Analysis of the Properties of Lightweight Concrete with the Technogenic Waste Material

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During the production of higher density lightweight concretes filler aggregates can be used instead of the part of the binding material. One type of filler aggregates is active filler aggregates that change the course of the reactions of hydration. The technogenic waste material – catalyst utilised in the reactor of catalytic cracking can be used as filler aggregate. Lightweight concrete (expanded – clay lightweight concrete), with the filler aggregates – technogenic waste materials is analysed in the research. During the analysis, the influence of the filler aggregate on the properties of concrete mixture was identified, thermographic analysis of exothermic effect was carried out, strength, structural properties were analysed, X-ray structural analysis was carried out. Additionally, the analysis of crush resistance of the coarse aggregate is carried out and described during the research. Article covers the information on the changes of the investigated properties in relation to the amount of the filler aggregates.

Keywords: lightweight concrete, expanded-clay aggregate, waste catalyst, structural parameters, exothermic effect, filler aggregate.

1. INTRODUCTION

Liquid residue of the catalyst of catalytic cracking (FC3R) is a waste material produced in the liquid unit of the catalytic cracking (FCC) of the oil refinement furnace (refinery). The scientific investigations had shown high FC3R pozzolanic activity not only in the lime putty [1], but also in the cement paste [2]. Scientists, who further developed similar investigations [3, 4] with various FCC catalyst samples, in all cases have found high pozzolanic activity in FCC waste material.

Paya in his research works [5] has described high FC3R reactivity in the cement paste, when pozzolana material is ground theretofore. Others [6] have analysed the pozzolanic activity of the used catalyst by using thermal and spectroscopic method. They have proved that catalyst is able to react with calcium hydroxide similarly as silica.

After the repeated usage of catalyst waste material it was found [7] that this additive could replace 15 % - 20 % of the amount of binding material or 10 % fine-grained aggregates without worsening the qualitative properties of the grout.

Scientists [8] who investigated the construction mixtures and grouts, have found that mixture, with water/cement ratio of 0.25 and with 15 % of catalyst waste material, reached the maximal compressive strength of 92.3 MPa.

Considering a special chemical composition and good thermal characteristics, this catalyst can be used for the production of fire resistant [9] and ceramic products [10], or as an aggregate in the production of asphalt concrete or as a pozzolanic component for Portland cement [11].

The fine-grained catalyst waste material can be assigned to the group of filler aggregates, and, according to its influence during the cement hydration process, to the active filler aggregates. In references [12] it is noted that active filler aggregates can be produced from the natural rocks, industrial waste materials. The amount of active SiO_2 in these filler aggregates should not exceed 50 % and should be not less than 5 % (mass). Researchers [9, 13] indicate that this utilised catalyst actively participates in the cement hydration process, puts forward the beginning of the binding, influences the formation of the crystallohydrates of aluminate cement.

In the scientific literature it was not possible to find the results of the comparable analysis proving that the properties of lightweight concrete are improved or not improved when this waste material is used.

Lithuanian oil refinery company "Orlen Lietuva" utilises more than 40 types of various catalysts. Two types of catalyst waste materials are produced during the processing: coarse-grained and fine-grained. During late years the scientists carry out widely the research on the secondary usage of catalyst waste materials. Main components of the catalyst waste materials are SiO₂ and Al₂O₃.

These aluminium silicate technogenic waste materials can be utilised for the production of construction materials as well as, and scientific works are carried out in this direction.

In this research the possibility to utilise the catalyst waste materials in the lightweight concretes is analysed. The main task of this research is to analyse the catalyst waste material and estimate the possible influence on the properties of lightweight concrete.

2. RESEARCH MATERIALS AND METHODS

During the research the following waste materials were used for the production of lightweight concrete (expanded – clay lightweight concrete):

Cement: composite Portland cement CEM II/A-L 42.5 N, satisfying the requirements of the standard LST EN 197-1 "Cement – Part 1: Composition, specifications and conformity criteria for common cements".

