Design of ceramic microstructures based on waste materials

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Abstract

The progressive changes in ceramic raw materials during firing processes are a complex area. This is partly due to the large number of raw material characteristics, primarily mineral composition, and partly to the relatively inadequate particle distribution in the unfired clay body. The most important starting point is always the optimal raw material composition which should give appropriate physical and mechanical characteristics to the final products after firing processes and should provide an efficient and economical production.
The paper analyzes the influence of some additives (fly ashes and waste glass materials) on the development of the ceramic roofing tile microstructure during the thermal treatment. The analyzed raw material mixtures were: the standard raw material mixture (from Kanjiza, Northern part of Serbia) and the modified one, i.e. the mixture of the standard raw material and corresponding additive. The silica phase obtained during the thermal collapse of the clay minerals in the presence of the glass additive bounded better CaO and MgO components released from the carbonates. The crystalline phases like plagioclases were performed in a considerable quantity and the products with new physical characteristics were formed.

Keywords: raw clay materials, fly ash and waste glass additives, microstructure

I. Introduction

The properties of raw material mixtures (clay mineral compositions, type of a non plastic components) are of decisive importance for the processes of sintering and therefore for the quality of the final product in the production of structural clay products [1]. Raw materials with significant carbonate content, as Kanjiza clay material, need a particular approach since carbonates could play the role of stabilizer and mineralizer, but could also present the starting point for the most dangerous failures. To avoid this, the carbonates have to be finely ground and dispersed in the clay mixture. A close contact with the clay minerals has to be provided [2]. Additives could be of a crucial importance in this area and very often, even if the potentials of mineral components (clay minerals, carbonates and feldspars) are not so high during the process of firing, some unexpected crystalline forms could be created in the presence of the additives. Waste glass promotes a more effective melting of quartz and a partial dissolution of mullite, leading to a more abundant and less viscous liquid phase, which accelerates the sintering kinetics [3]. Some additives are used in order to improve thermal behavior of the clay bodies, or for designing a ceramic microstructure resistant to aggressive environmental conditions [4].

In Serbia until now, there have been no generally applicable systematized observations (energy saving) regarding the use of additives, particularly not in the case of recycled waste materials. In this work, the influence of some industrial waste materials (fly ashes and waste glass materials) on the physical and mechanical characteristics of the clay roofing tiles and the development of the ceramic microstructure during the thermal treatment of the clay-waste glass mixture are analyzed. The investigation opens up some new perspectives in the production of clay roofing tiles, the reusing of the recyclable waste glass and the reducing of CO_2 emission.

II. Experimental

Material
• Raw clay material with a relatively large amount of carbonates (calcite and dolomite, 13 wt.%), illite-montmo-

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Table 1. Composition of the raw material mixtures

Notation of raw material mixture	Composition [wt.%]								
	1	2	3	4	5	6	7	8	9
Standard raw material	100	90	90	90	90	90	90	90	90
Fly ash (Vreoci)	-	10	-	-	-	-	-	-	-
Fly ash (Crljeni)	-	-	10	-	-	-	-	-	-
Fly ash (Drmno)	-	-	-	10	-	-	-	-	-
Fly ash (Svilajnac)	-	-	-	-	10	-	-	-	-
Waste glass K1	-	-	-	-	-	10	-	-	-
Waste glass K2	-	-	-	-	-	-	10	-	-
Waste glass K3	-	-	-	-	-	-	-	10	-
Waste glass K4	-	-	-	-	-	-	-	-	10

rillonite clay minerals, quartz, mica and feldspars – the standard raw material composition.

• Mixture of the standard raw material and a glass additive (fly ash or waste glass). In Table 1 is shown the nomenclature of the used raw material mixtures.

Procedures

The test samples were prepared on laboratory scale. The dry-prepared clay powder was moistened and used as the standard raw material mixture. The additives like fly ashes were directly mixed with the standard clay mixture (without any special preparation), while the waste glass was first ground in ball mill during a period of 2 hours. The first type of samples (100×70×15 mm) was formed with a laboratory extruder, dried to the constant weight in a laboratory dryer. The obtained samples were fired in a laboratory kiln, with a large preheating zone and a holding time of 4 hours at 960, 985 and 1010°C. The firing procedure of the second type of samples (50×5×5 mm) was done in a dilatometer with a heating/cooling rate of 5 and 20°/min at T_{max}=1010°C.

