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THE PROPERTIES OF A SINTERED PRODUCT BASED ON ELECTROFILTER ASH

LASTNOSTI SINTRANEGA PRODUKTA IZ ELEKTROFILTRSKEGA PEPELA

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The aim of this investigation was to obtain a sintered product based on electrofilter ash as a component of the raw-material mixture with satisfactory characteristics with regard to linear and volume shrinkage, total porosity and compression strength. The second component of the raw-material mixture is illite-kaolinite clay. The product obtained by sintering this raw-material mixture, based on its mechanical properties and total porosity, can be employed as a useful building material. On the basis of the obtained results the optimum sintering regime will be defined, taking into account the economic character of the process.

Keywords: electrofilter ash, clay, linear shrinkage, total shrinkage, sintering, porosity

Cilj raziskave je bil pridobiti sintran produkt z elektrofiltrskim pepelom kot komponento zmesi surovin in z zadovoljivimi linearnimi ter volumenskim skrčkom, skupno poroznostjo in tlačno trdnostjo. Druga komponenta surove zmesi je bila illitno-kaolinitna glina. Produkt sintranja te zmesi je zaradi mehanskih lastnosti in skupne poroznosti primeren za uporabo kot gradbeni material. Na podlagi rezultatov te raziskave bo opredeljen optimalen režim sintranja z upoštevanjem ekonomike procesa.

Ključne besede: elektrofiltrski pepel, glina, linearni skrček, skupni skrček

1 INTRODUCTION

Electrofilter ash contains silicates, carbonates and phosphates of calcium, magnesium, iron, aluminium and other elements[1]. Illite-kaolinite clays, apart from illite and kaolinite minerals, also contain a-quartz, Fe_2O_3 and $CaCO_3$[2]. This composition of the components from the raw-material mixture qualifies, depending on the sintering temperature, the reactions in the solid state, the polymorphic transformations of quartz and the liquid-phase formation[3]. Apart from the ceramic mass-sintering rate, i.e., the firing regime, the mineral content of the raw materials has an important role in the relations between particular microstructural elements[4]. The liquid phase accelerates the solid-state reactions (the diffusion coefficient in such systems increases by 1000 times)[5]. The new crystal phases, i.e., the compounds formed as a crystal phase during the sintering process, apart from the above-mentioned factors, were determined by the mineral and chemical content of the clay[6,7]. During the sintering of the samples with electrofilter ash, as a component of the raw-material mixture, the process is based on the heating of the samples at a temperature sufficient for the oxidation of the free carbon present in the ash, which could cause surface defects and a decrease of the sintered product's strength. In the following phase the samples are heated to the sintering temperature to obtain products with satisfactory characteristics with regard to the porosity and strength[8]. The content of electrofilter ash in the raw-material mixture can be 20–70 %[9], depending on the shaping method, the sintering temperature and the flux addition.

2 EXPERIMENTAL

The raw-material mixture for the production of samples was formed on the basis of "Pljevlja" clay as a binder, with five different mass fractions of electrofilter ash (10, 20, 30, 40 and 50 %). The samples were formed by plastic shaping in a mould corresponding to a parallelepiped with the dimensions 7.7 cm × 3.9 cm × 1.6 cm. For the components of the raw-material mixture the mineral and chemical composition, and the grain size distribution with granulometric analysis, were determined. The density and humidity of the components of the raw-material mixture were also determined. For the raw, unfired products, the linear and volume shrinkage during drying in air to a constant mass and drying in a dryer at a temperature of 110 °C were determined. The sintering of the samples with different amounts of electrofilter ash (Thermal plant "Pljevlja") was performed at a temperature of 1100 °C. This temperature was chosen on the basis of previous investigations of the temperature's influence on the properties of the sintered products on the basis of the composition of the raw-material mixture.

For the sintered products with different amounts of electrofilter ash we determined:

– the total porosity,
– the linear and volume shrinkage during sintering,
– the compression strength,
– the microscopic and X-ray analysis of the sintered products.

