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STRUCTURE AND PROPERTIES OF LIGHTWEIGHT CERAMIC AGGREGATES BASED ON LOCAL SILESIAN WASTE MATERIALS

This paper is focused on the manufacturing and properties of light weight aggregates made from local waste materials. The waste materials were car windshield glass contaminated by PVB foil, fly ash, mine slates as well as wastes after toothpaste production. The main aim of the research was to combine car windshield glass and the aluminosilicate coal mine slates as a basis for light weight aggregates manufacturing. Fly ash were added in order to modify rheological properties of the plastic mass. Toothpaste wastes were introduced as a source of carbonates and CO_2 evolution during thermal treatment. After milling and mixing all materials they were pressed and sintered at temperature range of 950°C-1100°C in air. The results show that it is possible to receive light weight aggregates only from the Silesian local waste materials. The significant influence of sintering temperature on properties of aggregates was observed.

Keywords: light weight aggregates, waste material, windshield glass, recycling

1. Introduction

The area of Upper Silesia is one of the most industrialized and thus the most contaminated areas in Poland. The amount of industrial waste produced in the Silesian voivodeship in years 2002-2015 is presented in Fig. 1.

A waste, difficult to reuse, is laminated automotive glass which is obtained in the processes of dismantling and recycling of cars. The problem is a polymer interlayer made of polyvinyl butyral (PVB) placed between two glass layers. Precise separation of PVB films from glass and cleaning glass is so complicated that waste glass cannot be used as a cullet in glass industry. It is stored at landfill sites being waste hard to manage. Our idea was to look for the method suitable for a recycling of the waste glass in a way to produce a new product with some social and commercial value. The light weight aggregates (LWA) has been chosen as a suitable target since they have a silica-based composition and they have a large application in building, construction and agriculture industry.

Nowadays, light weight aggregates are produced with the use of wastes from sewage sludge [2-6], recycled bricks and plaster from demolished buildings [7] or combinations of differ-

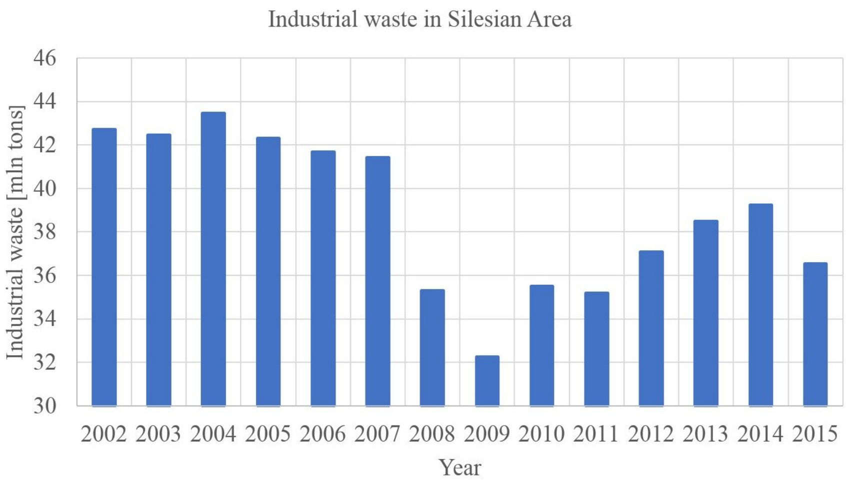

Fig. 1. Industrial waste in Silesian area in years 2002-2015 [1]

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ent types of waste [8-10]. Such aggregates have high porosity, low density and a suitable high mechanical strength. In order to obtain plastic mass from glass powder with sufficient rheological properties for granule formation we proposed application of the coal mine slates, residues after a coal classification since they contain alumina-silicates minerals and they are abundant in the Silesian area. Additionally, the use of components containing some amount of carbon and organic matter would help in the pore formation and increase the porosity of the material. One of them may be a PVB which is a contamination of windshield cullet. This foil decomposes at 300°C with gas release and causes the increase in porosity of aggregates. In a similar way works burning out carbon from coal slates. Both, PVB foil and slate, are introducing some amount of energy, what, in the future, will improve economy of the process in industrial conditions. In the research also other waste materials have been used. They can improve the effect of gas releasing and prevent too intensive sintering of aggregates during thermal treatment. A chalk, which is an ingredient of toothpaste waste, is a pore-forming agent, because it contains mostly calcium carbonate. On the other hand, fly ash are waste from local power plants and they are, in fact, gangue processed in fire which accompanies carbon fuel. Thus, they have chemical composition which is similar to coal slates, but after thermal treatment which takes place during the burning of carbon they have structure with defects, do not have plastic properties and have some amount of not burned carbon [11]. Therefore, they can introduce additional porosity Their structure with defects will be helpful in increasing reactivity of ceramic mass in high temperature and will let to improve economical affectivity of the whole process. The final result of sintering this type of material depends on many factors, such as type of material, mass densification, homogeneity of powder packaging, fragmentation rate, reaction, phase changes and burning conditions. The aim of the study was to determine the suitability of before mentioned raw materials to obtain porous product and to confirm the research hypotheses.

