

Pore structure of lightweight clay aggregate incorporate with non-metallic products coming from aluminium scrap recycling industry

D. Bajare^{a,*}, A. Korjamins^a, J. Kazjonovs^a, I. Rozenstrauha^b

^a Faculty of Civil Engineering, Riga Technical University, Azenes 16/20, Riga LV-1048, Latvia

^b Faculty of Material Science and Applied Chemistry, Riga Technical University, Azenes 14/24, Riga LV-1048, Latvia

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Abstract

This paper deals with the non-waste utilisation of aluminium recycling waste called non-metallic products (NMP) and their reprocessing into environmentally friendly material. In the present studies, lightweight expanded clay aggregates were produced from natural plastic clay and NMP. They were obtained recovering Al metal from black dross by using conventional metallurgical process. Based on the results obtained from chemical and mineralogical investigations of NMP, heat treatment in the temperature range from 1150 °C to 1280 °C was selected as an appropriate method to eliminate impurities of residues, such as aluminium nitride (AlN), iron sulphite (FeSO₃), aluminium chloride (AlCl₃). Emissions of gases during high-temperature treatment of NMP act as initiators to create extra porous structure of sintered ceramic bodies. The effect of raw material composition, previous treatment of NMP and sintering temperatures on the aggregate's properties were evaluated. Physical and microstructural properties of sintered aggregates were determined.

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1. Introduction

Large amount of dross is being generated during the aluminium scrap recycling process in the secondary industry. On average, 15–25 kg of dross is produced per every ton of molten aluminium.¹ One of the main constituent elements of dross is aluminium metal, which content varies from 8 to 80% depending on grades.² The dross obtained as a result of the aluminium scrap recycling process could be classified into three different categories based on the metal content, i.e., white dross, black dross and salt cake. White dross is characterised by the higher aluminium metal content and it is produced from primary and secondary aluminium smelters, whereas metal content in black dross is lower and it is generated during aluminium recycling (secondary industry sector). Black dross typically contains a mixture of aluminium oxides and slag with recov-

erable aluminium content ranging between 5 and 20%. The amount of aluminium present in salt cake is low (5–10%) with large quantity of soluble salts.^{2–4} Apart from aluminium metal, dross may also contain other chemical compounds and minerals, e.g. corundum (Al₂O₃), spinel (MgAl₂O₄), bayerite (Al(OH)₃), aluminium nitride (AlN), aluminium sulphide (Al₂S₃), halite (NaCl), sylvite (KCl), aluminium carbide (Al₄C₃), iron sulphite (FeSO₃), quartz (SiO₂), magnesium oxide (MgO), etc.^{2,3,5–7}

The recovery of metal from black or white dross is done worldwide through the conventional metallurgical process. Residual aluminium recycling waste containing alumina, salts, impurities and a small amount (3–5%) of metallic aluminium was obtained during the second recovery process. The given types of waste may have different names in various scientific publications, for example: non-metallic product (NMP), the aluminium recycling, the residual oxide mix, the residues and even recycled or residual dross.^{5,8–11}

It is generally considered that non-metallic product is a process waste and a subject to the disposal after the metal has been recovered from dross.

The consumption of aluminium waste is rising continuously worldwide, which is great stimulus for developing a non-waste

* Corresponding author. Tel.: +371 29687085; fax: +371 67089248.

E-mail addresses: diana.bajare@rtu.lv (D. Bajare), aleks@latnet.lv (A. Korjamins), janis.kazjonovs@rtu.lv (J. Kazjonovs), ineta.rozenstrauha@rtu.lv (I. Rozenstrauha).

technology.^{2–4,6} This case study investigates the application of the process waste or non-metallic product (NMP) generated from dross processing. The terms non-metallic product and NMP are used interchangeably in this case study.