3 RESULTS AND DISCUSSION

The mineral content of "Pljevlja" clay (**Figure 1**) determined by X-ray analyses shows that the clay is an illite-kaolinite type, with the presence of quartz, muscovite, calcite and clinochlor. The X-ray analysis of electrofilter ash (**Figure 2**) shows the presence of quartz, rankinite and albite. The DTA analysis of the "Pljevlja" clay does not indicate any particularly endothermic and exothermic "peaks"; therefore, TG analyses (**Figure 3**) and DTG (**Figure 4**) analyses were performed. On the curved line of the DTG (the rate of mass change during sample heating) some changes, i.e., peaks, at a temperature of 529 °C were noticed, which probably correspond to the dissolution of the illite and kaolinite, as well as peaks at a temperature of 731 °C (carbonate dissolution). The DTA analysis of the electrofilter ash (**Figure 5**) does not show any precisely defined peaks that correspond to endothermic and exothermic reactions. The changes in the heating were registered in the form of slight inflections, where the first one was registered in the temperature range (305–520) °C ($MgCO_3$), and the second with an endothermic effect at a temperature of 728 °C, as a consequence of CO_2 formation with the thermal dissociation of $CaCO_3$. The most significant mass change, according to the results of the TG analysis (**Figure 5**), was registered in the interval from 654.9 °C to 827.3 °C, which corresponds to the thermal dissociation of $CaCO_3$, according to the results of the X-ray analysis. The mass loss for this temperature interval was 3.78 %.

The granulometric analysis (**Table 1**, **Table 2**,) shows that the electrofilter ash has a greater average grain size (109 µm) than clay (21.90 µm). For the electrofilter ash the most common fractions are: from 99 µm to 114 µm (13.7 %); from 114 µm to 131 µm (14.3 %); and from 131 µm to 150 µm (12.4 %). For the "Pljevlja" clay the most common fractions are: from 57.2 µm to 65.7 µm (4.6 %); from 65.7 µm to 75.4 µm (4.7 %); and from 75.4 µm to 150 µm (4.4 %).

The results of the chemical analysis of the "Pljevlja" clay and the electrofilter ash (**Table 3** and **Table 4**) show a larger mass fractions of Al_2O_3 in the electrofilter ash (21.77 %) than in the clay (10.55 %). The amount of SiO_2 is lower in the electrofilter ash (49.45 %) than in the clay (71 %). The "Pljevlja" clay does not contain the

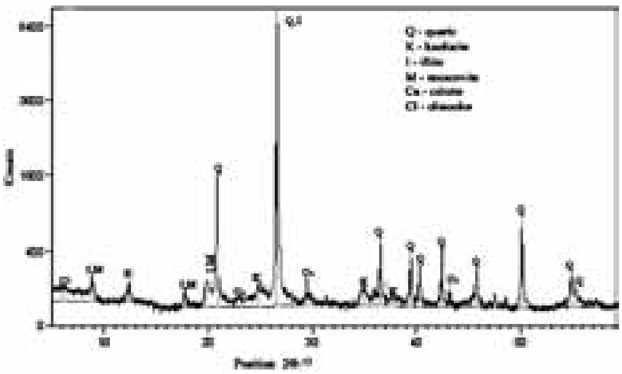

Figure 1: X-ray diffractogram of "Pljevlja" clay
Slika 1: X-difraktogram gline Pljevlja

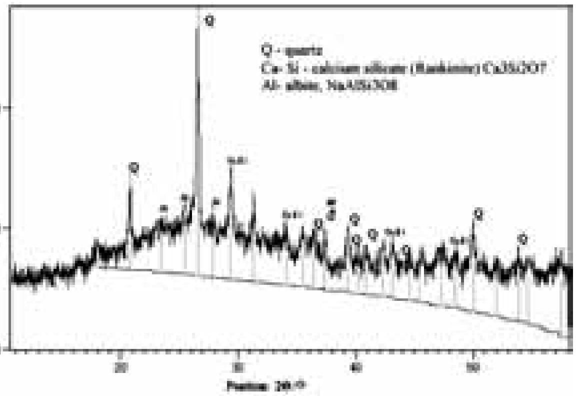

Figure 2: X-ray diffractogram of electrofilter ash from TE "Pljevlja"
Slika 2: X-difraktogram elektrofiltrskega pepela iz TE Pljevlja