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Concrete marking	Composition							
	Cement, kg/m³	Expanded-clay aggregate, kg/m ³		Sand,	Water,	Waste catalyst,	V/C	V/K
		0 mm - 4 mm	4 mm - 10 mm	kg/m³	l/m³	kg/m³	v/C	v/K
А	418	396.5	_	822.8	215.8	_	0.52	0.13
В	355.3	158.6	237.9	822.8	215.8	62.7	0.61	0.13
С	292.6	396.5	_	822.8	215.8	125.4	0.74	0.13

Fine aggregate: natural sand, with the maximal grain size smaller than 5 mm.

Coarse lightweight aggregate: sand of expanded clay with the grain size of 0 mm-4 mm and expanded clay gravel with the grain size of 4 mm-10 mm. The characteristics of coarse aggregate are provided in Table 2.

 Table 2. Characteristics of the expanded clay sand and expanded clay gravel

Fraction of the	Properties			
expanded clay	Bulk density, kg/m³	Particle density, kg/m ³	Bulk porosity, %	
0 mm - 4 mm	543	1520	63.80	
4 mm - 10 mm	428	1480	71.47	

Filler aggregate: catalyst waste material from the reactor of catalytic cracking. Chemical composition of the ungrounded catalyst waste material is provided in Table 3. Silica and aluminium oxide dominate in the filler aggregate, and the amount of titanium, lanthanum, ferric and phosphorus oxides varies respectively from 1.48 % to 0.11 %. The remains of the following materials exist as well: CaO, MgO, K₂O and Na₂O. Catalyst waste particle size are provided in Figure 1. The particle size distribution was measurements with Cilas 1090 dry analyzer.

 Table 3. Chemical composition of the catalyst waste material





Fig. 1. Catalyst particle size distribution

In Figure 1 the particle size of the catalyst waste varies from $0.2 \ \mu m$ to $112 \ \mu m$. Catalyst particles are spherical.

3 concrete mixtures, marked as A, B, C, were prepared during the research. Compositions of concrete mixtures A,

B and C are provided in Table 1. Additionally, used catalyst from the reactor of catalytic cracking was added to the concrete mixtures: 15 % to concrete mixture B, and 30 % to C (comparing to the amount of cement).

For the concrete mixtures A, B and C the lightweight coarse aggregate - expanded clay was used. The following was used during the preparation of concrete B: 0 mm - 4 mmfraction expanded clay sand and 4 mm - 10 mmfraction expanded clay gravel. 0 mm-4 mm fraction expanded clay sand was used to prepare concrete mixtures A and C. Content selection of the expanded clay - lightweight concrete A, B and C was carried out by implementing calculation-experiment method, in accordance with the methodology described in the references [14]. The class of the compressive strength of concrete A, B and C is LC16/18.

All concrete mixtures were prepared manually at the laboratory. The prepared concrete mixture of the required consistence was poured into the lubricated moulds. The samples were compacted by vibrating on the laboratory vibrating platform for 1 min. Then samples were taken out from the moulds and immediately soaked into the water of $20 \,^{\circ}\text{C} \pm 2 \,^{\circ}\text{C}$ temperature, as it is specified in LST EN 12390-2 "Testing hardened concrete - Part 2: Making and curing specimens for strength tests". These samples were stored in water until the estimation tests of the mechanical properties. 20 samples (100×100×100 mm) were selected from three concrete batches prepared at laboratory conditions for the estimation of compressive strength and other physical characteristics. The compressive strength of the expanded clay - lightweight concrete was estimated after 2, 14 and 28 days of hardening. The main physical and mechanical characteristics of the samples were estimated through the standard methods: density of the samples according to LST EN 12390-7 "Testing hardened concrete - Part 7: Density of hardened concrete", compressive strength according to LST EN 12390-3 "Testing hardened concrete - Part 3: Compressive strength of test specimens".