The composition of NMP is highly variable and usually unique to the plant generating the waste, hence finding potential application for this material is often seen as a difficult task.^{5,7,12} The task becomes even more challenging due to the toxic nature of NMP. It emits flammable gases, such as acetylene, or it is liable to give off toxic gases, such as ammonia, in dangerous quantities in contact with water.¹³ Apart from this, the NMP contains compounds like soluble salts, oxides, carbides and sulphides as well as metallic aluminium.^{5,7,8,12}

However, there are a lot of patents and scientific proof for the possibility to use NMP as a source of aluminium compounds for chemical,^{4,14–18} metallurgy¹⁵ and building industry.^{2,4,19} Waste could be utilised together with other alternative materials to produce premixes for clinker and ceramic products^{9,20} as well as it can be used as a raw material for the production of concrete, mineral wool and materials with ultra-high resistance to fire.^{2,9,21–22} The goal of the research is the same – to develop the processes for converting NMP into the products with high benefit. Scientific justification of the successful application of waste in the different fields lays in the changes happening in the mineralogical and chemical composition of NMP during the high temperature treatment.

The main goal of the research is to investigate the possibilities of NMP recycling for production of several useful commercial products – porous ceramic building materials with an extra high porosity and unique pore structure.

The lightweight expanded clay aggregate (LECA) is an important building material in the regions where natural lightweight aggregates are not available. On the other hand, LECA can be manufactured from the widely available natural resource – clay. The properties of the end product mainly depend on the type of clay, the type and amount of NMP and the sintering temperature of the aggregates. The main goal of this experimental work is to examine the effect of NMP application on the physical and micro-structural properties of LECA produced at various sintering temperatures.

2. Materials and methods

2.1. Raw materials

In the current study, lightweight expanded clay aggregates (LECA) were produced from the clays with a high content of carbonates and NMP in different compositions. The chemical

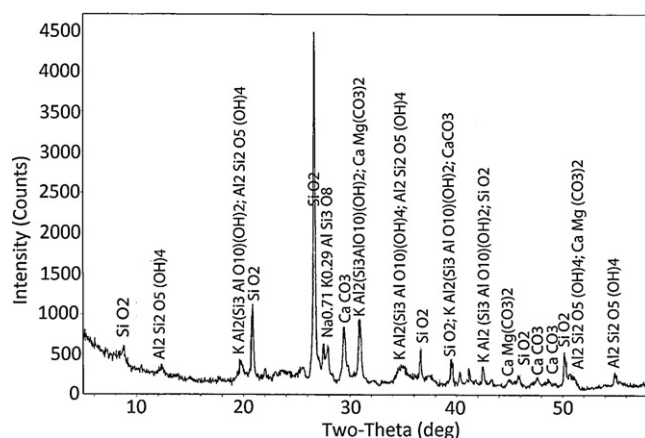


Fig. 1. X-ray diffraction pattern of clay used in the experiments.

composition of clay and NMP was determined according to LVS EN-196-2 with the sensibility of ± 0.5 wt% (Table 1).

Apart from that, the applied clay contained carbonates ($\text{CaCO}_3 + \text{MgCO}_3$) 21.66 wt%. X-ray diffraction (XRD) analysis of the applied clay can be seen in Fig. 1, which shows that the clay is composed of quartz (SiO_2), calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CaO}_3)_2$), illite ($\text{KAl}_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and anorthoclase ($\text{Na}_{0.71}\text{K}_{0.29}\text{AlSi}_3\text{O}_8$). According to the analysis, the clay used in these experimental studies is a typical carbonate clay.

Analysis of the elements that was carried out with the help of an inductive coupled plasma optical spectrometry (ICP-OES), an atomic absorption spectroscopy (AAS) and a potentiometer titration analysis, showed the following content of NMP: aluminium (Al), silicon (Si), magnesium (Mg), calcium (Ca), sodium (Na), potassium (K), sulphur (S), chlorine (Cl), iron (Fe), copper (Cu), lead (Pb), zinc (Zn) (Table 2).

These data correspond to the chemical composition of NMP, which is given in Table 1. In terms of the chemical composition and an additional calculation the analysed NMP also contains aluminium nitride (AlN) – on average 5 wt%, aluminium chloride (AlCl_3) – on average 3 wt%, potassium and sodium chloride ($\text{NaCl} + \text{KCl}$) – total 5 wt% and iron sulfite (FeSO_3) – on average 1 wt%. The mineralogical composition of NMP was determined by using the XRD analysis (Fig. 2; Table 3).