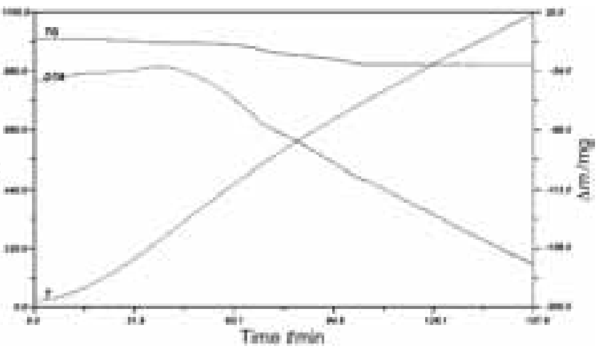

Figure 3: DTA and TG analysis of clay sample
Slika 3: DTA- in TG-analiza vzorca gline

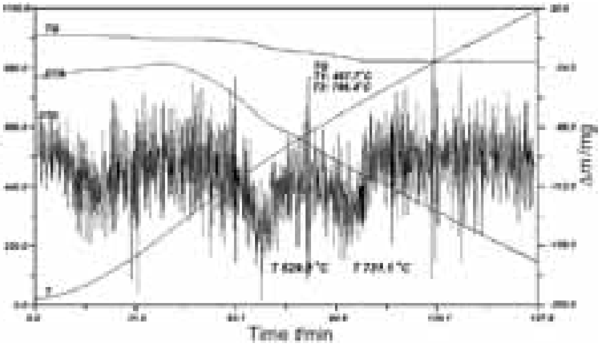

Figure 4: DTA, TG and DTG analysis of clay sample
Slika 4: DTA-, TG- in DTG-analiza vzorca gline

Table 1: Particle size distribution of clay
Tabela 1: Velikostna porazdelitev zrn gline

Particle size (μm)	<2	<5	<20	<30	>45	>60	<80	<100	<150
Percentage (%)	9.80	25.90	48.10	56.70	33.00	24.20	14.60	8.20	1.90

Table 2: Particle size distribution of electrofilter ash
Tabela 2: Velikostna porazdelitev zrn elektrofiltrskega pepela

Particle size (μm)	<2	<5	<20	<30	>45	>60	<80	<100	<150
Percentage (%)	1.50	1.90	5.00	7.60	88.30	80.90	73.40	58.10	18.50

Table 3: Chemical composition of clay
Tabela 3: Kemična sestava gline

Oxides	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	lg.loss
w/%	71	5.51	10.55	1.42	0.62	0.45	1.86	0.25	8.34

Table 4: Chemical composition of electrofilter ash
Tabela 4: Kemična sestava elektrofiltrskega pepela

Oxides	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	Na_2O	ZnO	MgO	MnO	P_2O_5	K_2O	lg.loss
w/%	49.45	5.23	21.77	0.66	13.34	0.46	0.004	1.29	0.02	0.24	1.40	4.35

following oxides, present in electrofilter ash: MnO, TiO_2, ZnO and P_2O_5.

The granulometric content of the components of the raw-material mixture has an important influence on the volume and linear shrinkage of the product during sintering. The values of the volume shrinkage during sintering decrease with the increase in the amount of ash in the raw-material mixture (**Figure 6**). With the increase in the amount of electrofilter ash the linear and volume shrinkage decreases. In the components of the raw-material mixture there is no significant difference in the amount of Fe_2O_3, but the amount of MgO in the ash is twice as high, and therefore the increase in the amount of ash in the raw-material mixture can cause a reaction between Mg (II) oxide and Fe (III) oxide, and an increase of the influence on the porosity as well as the extension of the system. The particles of soot present in electrofilter ash have an important influence on the linear and volume shrinkage. During sintering the carbon present is oxidized, defects are formed and the strength of the samples is reduced. Electrofilter ash contains TiO_2 and MnO, which have the role of mineralizers and affect the polymorphic transformations of the quartz. The activity of the TiO_2 is influenced by its content (0.66 %) and the sintering temperature.