Methods

Raw materials characterization: Determination of particle size distribution; Chemical composition (standard silicate chemical analysis); Qualitative and Semi-quantitative X-ray analysis (Philips PW 1410 Cu Kα).

Dried samples characterization: High-temperature dilatometry (DIL 802L, Bähr); DTA/TG analysis (STA 503, Bähr, measurement was done in temperature range 20–1000°C, with heating rate: 5, 10 and 20 °/min.); High-temperature X-ray diffraction analysis (Philips PW 1050 Co Kα).

Fired samples characterization: Water absorption (JUS B.D 8.010); Water absorption and apparent porosity (ASTM C373-88); T value (DIN 52251-part.3); Frost resistance capacity (DIN 52251-part.2); Breaking strength (JUS B.D1.310); Pore size distribution determined by mercury porosimetry (Carlo Erba 2000 VS); SEM-EDS analysis (JSM–6460LV, JEOL). In the SEM and EDS investigation, the fresh fracture of the ceramic tile specimens was sputter-coated with gold, using BAL-TEC SCD 005 instrument (180s / 30mA / 50mm). The final SEM imaging was undertaken at high-vacuum conditions with secondary electron imaging using a high-acceleration voltage of 25 kV and working distance of approximately 10 mm. EDS analysis was conducted under the same high-vacuum conditions and the same accelerating voltage as the SEM analysis.

III. Results and Discussion

3.1 Characteristics of raw materials

The mineral composition of the standard raw material mixture characterizes presence of clay minerals (illite, montmorillonite, chlorite and kaolinite) and a large amount of carbonates (calcite and dolomite) Tables 2 and 3.

Table 2. Phase composition of the standard raw material

Phase composition [wt.%]	
Quartz	26
Feldspars*	17
Ilite + muscovite	16
Kaolinite	6
Montmorillonite	5
Chlorite	6
Calcite	7
Dolomite	6

*Orthoclase, low temperature plagioclase

Table 3. Particle size composition of the standard raw material

Composition [wt.%]	
Clay (< 2 μm)	28
Silt (2 – 20 μm)	50
Sand (2 – 200 μm)	22
Total carbonates	13

3.2 Additive selection

Due to the lowest water absorption capacity (Table 4) of the designed ceramic systems, the raw material mixture with glass additive K4 (sample 9) was chosen as the most promising. The detailed investigation was carried out with this system and the standard ceramic system. Chemical composition of the selected additive

Table 4. Water absorption capacity of the different ceramic systems

System → T_firing [°C] ↓	Water absorption [wt.%]								
	1	2	3	4	5	6	7	8	9
960	9.84	14.21	14.01	13.26	13.77	9.83	8.70	9.81	8.43
985	9.57	14.17	13.76	12.76	13.41	9.51	8.24	9.52	7.76
1010	8.68	13.74	13.07	12.49	13.05	8.62	7.68	8.98	6.28

Table 5. Chemical composition of the waste glass K4

				Chemical composition [wt.%]				
Li	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Total
0.69	73.78	4.16	1.99	1.04	1.70	12.78	3.49	99.63

Table 6. Physical and mechanical characteristics of the standard and modified (sample 9 with glass additive K4) ceramic systems

System → T_firing [°C] ↓	Water apsorption JUS [wt.%]		Water apsorption ASTM [wt.%]		Apparent porosity [%]		Bending test [MPa]	
	standard	modified	standard	modified	standard	modified	standard	modified
960	9.88	8,43	10.36	9.35	20.03	18.44	19.96	19.54
985	9.05	7.76	9.09	8.09	17.75	16.05	20.21	24.37
1010	8.46	6.28	8.69	7.15	17.03	14.25	19.77	20.93

Table 7. Pore size distribution of the standard and modified (sample 9 with glass additive K4) ceramic systems