According to the XRD analysis data, the NMP contained metallic aluminium (Al), iron sulfite (FeSO_3), aluminium nitride (AlN), corundum (Al_2O_3), aluminium iron oxide (FeAlO_3), magnesium dialuminium (MgAl_2O_4), quartz (SiO_2), aluminium chloride (AlCl_3) and aluminium hydroxide ($\text{Al}(\text{OH})_3$).

The XRD analysis was used for determination of changes in the mineralogical composition of NMP during the heat treatment. According to the XRD NMP, which was treated at the

Table 1
Basic chemical composition of clay and NMP (wt%).

	Ignition loss, 1000 °C	Al_2O_3	SiO_2	CaO	SO_3	TiO_2	Na_2O	K_2O	MgO	Fe_2O_3	Others
Clay	13.60	14.34	50.22	8.54	0.07	0.56	0.43	3.09	3.07	5.74	
NMP	6.21	63.19	7.92	2.57	0.36	0.53	3.84	3.81	4.43	4.54	>2.6

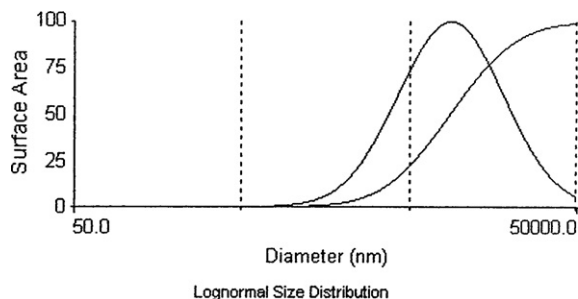


Fig. 5. Particle size distribution of NMP.

Light smell of ammonia was detected during the aggregate preparation procedure. According to analysis made by the Varian CP-3800 Gas Chromatograph and Varian Cary 50 UV–vis spectrophotometer, ammonia (NH_4) in the amount of 317 mg/m^3 and small amount (0.41 mg/m^3) of sulphur dioxide (SO_2) were identified. The prepared aggregates were dried in the oven for 3 h at temperature of 105°C to stop the reaction between impurities (AlN) of NMP and the water used to prepare the plastic mass.

Green aggregates were treated in the electric furnace for 5 min. at various sintering temperatures ranging from 1150 to 1270°C . The rate of temperature increase in the furnace was kept constant at 15°C/min . Green aggregate, and aggregates sintered at the temperature of 1170°C with and without NMP are shown in Fig. 6.

2.3. Characterisation methods

Chemical composition of clay and NMP was determined according to LVS EN-196-2 with sensibility $\pm 0.5 \text{ wt\%}$. Analysis of the NMP elements was carried out with the help of inductive coupled plasma optical spectrometry (ICP-OES), atomic absorption spectroscopy (AAS) and potentiometer titration analysis. The mineralogical composition of the NMP and clay was determined by using the XRD analysis (RIGAKU ULTIMA+). The same method was used to determine changes in the mineralogical composition of the heat-treated NMP. Laser diffraction method (Particle Size Analyzers Zeta Plus) was used to determine particle size of the raw material mix. Gases, which give off in the reaction between NPM and water, were determined by the gas chromatography (Varian CP-3800) and spectrophotometry (Varian Cary 50 UV–vis).

The volume expansion of aggregate was measured by the percentage of volume increment of the particle, where the volume was calculated considering an average diameter of particle.



Fig. 6. View of the aggregates: (a) green aggregate. Aggregates sintered at the temperature of 1170°C , (b) the comparative aggregate made from clay with no added NMP and (c) the aggregate made from clay with NMP (9%).