2. Experimental

In this work, waste which is broadly available in Silesia from production processes and recycling, was chosen to obtain granules. For the investigations following raw materials were selected:

– layered automotive glass cullet, obtained by car dismantling, supplied by KAPADORA recycling company (Żory, Poland),
– coal mine slates from Krupiński coal mine (Suszec, Poland),
– fly ash from HALDEX company (Katowice, Poland)
– wastes after toothpaste production (manufacturer from Silesian region).

All raw materials for the granules production are waste materials delivered with high amount of moisture (storage in open air areas) requiring purification, drying, mechanical separation of PVB fragments and other solid contaminants. Windshield cullet and coal slates were delivered in crushed, irregular pieces. The post-production toothpaste waste was condensed semi-liquid slurry. Fly ash was in the form of fine grained powder.

TABLE 1

Some physical properties of waste materials

Material	Moisture content [wt%]	Weight loss at 850°C [wt%]	Phase composition by XRD
Windshield glass (with PVB)	3.43-7.75	0.70-1.98	amorphous
Mine slates	3.32-4.47	7.99-9.30	kaolinite, pyrophillite, ferripyrophyllite quartz
Toothpaste	51.14-57.70	48.88	calcium carbonate
Fly ash	0.33-0.40	2.9-3.15	amorphous, quartz

Weight losses were determined by heating the powdered material at 850°C for 1 hour in air atmosphere in a chamber furnace. Differential scanning calorimetry (DSC) measurements of milled materials were performed (DSC 404 Netszch) at the range from room temperature up to 1100°C, in argon flow and with heating rate of 5°C/min.

Morphology of tested waste materials were carried out in the scanning electron microscope (SEM Hitachi S-4200). The Thermo Noran System 7 was used for measurements of the chemical composition (EDS). The results are presented in Table 1 and Fig. 2. The phase analysis of selected specimens was performed on Panalytical Empyrean Alpha diffractometer.

Milling of raw materials was performed separately in a cross-beater mill (Retsch SK 100 and/or SK 300) with 0.5 mm separation sieves. Drying of milled windshield glass and coal slates was performed in conventional laboratory driers at 110-120 ^{o}C until constant weight was obtained. The separation and multi-stage milling were carried out. Fly ash did not require any special processing.

For the investigations several series of specimens with different amounts of waste additions were chosen. All mixtures contained 30wt% of windschield cullet with PVB.

TABLE 2

Composition of mixtures [wt%]

Name	Glass contents	Mine slates	Toothpaste waste	Fly ash
F	30%	20%	20%	30%
G	30%	20%	30%	20%
H	30%	30%	10%	30%
I	30%	40%	10%	20%
J	30%	30%	20%	20%
K	30%	40%	20%	10%
L	30%	30%	30%	10%
M	30%	40%	30%	0%

All of the components were mixed and homogenized in an agate mortar to obtain homogenous mixture. Then, samples with