Pore radius intervals	Pore size distribution [%]						
	< 0.01 μm	0.01–0.05 μm	0.05–0.1 μm	0.1–0.5 μm	0.5–0.75 μm	0.75–1.0 μm	>1.0 μm
Standard – dried	22.15	14.11	21.87	21.62	6.13	0.32	13.15
Modified – dried	18.45	13.91	14.72	10.22	28.76	0.27	13.14
Standard – 960°C	7.11	7.49	6.16	60.76	4.93	0.41	13.14
Standard – 985°C	6.20	6.72	5.35	67.84	2.58	0.36	10.95
Standard – 1010°C	6.83	8,30	6.04	39.04	20.92	2.80	15.64
Modified – 960°C	6.66	7.40	5.58	39.03	26.72	2.12	12.50
Modified – 985°C	0.16	7.73	6.49	35.81	31.17	4.27	14.38
Modified – 1010°C	0.16	7.37	8.02	27.61	10.45	10.07	36.49

Table 8. Average pore radius [4], Maag's factor [5] and T values [6] of the standard and modified (sample 9 with glass additive K4) ceramic systems

	Average pore radius [μm]	Maage's factor	T value
Standard – 960°C	0.771	50.1	0.730
Standard – 985°C	0.848	46.3	0.704
Standard – 1010°C	1.071	55.0	0.660
Modified – 960°C	0.693	49.6	0.661
Modified – 985°C	0.999	51.1	0.612
Modified – 1010°C	1.580	73.9	0.520

Table 9. Phase composition of the standard and modified (sample 9 with glass additive K4) ceramic systems fired at T_{max}=1010°C

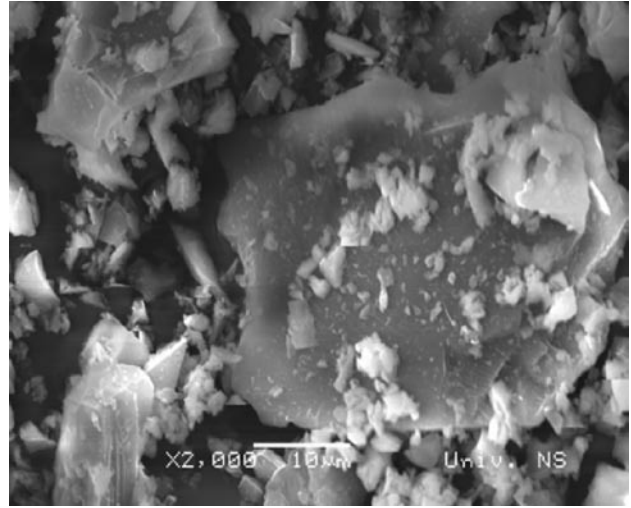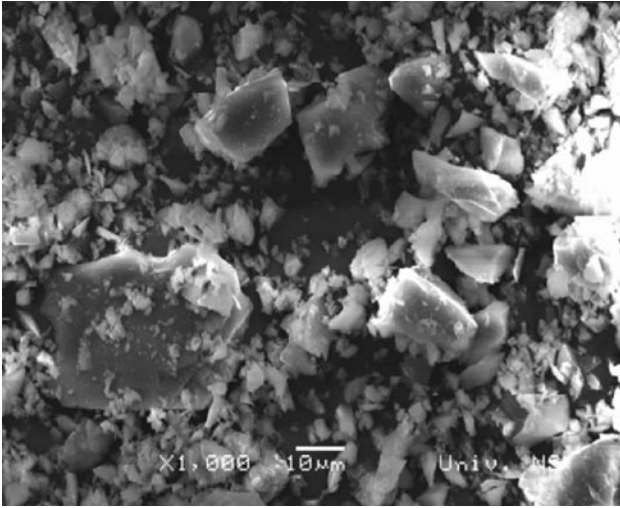| Crystal forms	Phase composition [wt.%]	
	Standard system	Modified system
Quartz	33	26
Plagioclases (high temperature form)	38	44
Hematite	10	9
Diopside	4	4
Rö-amorphous phase	10–15	15–20

Figure 1. SEM micrograph - morphology of the waste glass particles

is shown in Table 5, and the morphology of the waste glass particles on Fig. 1.