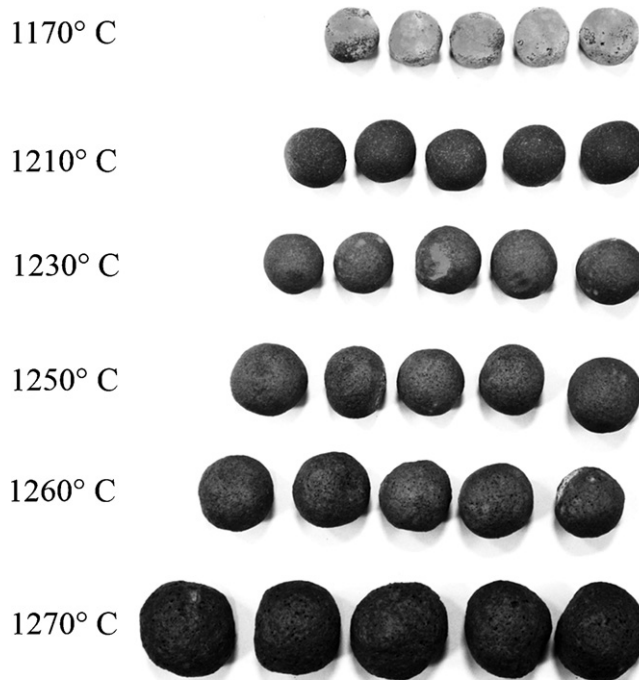


Fig. 7. Volume expansion of aggregates made from clay mass with 37.5% NMP and sintered in the different temperatures.

The density of aggregates was measured in accordance with EN 1097-7. Measurements of LECA water absorption were carried out according to EN 1097-6.

The microstructure of sintered LECA was studied by using the high-pressure mercury porosimeter Pore Master 33 Quantachrome and optical microscope Leica M 420. The samples for mercury porosimetry and optical microscopy were prepared as cylindrical specimens of 4 mm diameter and 10 mm height.

3. Results and discussion

3.1. Particle volume expansion and particle density

Particle density is one of the traits of expanded clay aggregates (LECA), which is also referred as an apparent density; it is the relation between the mass and the total volume of the single aggregate, pores included. The apparent density of LECA depends on the type of raw material manufacturing process, which is normally at $\frac{1}{2}$ to $\frac{1}{4}$ of the density of non-sintered aggregates.^{23,24}

As it has been explained earlier in this text, the particle density plays an important role in the designing of concrete

structure and thermal isolation properties of building members. The evaluation of aggregate expansion resulting from the increase in the sintering temperature was determined by measuring the single aggregate density and volume. Density of LECA noticeably depends on the two factors: amount of added NMP and sintering temperature. Density of non-sintered aggregates is 1.85 g/cm^3 on the average, but it can be decreased to 0.45 g/cm^3 through modification of the composition and production temperature.

The optimal sintering temperature, at which maximum expansion of LECA takes place, increases with the increased amount of NMP added to the clay mass. The maximum expansion of aggregates sintered at the optimal temperature reaches approximately 4 times compared to non-sintered units (Figs. 7 and 8).

LECA has a distinct difference between the glassy outer shell and the porous interior.^{23,24} It means that the outer shell exerts notable influence on the absorption capacity of aggregates, because homogenous outer glassy film makes particles impervious to water.²⁴

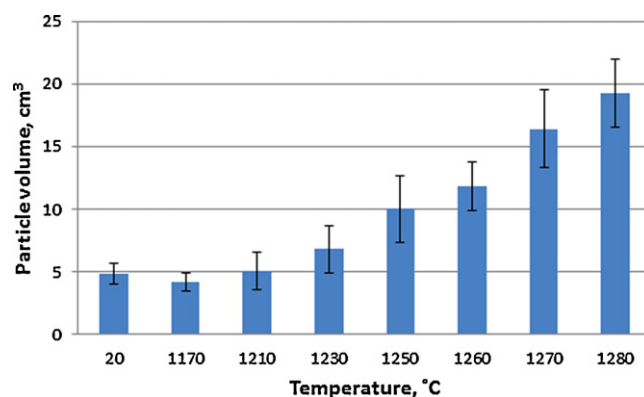


Fig. 8. Volume expansion of aggregates made from clay mass with 37.5% NMP and sintered in the different temperatures.