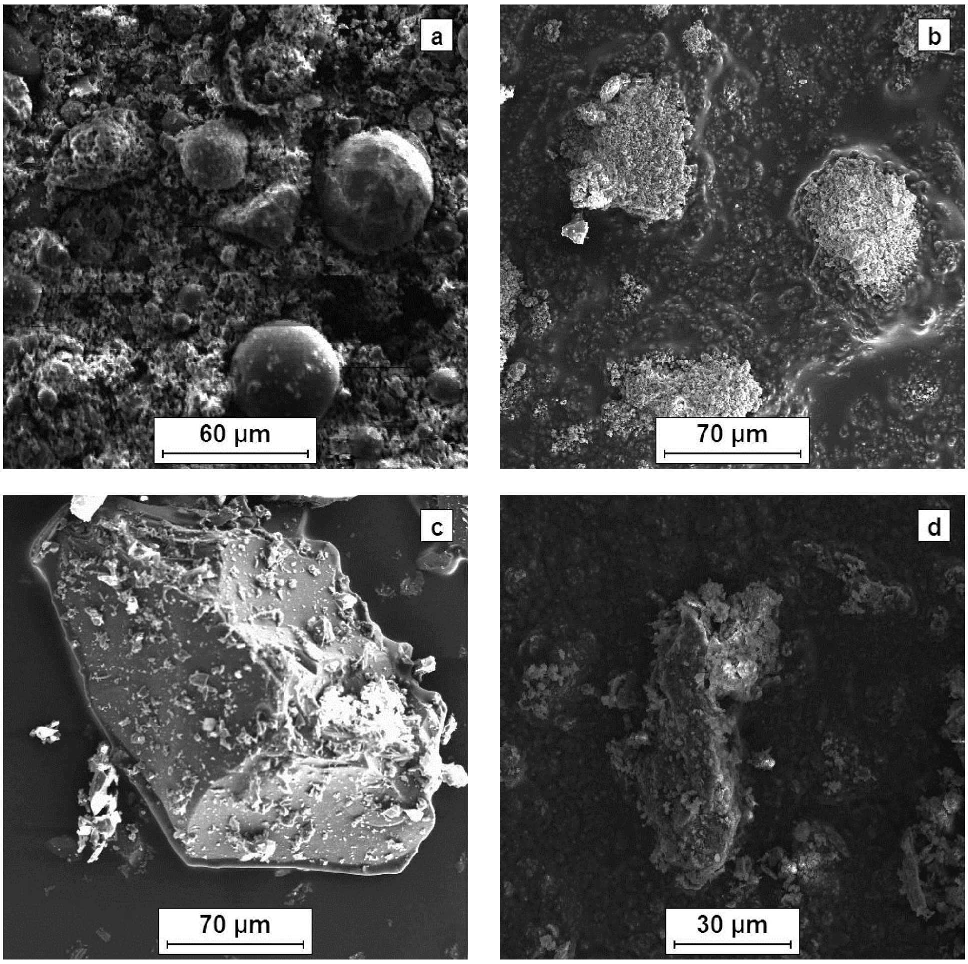

Fig. 2. Morphology of the crushed waste materials” a-fly ash, b-toothpaste, c-milled glass, d mine slates (SEM)

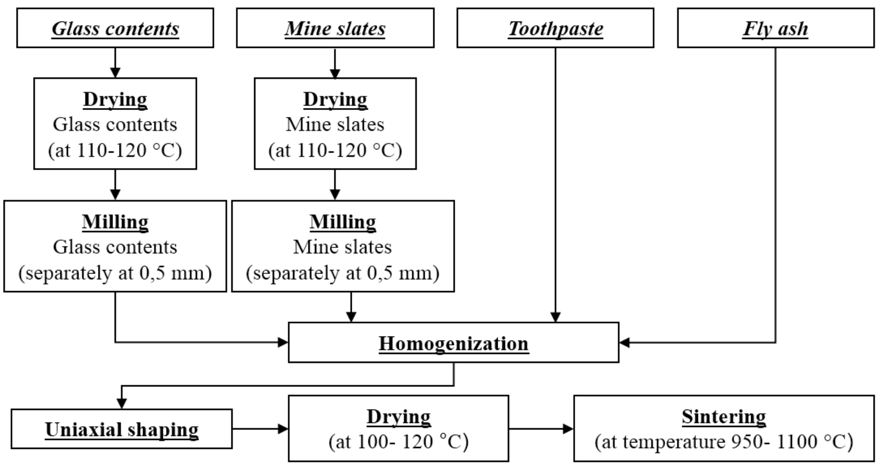

Fig. 3. General overview of the work

a diameter of 25 mm were formed by uni-axial pressing with a pressure of 10 MPa. Next, after drying, samples were sintered in a laboratory chamber furnace (Carbolite) in the air atmosphere for 0.5 h at the temperatures 950-1050°C. For the sintered specimens, parameters like weight loss, apparent density and open porosity were characterized. Microstructure investigations were performed on the stereoscopic microscope Nikon SMZ 745T.

A general overview of the work is presented in the Fig. 3.