Crush resistance of the grains of expanded clay in dry and impregnated status is estimated according to LST EN 13055-1 "Lightweight aggregates – Part 1: Lightweight aggregates for concrete, mortar and grout".

Thermographic analysis of exothermic effect was implemented on all concrete mixtures as well. Temperature variations during binding and hardening of the concrete were estimated according to the methodology created by company "Alcoa" [15]. During the testing, exothermic effect is identified in three different samples: in first expanded clay – lightweight concrete A, where only



Fig. 2. The temperatures of the exothermic effect of the expanded-clay lightweight concrete during the hardening: A – expanded-clay lightweight concrete without the waste material, when water/concrete ratio is 0.52; B – expanded-clay lightweight concrete with 15 % of waste material, water/cement ratio is 0.61 and C – expanded-clay lightweight concrete with 30 % of waste material, water/cement ratio is 0.74

cement is included, in second expanded clay – lightweight concrete B, where 15 % of used catalyst waste material is included, and third expanded clay – lightweight concrete C, where 30 % of used catalyst waste material is included.

According to the results of water absorption the following parameters were calculated: effective porosity $(W_{\rm E}, \%)$, total open porosity $(W_{\rm R}, \%)$, reserve of pore volume (R, %), degree of structural in homogeneity (N), and water absorption by capillaries under normal conditions $(g, g/{\rm cm}^2)$ after 30 minutes [16].

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

Initially, crush resistance of 0 mm - 10 mm fraction grains of expanded clay was estimated during the research. The results of crush resistance of dry and soaked expanded clay are provided in Table 4. Results show that crush resistance of the expanded clay soaked for 2 days has decreased by 67 % comparing to the dry expanded clay. This result is typical for the ceramics. Crush resistance of the expanded clay soaked for 14 days is lower only by 12.65 %. After 28 days, crush resistance increased almost by 63 % comparing to the crush resistance of dry expanded clay grains. It can be assumed that the carbonization processes are taking place in the expanded clay [17].

Table 4. Crush resistance of expanded-clay

Fraction of the expanded	Crush resistance, MPa					
	Dry	Soaked in water after				
ciay, iiiii	Diy	2 days	14 days	28 days		
0-10	6.56	2.16	5.73	10.67		

During research the mean values of physical and mechanical properties of the samples were calculated. Mean densities and compressive strengths of the samples produced from the mixtures A, B and C are provided in Figures 3 and 4.

The obtained data show (Figure 3) that the density of the lightweight concrete samples produced from the mixture B is highest, and C – lowest.

Compressive strength values of the concrete samples produced from the mixture C are lowest, and A – highest.

However, the maximal compressive strength after 28 days of hardening was achieved in concrete samples B (Figure 3). Class requirements after 28 days of hardening are satisfied by the concrete samples produced from the mixtures A and B.



Fig. 3. Average density values of the concrete produced from the mixtures A, B and C



Fig. 4. Average compressive strength values of the concrete produced from the mixtures A, B and C after 2, 14 and 28 days of the hardening

During the thermographic analysis of the exothermic effect the influence of the catalyst waste material on the thermal properties of the mixture during the hydration of the binding material. Figure 1 shows that the heat dissipation in the mixture A starts after 106 minutes and reaches the maximal temperature of 27 °C after 1179 minutes. In mixtures B and C heat dissipation process starts a lot earlier, after 34 and 75 minutes respectively. The maximal exothermic temperature of 27.5 °C in mixture B is reached exactly after 880 minutes. The mixture of expanded clay – lightweight concrete C, where 30 % of

Table 5. Average structural parameters values of the concrete

Concrete marking	Degree of structural inhomogeneity, N	Capillary rate of mass flow g , g/cm^2	Effective porosity $W_{\rm E}$, %	Total open porosity $W_{\rm R}$, %	Reserve of pore volume <i>R</i> , %
А	1.08	0.63	29.52	30.25	2.41
С	0.57	0.91	16.69	27.67	39.66

used catalyst waste material is included, reached the maximal exothermic temperature of 24.7 °C after 891 minutes. The results of analysis showed that the larger additive quantity the shorter inductive hydration period of Portland cement is and the earlier maximal exothermic temperature is reached. However, when the amount of catalyst waste material is increased, the maximal temperature of hydration process decreases. It is obvious that the kinetics of these processes determines physical, mechanical and structural properties of the composite concrete and their characteristics' values as well.