3.2. Water absorption

Water absorption increases along with the increase in the sintering temperature of LECA due to increase of the volume

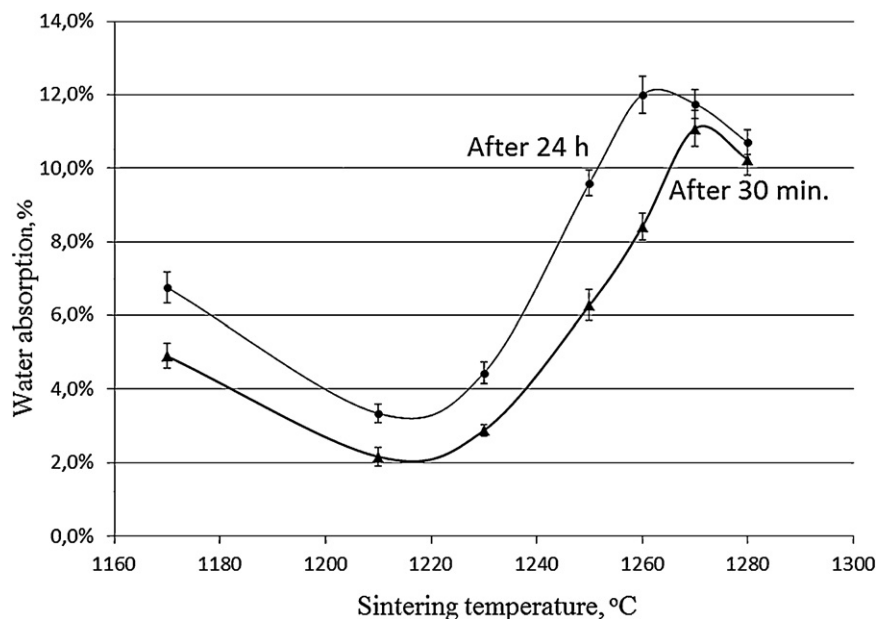


Fig. 9. Water absorption of ECA made from clay mass with 37.5% of NMP and sintered at different temperatures.

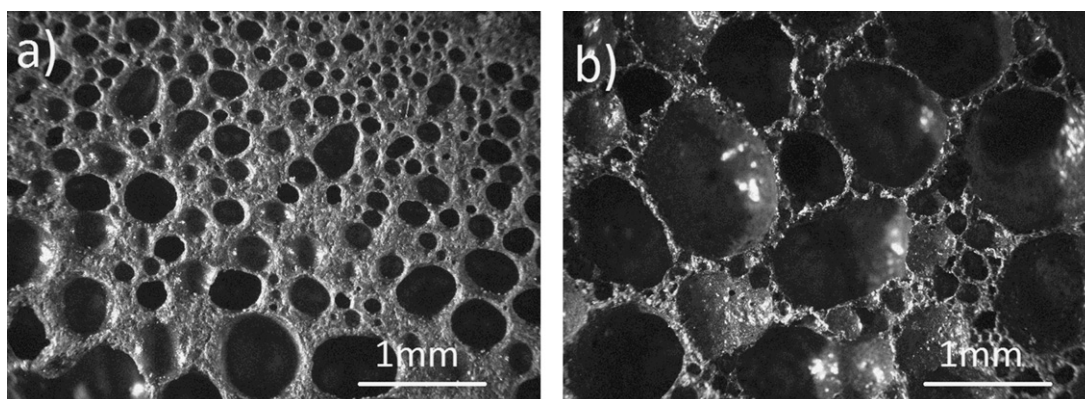


Fig. 10. The pore structure of the expanded clay aggregates sintered at the temperature 1160°C : (a) made of pure clay and (b) made of clay by adding NMP.