The total porosity during sintering increases with the increase of ash content in the raw-material mixture (**Figure 7**). The mineral and granulometric content of the components of the raw-material mixture, as well as the shaping method, have an important influence on the porosity. A higher mean value of the grain of electrofilter ash with relation to the clay causes an increase in the porosity of the raw, unfired product, and therefore an increase in the porosity of the sintered product. During the formation of the raw-material mixture the flux was not added, but the content of alkalis in the clay is higher than in the electrofilter ash (chemical analysis), which causes a reduction in the amount of liquid phase with the in-

Figure 5: DTA and TG analysis of electrofilter ash sample
Slika 5: DTA in TG analiza vzorca elektrofiltrskega pepela

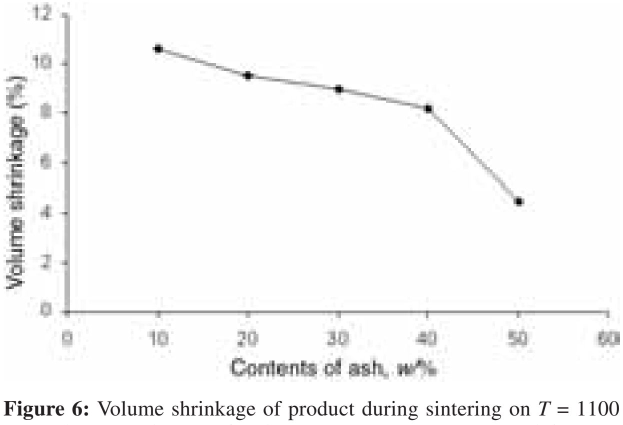

Figure 6: Volume shrinkage of product during sintering on T = 1100 °C, (ash content in mass fractions *w*/% = (10, 20, 30, 40 and 50)
Slika 6: Volumenski skrček zmesi pri sintranju pri T = 1100 °C (vsebnost pepela v masnih deležih *w*/% = (10, 20, 30, 40 in 50)

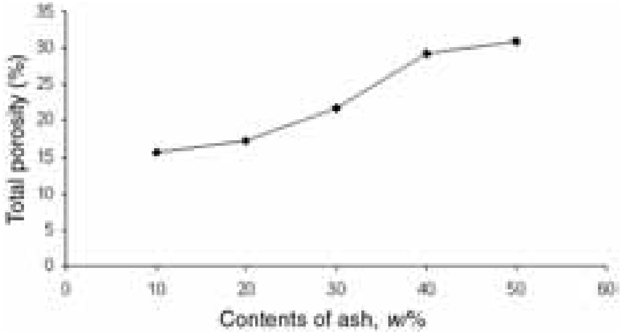

Figure 7: Total porosity of products during sintering at T = 1100 °C, (ash content in mass fractions w/% = (10, 20, 30, 40 and 50)
Slika 7: Skupna poroznost zmesi pri sintranju pri T = 1100 °C (vsebnost pepela v masnih deležih w/% = (10, 20, 30, 40 in 50)

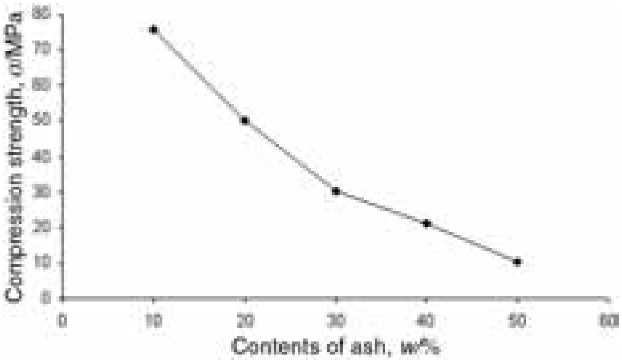

Figure 8: Compression strength of product during sintering at T = 1100 °C, (ash content in mass fractions w/% = (10, 20, 30, 40 and 50)
Slika 8: Tlačna trdnost po sintranju pri T = 1100 °C (vsebnost pepela v masnih deležih w/% = (10, 20, 30, 40 in 50)

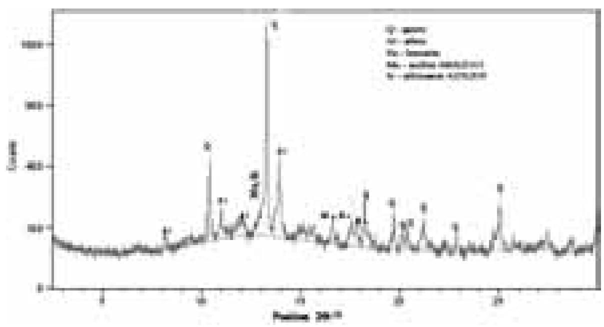

Figure 9: X-ray diffractogram of sintered product (ash 40 %, clay 60 %, T = 1100 °C)
Slika 9: X-difraktogram sintranega proizvoda (T = 1100 °C, masni delež pepela 40 %, gline 60 %)

crease in the amount of ash. The liquid phase accelerates the reactions in the solid state as a result of the increase in the diffusion coefficient.