3.3 Standard and modified ceramic systems

Physical and mechanical characteristics

The first positive effect of the additive, as stabilizer and activator of the firing process, is seen on the base of water absorption and mechanical characteristics of the fired products, Table 6.

Finely dispersed in the composition batch, the additive during firing process approached the silica phase of the clay minerals to CaO and MgO components. In new thermal conditions these were the right reaction partners of the clay minerals and feldspars.

Pore structure characteristics and frost resistance

The pore structure of the selected ceramic systems was determined by the mercury porosimetry. The analysed pore radius interval was between 0.001 – 30 μm, Table 7, Fig. 2. The characteristics, which also distinguish the modified system from the standard one, are the complete sealing of the pores with the radius below 0.01 μm, and the growth of the pores with the radius larger than 0.5 μm, Fig. 3.

The indirect criteria for the frost resistance prediction, including all types of firing conditions, con-

firm a higher stability in the case of modified system, Table 8.

Firing performances

The values of the sample dilatation show a particular thermal behavior in the case of the modified system, Fig. 4. The content of silica phase is dramatically increased in comparison with the standard one. Thus, at one point (Shrinkage = 1.4; T=1000°C), the dilatation value of the modified sample at heating rate 20°/min is simultaneous with the value of the standard heating, which is four time less (5°/min.). This part shows a thermal advantage of the clay body in the presence of the glass additive, which plays a decisive role in the microstructure design based on the most possible silicatization reactions.

Phase composition

In the case of XRD analysis beside failure to identify phases, quantification of clay minerals seems to be the greatest source of error. If we speak of an experienced laboratory, an average difference of 2 wt.% from the actual value for each phase is acceptable [8]. Considering our systems, the content of quartz is decreased, but the high temperature plagioclase form based on the presence of calcium, is increased in the case of the modified system,
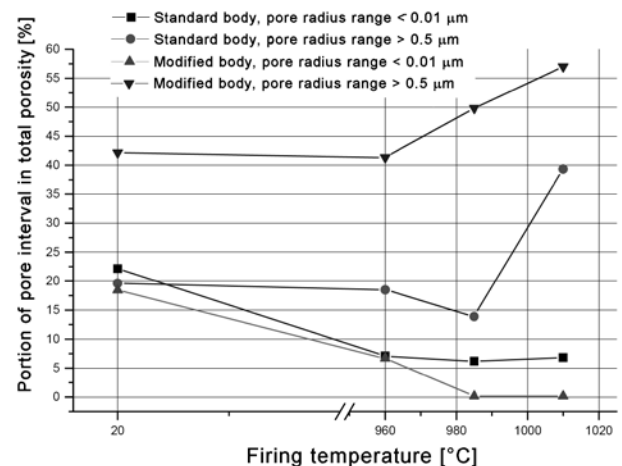

**Figure 2. Pore size distribution
of the standard and modified ceramic systems**

**Figure 3. Conversion of the rate of the pore intervals
(pore radius below 0.01 μm and above 0.5 μm)**

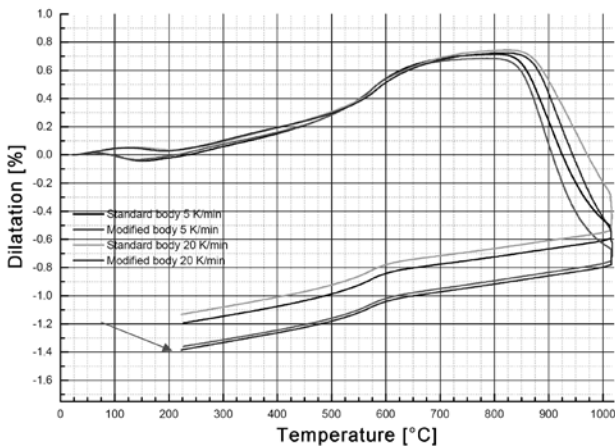**Figure 4. Dilatometric behaviour of the standard and modified ceramic systems, T$_{max}$=1010°C**
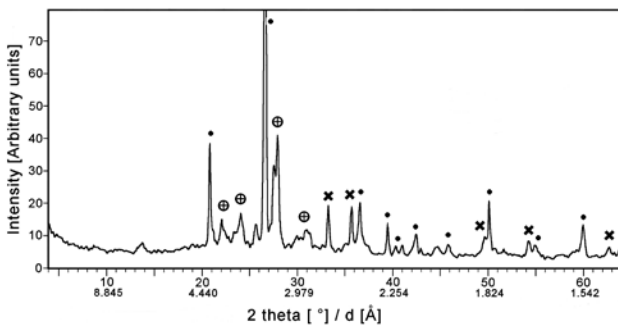