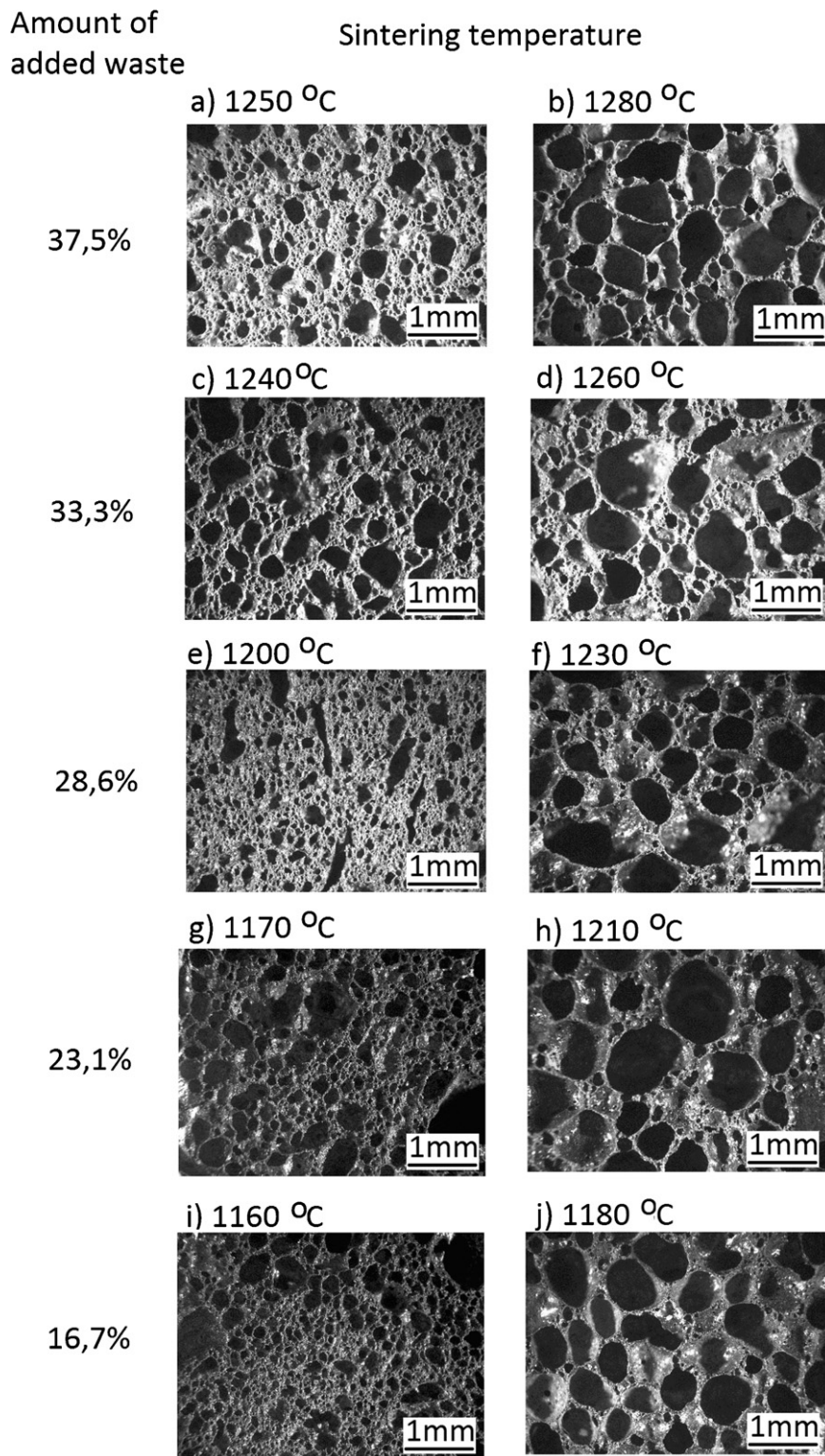


Fig. 11. Pore structure of LECA produced by adding different amount of NMP and sintered at different temperatures.

and porosity of aggregates. The maximum water absorption (after 30 min. immersion in water) of LECA sintered at the optimal expansion temperature reaches 10–12% on the average. Water absorption of LECA was increased by 2–3% when immersion in water was prolonged to 24 h (Fig. 9). The highest water absorption after 30 min (11%) was measured on LECA

produced from clay mass with addition of 37.5% NMP and sintered at the temperature of 1270 °C. The water absorption of these aggregates slightly reduced (10.5%) when sintering temperature was increased to 1280 °C. This probably can be explained by the sintering temperature when melting of LECA begins.