The compression-strength value decreases with the increase in the amount of ash in the raw-material mixture (**Figure 8**). With the increase in the amount of ash the total porosity is increased, which decreases the compression-strength values. The amount of mullite and sillima-

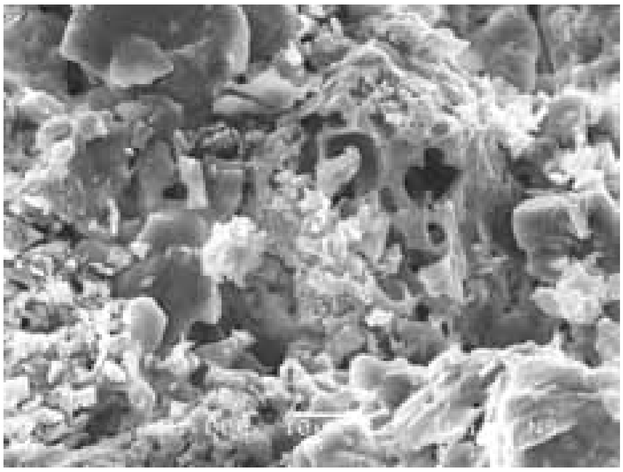

Figure 10: Microstructure of sintered product (T = 1100 °C, ash 40 %, clay 60 %, enlarged 1000-times)
Slika 10: Mikrostruktura sintranega produkta (T = 1100 °C, masni delež pepela 40 %, gline 60 %) pov. 1000-kratna

nite in the sintered product decreases with the increase in the content of ash (X-ray analysis of the sintered product), which has an important influence on the mechanical characteristics of the sintered product. The X-ray diffractogram of the sintered product (40 % of ash; 60 % of clay) shows the presence of quartz, albite, hematite, mullite and sillimanite (**Figure 9**). Mullite is formed at temperatures from 900 °C to 1100 °C. The presence of TiO_2 in the electrofilter ash (0.66 %) can partly enhance the mullitization, while the presence of a small amount of MnO (0.022 %) probably has a minor effect as a mineralizer in the polymorphic transformations of quartz. The microstructure of the sintered products (**Figure 10** and **Figure 11**) shows that it is a very complex structure: crystal phase (mullite, sillimanite, quartz) with the presence of the glass phase and pores.

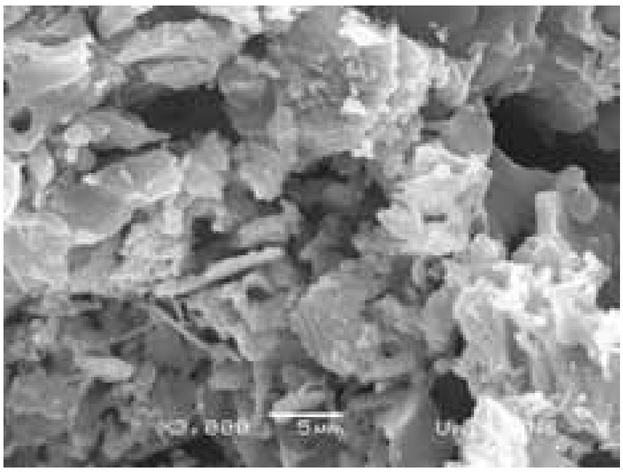

Figure 11: Microstructure of sintered product (T = 1100 °C, ash 40 %, clay 60 %, enlarged 3000-times)
Slika 11: Mikrostruktura sintranega produkta (T = 1100 °C, masni delež pepela 40 %, gline 60 %), pov. 3000-kratna

4 CONCLUSION

The investigations of the properties on the basis of the raw-material mixture of electrofilter ash and clay show that:

- on the basis of this raw-material mixture satisfactory characteristics of the sintered product with regard to volume shrinkage, total porosity and compression strength are obtained;
- without the presence of flux, a component for the reduction of shrinkage and electrolytes in the raw-material mixture, the mass fraction of electrofilter ash should not be higher than 30 %;
- investigations were performed without the pulverization of electrofilter ash, which would definitely have an influence on the properties of the sintered product.

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