3. Results and discussion

All raw materials had grains with different morphology and size. Surface analysis (SEM) was performed on milled powders and showed characteristics of each raw material. Despite the use of 0.5 mm separating sieves, for glass and slate the actual size of grains is smaller. This phenomenon can be explained by the nature of materials and grinding method.

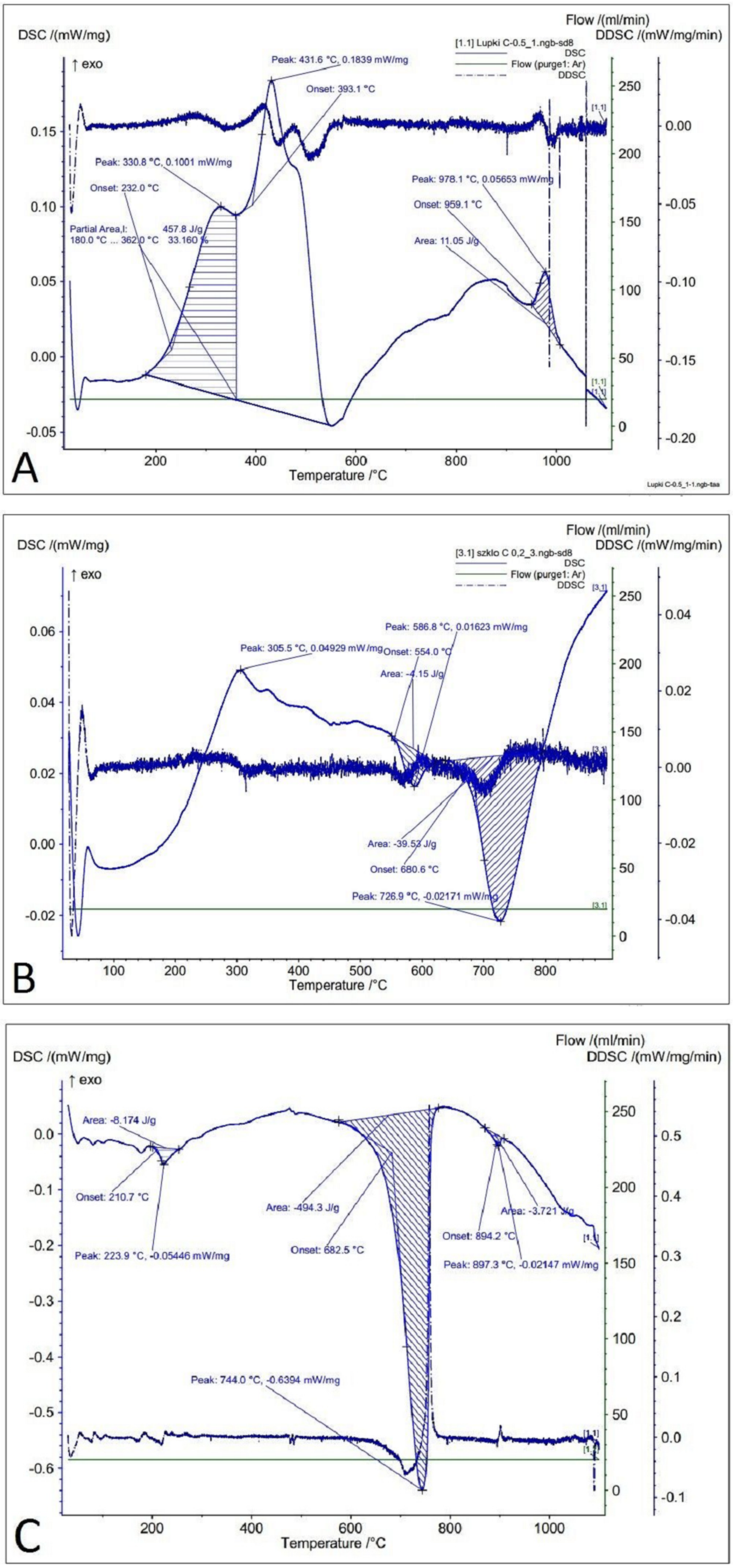

Fig. 4. Differential scanning calorimetry of mine slates (a), glass (b) and toothpaste (c)