Water absorption of LECA depends not only from the open porosity but also from the outer layer of aggregates. The interfacial zone between lightweight aggregate with a weaker and more porous outer layer and cement paste is more dense and homogeneous. In addition, bonds between the aggregates and cement paste appear stronger due to an improved mechanical interlocking between the aggregate and the cement paste. The cement paste can penetrate in the open pores of outer layer of the aggregate during mixing of lightweight aggregate concrete. It depends on the microstructure of the surface layer of the aggregate, the particle size distribution of the cement and the viscosity of the paste.

There are also some disadvantages of increased open porosity of aggregates. The change of workability of lightweight concrete after mixing indicated a movement of water into pore structure of aggregates. It is affected additionally by the water requirement of the cement paste, i.e., its water–cement ratio.

3.3. Microstructure of LECA

Microstructures of the lightweight aggregates produced at different temperatures were examined with the help of an optical microscope. The pore structures of LECA are illustrated in Figs. 10 and 11. It is clear that the amount of NMP added and the sintering temperature significantly affects the pore structure of LECA.

Two types of the pores were observed during microstructural studies of LECA. Pores of the first type, which may be called macropores, have the diameter larger than 1 mm and they are incorporated through smaller pores. The macropores have rounded morphology and they are mainly closed. They are typical for the aggregates sintered at the maximum expansion temperature, which depends on the amount of NMP added (Fig. 10). These pores are typical also for the aggregates made from pure clay and sintered at the maximum expansion temperature (1160 °C), where decomposition process of carbonates is completed (Fig. 11).

The second type of pores (micropores) is smaller than 1 mm. Pore size distribution of LECA was detected by Hg-porosimeter Pore Master 33 Quanta-chrome (Figs. 12 and 13). The main reason for appearance of incorporated small size (<0.2 µm) pores in the structure of LECA can be explained by decomposition of NMP minerals (FeSO_3 , $\text{Al}(\text{OH})_3$) during sintering process of aggregates (Fig. 12b). Micropores were not observed in the microstructure of the aggregates made from pure clay and sintered at the maximum expansion temperature (1160 °C). Micropores also were not typical for the LECA, which are not sintered at the maximum expansion temperature. In that case, pore structure of LECA is not completely developed and the pores, which become larger than 1 mm at the maximum expansion temperature, still range from 10 to 1000 µm (Figs. 12a and 13a).

Finally, it was discovered that properties of lightweight expanded clay aggregates (LECA) depend from the amount of NMP added to the composition and from the sintering temperature of green aggregates. Test results show that enlarged amount of NMP in the composition may influence the pore struc-

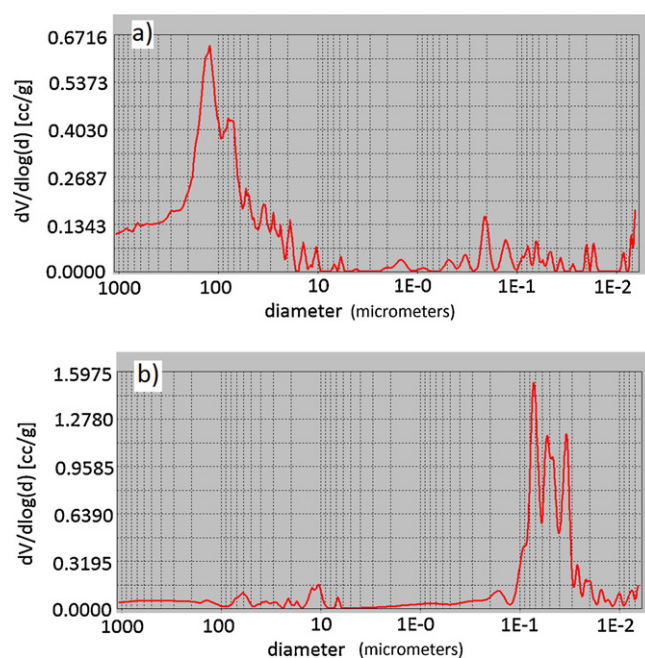


Fig. 12. Pore size distribution of lightweight expanded clay aggregates (LECA) made of clay by adding 16.7% of NMP: (a) sintered at the temperature 1160 °C and (b) sintered at the temperatures 1180 °C, which is maximum expansion temperature of aggregates.

