulder, A Mixture of Fly Ash as Road Base Construction Material, Waste Management, 1996, **16** (1-3) 15.
10. A. Guerrero, S. Goni, and V. Allegro, Durability of class C fly ash belite cement in simulated sodium chloride radioactive liquid waste: Influence of temperature, Journal of Hazardous Materials, 2009, **162**, 1099.
11. V. Lilkov, O. Petrov, Y. Tzvetanova, and P. Savov, Mössbauer, DTA and XRD study of Portland cement blended with fly ash and silica fume Construction and Building Materials, 2012, **29**, 33.
12. M. Erol, S.Kucukbayrak, and A. Ersoy-Mericboyu, Comparison of the properties of glass, glass–ceramic and ceramic materials produced from coal fly ash, Journal of Hazardous Materials, 2008, **153**, 418.
13. Z. Haiying, Z. Youcai, and Q. Jingyu, Study on use of MSWI fly ash in ceramic tile, Journal of Hazardous Materials, 2007, **141**, 106.
14. J Davidovits, Geopolymers: inorganic polymeric new materials, Journal of Thermal Analysis, 1991, **37**, 1633.
15. M. Izquierdo, X. Querol, C. Phillipart, D. Antenuc, and M. Towler, The role of open and closed curing conditions on the leaching properties of fly ash-slag-based geopolymers, Journal of Hazardous Materials, 2010, **176**, 623.
16. R. Williams, and A. van Riessen, Determination of the reactive component of fly ashes for geopolymer production using XRF and XRD, Fuel. 2010, **89**, 3683.
17. V. Malhotra, and P. Mehta, High-performance, high-volume fly ash concrete,supplementary cementing materials for sustainable development. Otawa:Marquardt Printing; 2002.
18. S. Aydin, and B. Baradan, Effect of pumice and fly ash on high temperature resistence of cement based mortats, Cement and Concrete Research, 2007, **37**, 988.
19. Y. Xu, Y. Wong, C. Poon, and N. Anson, Impact of high temperature on PFA concrete, Cement and Concrete Research, 2001, **31**, 1065.
20. L. Vilches, C. Leiva, J. Vale, and C. Fernández-Pereira, Insulating capacity of fly ash pastes used for passive protection against fire, Cement and Concrete Composites, 2005, **27**, 776.
21. L. Vilches, C. Leiva, J. Vale, and C. Fernández-Pereira, Coal fly ash containing sprayed mortar for passive fire protection of steel sections, Materiales de Construcción, 2005, **55**, 25.
22. C. Leiva, L. Vilches, C. Fernández-Pereira, and J. Vale, Influence of the type of ash on the fire resistance characteristics of ash-enriched mortars, Fuel, 2005, **84**, 1433.
23. M.Barbuță, M.Harja, and D.Babor, Concrete polymer with fly ash: morphologic analysis, based on scanning electon microscopic observations, Romanian Journal of Materials, 2010, **40** (1), 3.
24. C. Leiva, C. García Arenas, L. Vilches, J. Vale, A. Giménez, J. Ballesteros, and C. Fernández-Pereira, Use of FGD gypsum in fire resistant panels, Waste Management, 2010, **30**, 1123.
25. A. Terzić, Lj. Pavlović, N. Obradović, V. Pavlović, J. Stojanović, Lj. Miličić, Z. Radojević, and M. M. Ristić, Synthesis and Sintering of High-temperature Composites Based on Mechanically Activated Fly Ash, Science of Sintering, 2012, **44** (2), 135.
26. A. Terzić, Lj. Pavlović, and Lj. Miličić, Evaluation of Lignite Fly Ash for Utilization as Component in Construction Materials, International Journal of Coal Preparation and Utilization, 2013, **33** (4), 159.
27. A. Terzić, Z. Radojević, Lj. Miličić, Lj. Pavlović, and Z. Aćimović, Leaching of the potentially toxic pollutants from composites based on waste raw material, Chemical Industry & Chemical Engineering Quarterly, 2012, **18** (3), 373.

****