Results of thermal decomposition of waste materials (Fig. 4) are consistent with their phase composition. An amount of carbon in coal mine slates is sufficient to cover the endothermic effect of clay-based mineral decomposition since only exothermic effect of carbon oxidation is visible. Additionally, exothermic effect of metakaolinite crystallization below 1000°C is present. On the other hand, thermal treatment of toothpaste shows a negligible effect of organic part decomposition and a strong endothermic effect related to calcium carbonate decomposition at temperature below 800°C. DSC results of glass powder demonstrate a strong exothermic effect of PVB oxidation in the temperature range of 200-500°C and endothermic peak over 700°C related to glass melting. DSC of fly ash (not shown here) does not show any reactions since they are the product from thermal treatment during coal burning out. Thus, we could summarize that organic matter and coal oxidation produce gas evolution during the formation of the pyroplastic state of the mass while carbonates decomposition produces evolution of gas after glass melting.

In the evaluation of properties of aggregates, parameters like open porosity and apparent density were considered as the most important. Results are presented in Fig. 5.

During the analysis of Fig. 5 it can be observed that apparent density increases with an increase of the process' temperature. It is the result of an increase of sintering rate and formation of more compact structure. These results confirm measurements of open porosity: as a temperature of the process increases, the open porosity decreases. It is clearly seen that temperature of 1050°C is the highest possible temperature for manufacturing porous granules since the highest growth of density occurs between 1050 and 1100°C. Additionally, some compositions reveal the minimal apparent density after heat treatment at this temperature.

The smallest apparent density and the highest open porosity have specimens from series F (30wt% glass, 20wt% slate, 20wt% toothpaste, 30wt% fly ash), while specimens from series K (30wt% glass, 40wt% slate, 20wt% toothpaste, 10wt% fly ash) have the highest apparent density and the lowest open porosity in nearly entire range of investigated temperatures. Both series contain the same content of toothpaste (20wt%). Significant differences in open porosity values between series F and series K, proof that the addition of toothpaste does not significantly affect their properties. One reason may be higher temperature of calcium carbonate decomposition in comparison to glass melting temperature. Another reason can be proportions of slates and fly ash. Higher slate content promotes sintering. The slate contains a significant amount of potassium which in combination with glass may favour a formation of low-melting eutectics.

The influence of fly ash replacing slates on the open porosity at given temperatures for specimens with constant glass and toothpaste contents is presented in Fig. 6. The influence of toothpaste replacing fly ash for the specimens with constant glass and slates contents is presented in Fig. 7. The influence of toothpaste replacing slates for the specimens with constant fly ash contents is presented in Fig. 8.

Analysing before mentioned results, it can be stated that the highest open porosity (33,22%) has the specimen G (30wt% glass, 20wt% slate, 30wt% toothpaste, 20wt% fly ash) sintered at 950°C. Depending on the process' temperature, the influence of each component on the structure is slightly different. However, for most temperatures, the highest open porosity is always observed for specimens with the highest content of fly ash, regardless of the amount of other components (Figs. 6-7). In case of the constant content of toothpaste, the open porosity decreases when the content of fly ash decreases (Fig. 6). Thus, the higher the content of slates, the lower is the open porosity (Figs. 6,8). When the fly ash is replaced by the toothpaste (Fig. 7), the influence of the composition on properties is slightly smaller, however the trend is true. Therefore, it can be stated that the open porosity is mostly affected by the slates to fly ash ratio.

Analysis of the morphology of specimens with constant toothpaste content (20wt%) showed a significant influence of