ture of LECA sintered in the same temperature and promote possibilities to produce lightweight aggregates with different physical and mechanical properties. Since the clay is a locally available material, production of LECA has good prospects in the countries where natural lightweight aggregate sources are unavailable. However, the relationship between the microstruc-

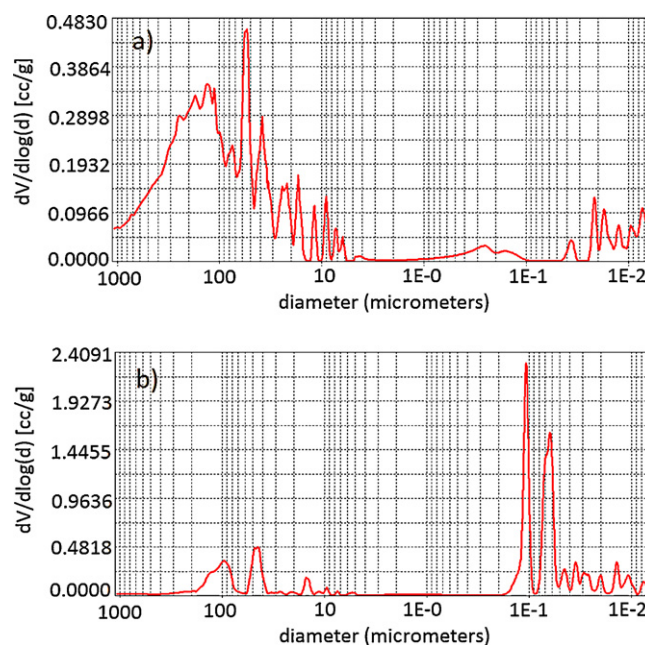


Fig. 13. Pore size distribution of lightweight expanded clay aggregates (LECA) made of clay by adding 37.5% of NMP: (a) sintered at the temperature 1250 °C and (b) sintered at the temperatures 1280 °C, which is maximum expansion temperature of aggregates.

ture and mechanical properties should be studied further in the next series of research.

As negative aspect must be noted that harmful gases can emit during sintering process in the industrial production of NMP-containing aggregates and therefore it is necessary to install a gas cleaning system for treating exhaust gases from the sintering furnaces.

4. Conclusions

Lightweight expanded clay aggregates with different properties and structure can be produced from local clay and hazardous solid waste from aluminium scrap recycling factories.

Expansion degree, density and pore structure of LECA depend on the composition and sintering temperature. This phenomenon should be used for modification of the relationships between physical and mechanical properties according to the actual needs.

The maximum expansion temperature of LECA increases resulting from enlargement of the NMP proportion in the clay composition, i.e., every composition has its own maximum expansion temperature.

Apparent density of LECA sintered at the maximum expansion temperature is between 0.4 and 0.6 g/cm³ irrespective of the composition.

The water absorption values of LECA sintered at the maximum expansion temperature increased along with the increase in the proportion of NMP in clay composition.

Considerable changes were observed in the pore structure of LECA sintered at the maximum expansion temperature and lower temperatures; fully developed pore structure, which is typical for LECA sintered in the maximum expansion temperature, consists from macropores with mean diameter 1 mm and micropores with diameter smaller than 0.2 µm. Macropores are incorporated through micropores.

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Glossary

NMP: non-metallic products

LECA: lightweight expanded clay aggregate

ICP-OES: inductive coupled plasma optical spectrometry

AAS: atomic absorption spectroscopy

XRD: X-ray diffraction