Figure 5. XRD diffractogram of the standard ceramic system fired at 1010°C
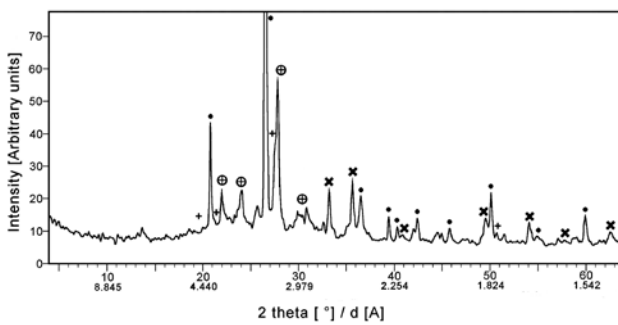(● quartz, ⊕ plagioclase, ✕ hematite, ✚ diopside)

Figure 6. XRD diffractogram of the modified ceramic system with glass additive K4, fired at 1010°C
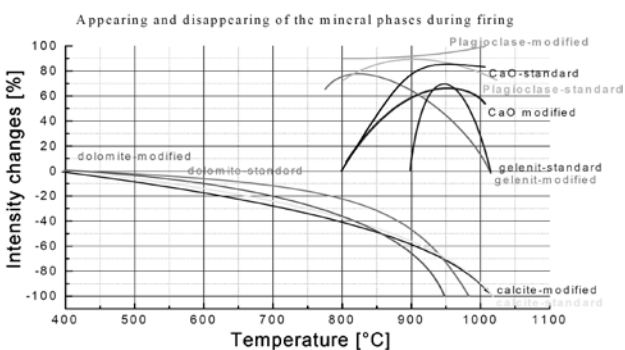(● quartz, ⊕ plagioclase, ✕ hematite, ✚ diopside)

Figure 7. Monitoring of crystalline phase evolution during the firing processes

Table 9. It is obvious that a part of quartz has already entered the silicatization reactions of the carbonates presenting a crystallization support for the next steps of mineral conversions (high temperature plagioclase formation) in the modified system. This state is the consequence of the presence of glass additive, which pushes the defined part of quartz into reactions with carbonates changing the phase composition of the modified system. (Figs. 5 and 6)

The high-temperature X-ray diffraction results support the above facts. Namely, the phases like dolomite and calcite disappear earlier in the case of the modified system. Phases such as gelenite and high temperature plagioclases appear earlier (at lower temperatures) and the plagioclase content continually grows in the case of the modified system. (Fig. 7) Obviously, the modified systems overcome easier the changes in the firing treatment.