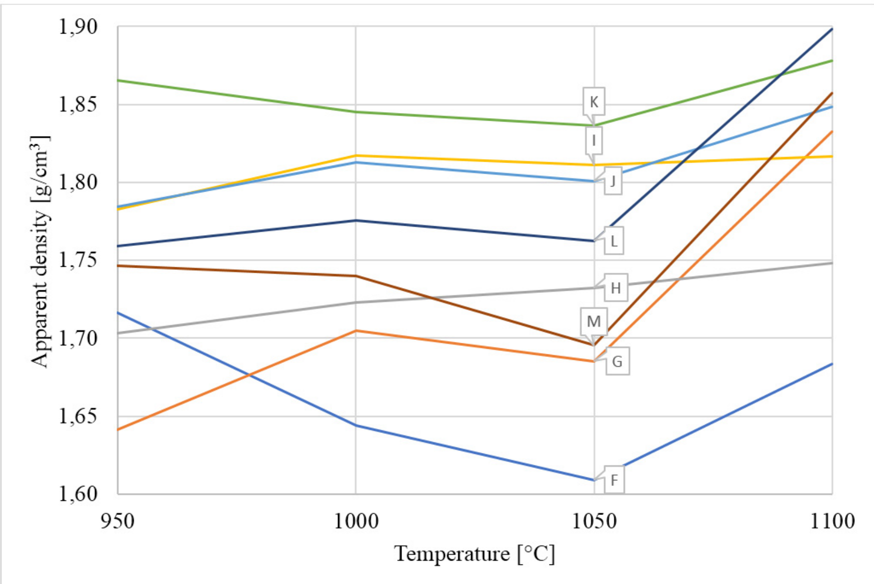

Fig. 5. Apparent density of tablets after sintering in the temperature range of 950-1100°C

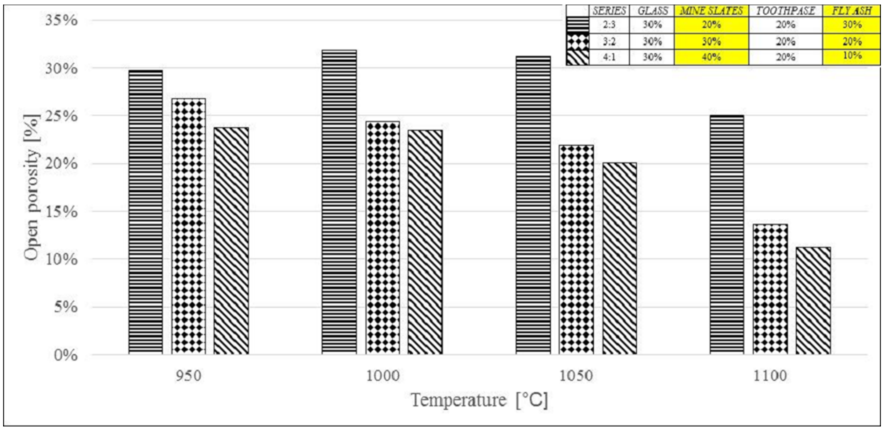

Fig. 6. The influence of the ratio of coal mine slates amount to fly ash amount at constant glass (30 wt%) and toothpaste (20 wt%) amount on open porosity of specimens annealed at various temperatures

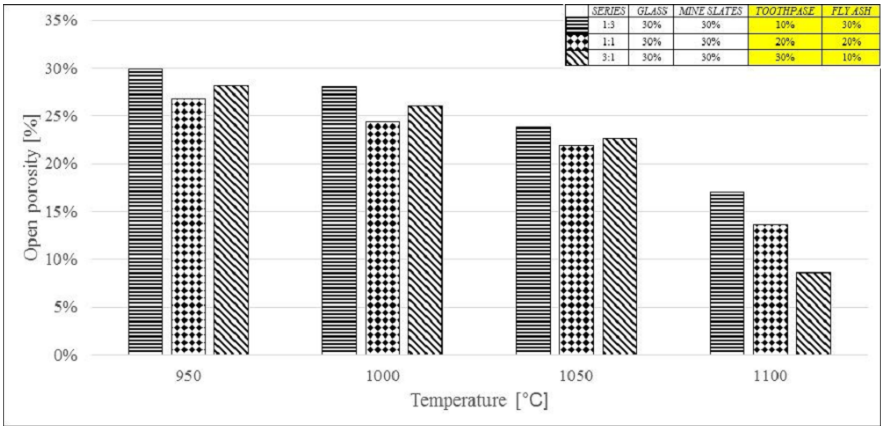

Fig. 7. The influence of the ratio of toothpaste amount to fly ash amount at constant glass (30 wt%) and coal mine slates (30 wt%) on open porosity of specimens annealed at various temperatures