X-ray diffraction examination was implemented on the samples of all batches. Considering the data of X-ray diffraction pattern provided in Figure 5, it was identified that the main minerals of the lightweight concrete produced from the mixture A are ettringite, dolomite, silica, calcite, portlandite, sunstone and cement minerals.



Fig. 5. X-ray diffraction patterns of the concrete sample produced from the mixture A

Considering the data of the X-ray pattern shown in Figure 6, it was identified that the main minerals of the samples of the lightweight concrete, where 15 % catalyst waste materials (B) were utilised, are illite, silica, calcite, portlandite, sunstone and cement minerals.



Fig. 6. X-ray diffraction patterns of the concrete sample produced from the mixture B

In Figure 7 the X-ray diffraction pattern of the samples of lightweight concrete produced form the formation mass C is shown. It was found that the main minerals of the lightweight concrete produced form the

mixture C are ettringite, dolomite, silica, calcite, portlandite, sunstone and cement minerals.

As scientists [18] state, the influence of hydrated cement minerals (for example ettringite), growing in the cracks, can be identified through the compressive strength of the concrete. In the course of time the strength can decrease due to the influence of these minerals.

Since X-ray diffraction examinations were implemented on the samples stored for 28 days in water, exactly due to the creation of ettringite in compositions A and C, comparing to the composition B, where no ettringite exist, it is possible to explain, the absolutely largest mean value of compressive strength of samples B after 28 days.



Fig. 7. X-ray diffraction patterns of the concrete sample produced from the mixture C

Theoretically, according to the scientist [19] a simple model of the porous body can be represented as a system consisting of small radius and identical, in the respect of the size, spherical particles and pores between them. In case of cubic packing, its porosity is 47.64 %, and for the limiting hexagonal packing -25.95 %. In this case rhombohedral pores form 18.58 %, and tetrahedral -7.37 %. The structure of pore volume is characterized by smoothness, anisotropy and heterogeneousness.

Estimated values of the structural parameters for the concrete samples, produced from the mixtures A and C, are provided in Table 5. By considering the parameters of the capillary rate of mass flow it is possible to predict that the conditional diameter of the effective pores and capillaries shall be bigger for the samples C. Degree of structural in homogeneity in samples A is almost two times larger comparing to samples C. Mean values of open porosity parameter are similar, but the effective porosity of composite A is significantly larger than the one of C.

Additionally, by considering the data of the references and by using the value of reserve of pore volume [10] it is possible to predict that samples C would have higher volumetric and actual frost resistance, and samples A would have lower volumetric and actual frost resistance. These investigations point out the essential differences of the structure of various samples. However, more accurate results would have to be obtained during further research.

CONCLUSIONS

During the investigations it was identified that the used catalyst in the mixture of lightweight concrete behaves as an active filler aggregate and changes considerably the course of hydration processes. Due to this the mineralogical structure composition and physical, mechanical as well as structural characteristics of the hardened concrete change.

After the investigations it was estimated the density of samples of the expanded – clay lightweight concrete, where 15 % of catalyst waste material from the reactor of catalytic cracking is added, has increased by 4.72 %, and compressive strength has increased by 4.17 %. This increase of the density and mechanical characteristics could be caused by the fact that ettringite was not created in the mixture.

Results of the investigations showed that the larger additive quantity, the shorter inductive hydration period of Portland cement and the earlier maximal exothermic temperature is reached.

It can be preliminary predicted that actual frost resistance should be larger for those samples, for which production the mixture with 30 % additive of catalyst waste materials (C) was used, comparing to the reference sample (A).

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