Microstructure characterization

The interactions between carbonates and clay minerals, in the presence of the glass additive K4, obviously take a different direction than in the case of the standard ceramic system. The reactions in the solid state (the standard ceramic body, Fig. 8) are partially changed
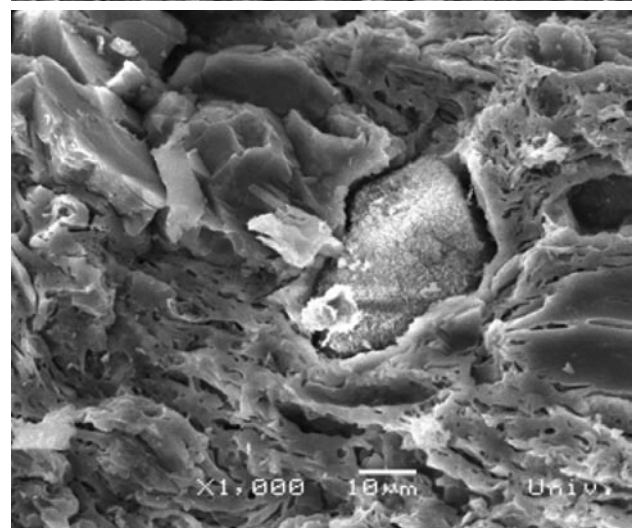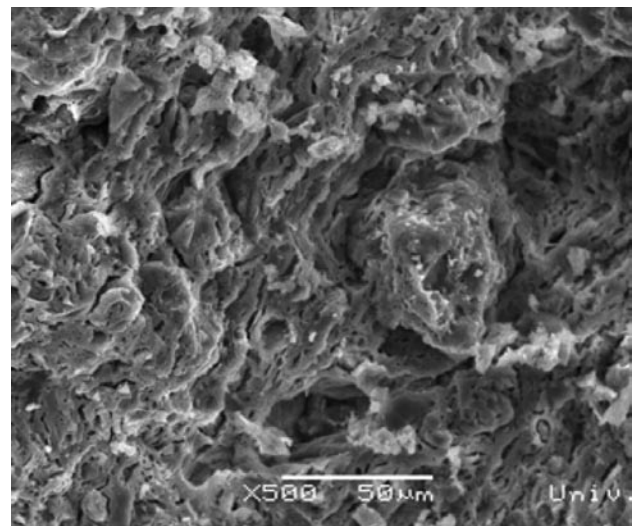

Figure 8. Microstructure of the standard ceramic body, T$_{firing}$ 1010°C - general view (500× up, 1000×, down)

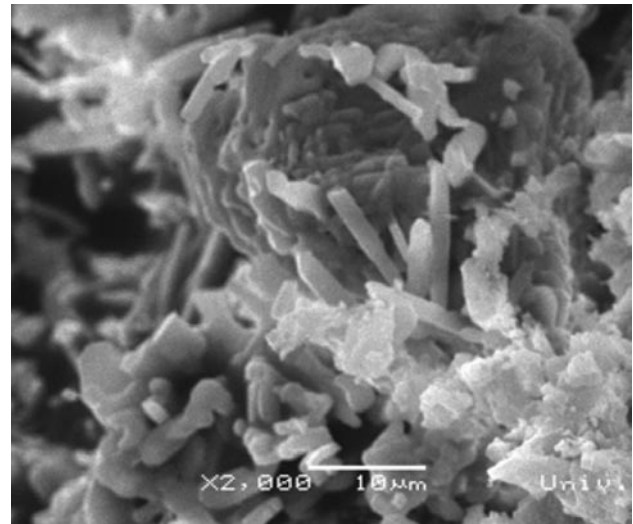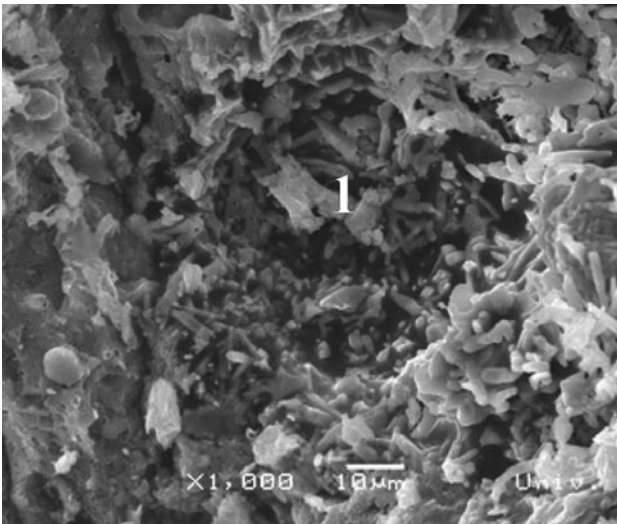**Figure 9. Microstructure of the modified ceramic body, T_{firing} 1010°C - general view (1000× left, 2000× –detail 1, right)**

compared to these carried out in the presence of glass phase (the modified ceramic body, Fig. 9), whose forming promoter is the used additive.