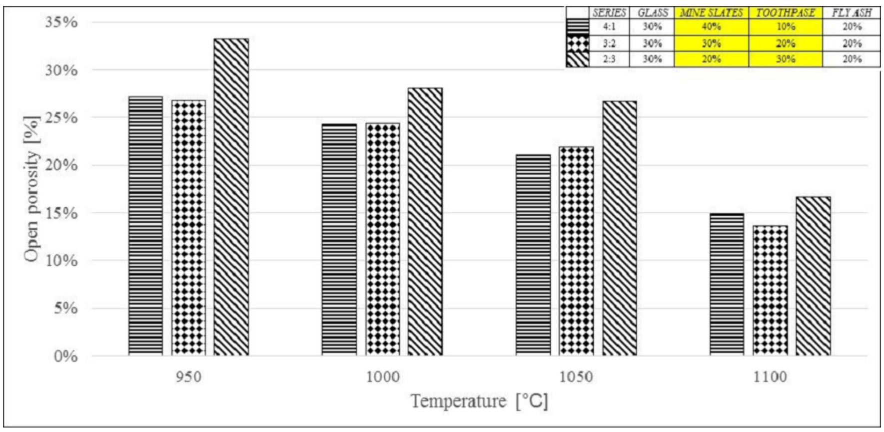

Fig. 8. The influence of the ratio of coal mine slates amount to toothpaste amount at constant glass (30 wt%) and toothpaste fly ash (20wt%) amount on open porosity of specimens annealed at various temperatures

composition on the microstructure of the material. Specimens with 30wt% of ash (F) have more homogeneous and porous microstructure. While as the amount of slates increases, the inhomogeneity of the material increases. It can be clearly seen that darker areas filled with the slate are non-porous inclusions.

Analysis of phase composition (Fig. 10) of specimens K and F, with varying slates and fly ash content, sintered at 1100°C, showed the similarity of phase composition, i.e. there are unreacted quartz and crystallized cristobalite in both of them.

This similarity is a result of similar chemical composition (aluminosilicate) of mine slates and fly ash. The main identified phases occurring in both investigated specimens are quartz, cristobalite, diopside, anorthite. The differences are only in the amounts of phases. There is slightly lower amount of quartz and

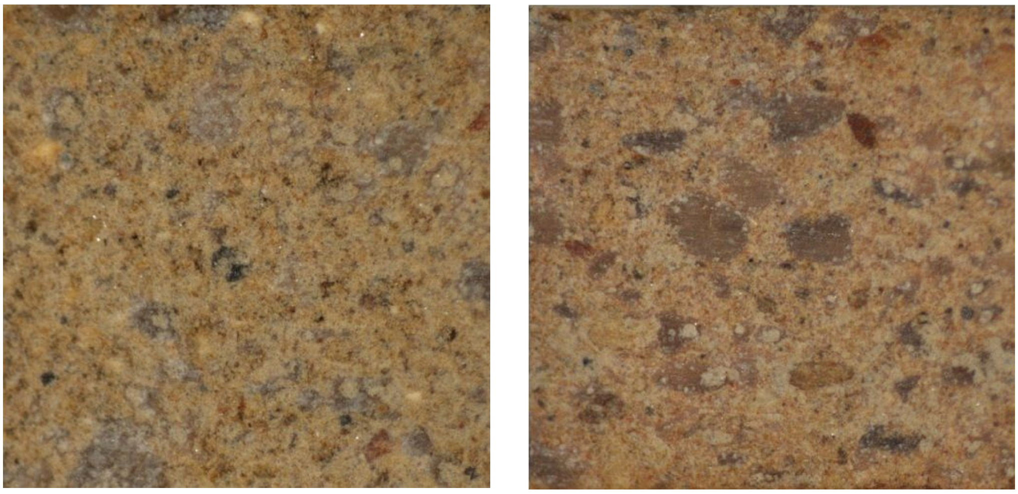

Fig. 9. The influence of the composition on the microstructure of specimens sintered at 1000°C (left side-F – 30wt% glass, 20wt% slate, 20wt% toothpaste, 30wt% fly ash), right side K – 30wt% glass, 40wt% slate, 20wt% toothpaste, 10wt% fly ash)

bigger amount of cristobalite in specimen F. The albite phase occurs together with diopside (mixed crystals) so it's presence cannot be excluded.

There is a tendency of peaks' intensities to increase for specimens sintered in higher temperatures, regardless the mixture composition. It is probably related to a higher degree of crystallization of the forming phases and decrease of the amount of an amorphous phase.

4. Conclusions

Therefore, it can be concluded that generally accessible, burdensome products such as laminated automotive glass cullet, coal mine slates, toothpaste waste and fly ash lay on the Silesian landfills are a valuable source of raw materials which enables production of valuable granules and, on the other hand, they improve the quality of the natural environment.

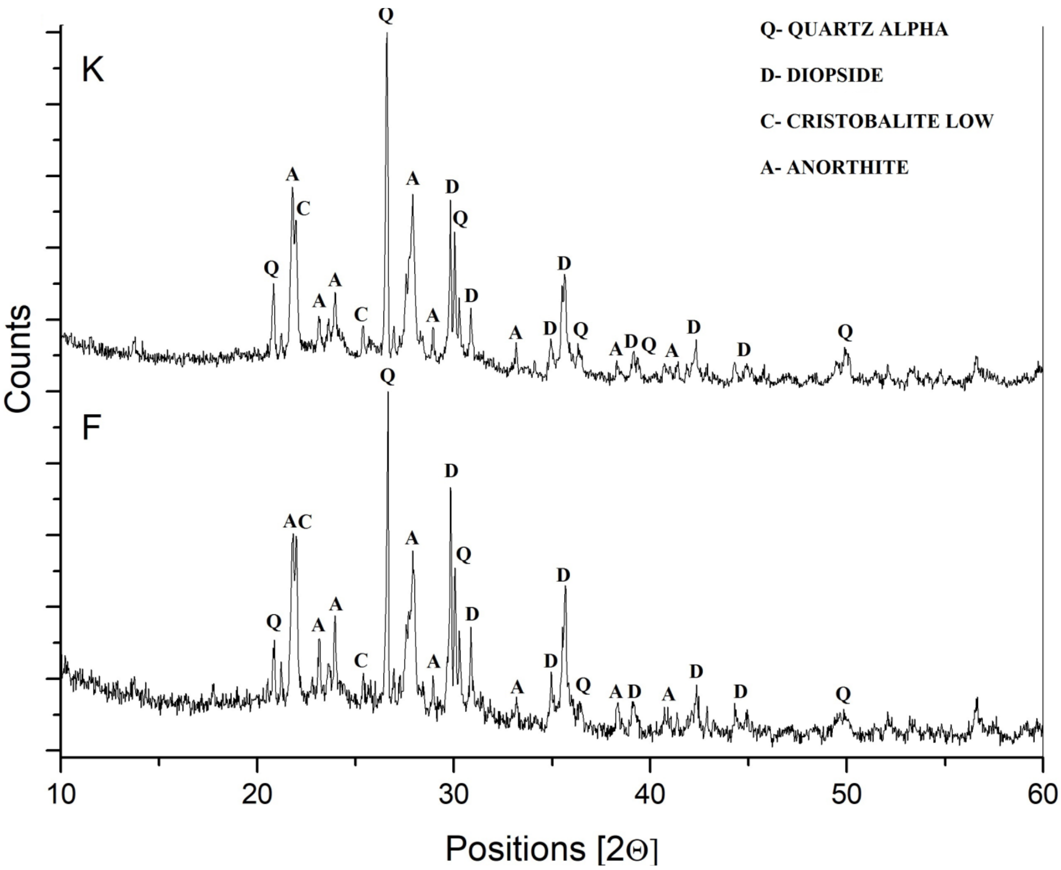

Fig. 10. Comparison of XRD pattern of samples F (glass 30wt%, mine slates 20wt%, toothpaste 20wt%, fly ash 30wt%) and K (glass 30wt%, mine slates 40wt%, toothpaste 20wt%, fly ash 10wt%) sintered at 1100°C

The significant influence of sintering temperature on LWA's properties was observed. As the temperature increases, the apparent density increases and the open porosity decreases. The highest open porosity and the lowest density have specimens sintered at 950°C. The strongest influence on an apparent density as a function of sintering temperature was observed for specimens composed of 30wt% glass, 20wt% slate, 30wt% toothpaste and 20wt% fly ash (specimen G). In case of open porosity, the strongest influence of sintering temperature was for specimen L containing 30wt% glass, 30wt% slate, 30wt% toothpaste and 10wt% fly ash.

The influence of waste containing calcium carbonate (toothpaste) on the open porosity and the apparent density was observed. Specimens with more than 10wt% of toothpaste had the lowest apparent density after sintering at 1050°C and a high open porosity. Replacing slate for fly ash addition had strong influence on properties and increase the open porosity. The most appropriate composition to obtain the low density and the high porosity was composition with: 20wt% slate, 30wt% toothpaste, 20wt% fly ash, when sintered at 950°C.

XRD measurements for specimens with strongly different porosity showed similar, aluminosilicate composition with small differences in the amounts of phases. Increasing the temperature of the process results in higher crystallization degree but is economically unfavourable.

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