The matrix of the modified ceramic microstructure presents the spread melt of the glass additive mixed with the silica phase provided by the clay minerals, Fig. 9. This phase mixture, absorbing a higher quantity of CaO and MgO components than in the case of the standard system, is responsible for the formation of an additional amount of plagioclase (Fig. 9). The formed microstructure has a significant effect on the physical properties of the fired products, especially on the frost resistance characteristics, Table 8.

EDS analysis

In order to clarify the conclusions of this paper clearer, three characteristic microstructural points of the modified ceramic were analyzed with the Energy Dispersive Spectrometer (Fig. 10). Point 1 can be described as the region mainly consisting from waste glass. Point 2 is the mixture obtained from the above mentioned waste glass and glassy phase obtained from the clay minerals. As this region contains carbon (Fig. 10, Spectrum 2), the system

obviously trapped a part of CO_2 component after the carbonate decomposition. Finally, point 3 could be characterized as the region with the newly formed crystalline phases from CaO, MgO and silica matrix.

IV. Conclusions

After the series of investigation with a few additives (different fly ashes or waste glasses), the waste glass of the defined chemical composition (Na_2O = 12.78 wt.% and
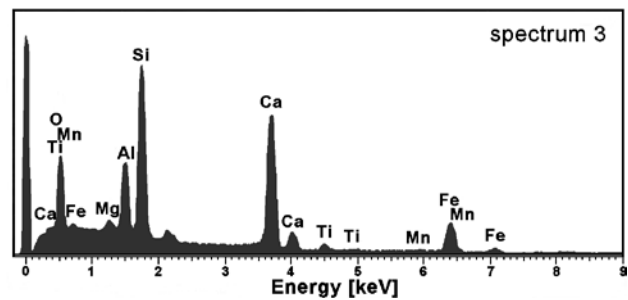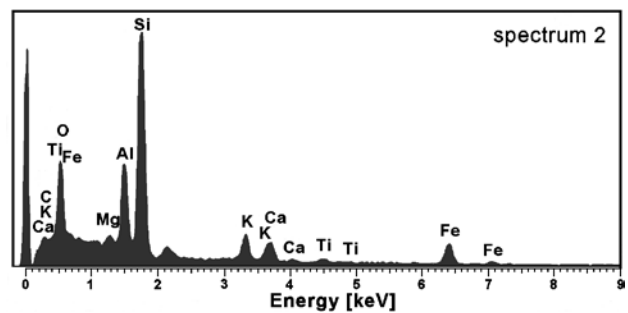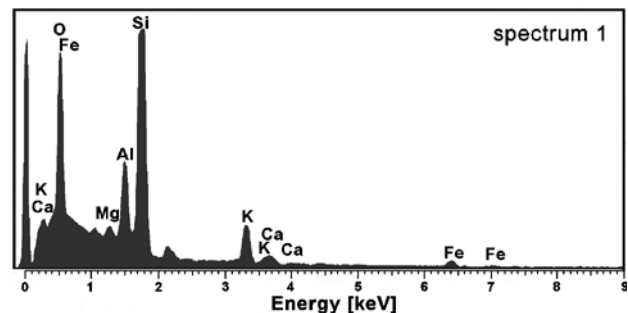

Figure 10. SEM micrograph and EDS spectrums (1-3) of the modified body, T_{firing} 1010°C

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K_2O = 3.49 wt.%) was chosen as a promising one. The positive effect of the additive lies in the stabilisation of the ceramic system during the preheating zone and in the supplying of the modified ceramic system with a higher liquid phase amount in comparison with the standard one. The modified ceramic system gets lower porosity and higher content of plagioclase. The deliberately changed glassy phase composition influenced the decrease of quartz content and the increase of plagioclase content.

The induced pore structure alteration lessened the portion of the pores smaller than 0.01 μm and increased the amount of pores above 0.5 μm. These changes influenced the frost resistance capacity criteria of the modified system providing a more frost durable product in the special climatic conditions. It showed the possibility of the revaluation of the lower quality raw clay materials which opens new perspectives for waste glass recycling as well as for the reduction of CO_2 emission.

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