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Application of Catalyst Waste to Ceramics Made of Raw Materials

Olga KIZINIEVIČ[1*], Ramunė ŽURAUSKIENĖ[1], Algis ŠPOKAUSKAS[2], Romualdas MAČIULAITIS[1]

[1]*Department of Building Materials, Vilnius Gediminas Technical University, Saulėtekio 11, LT-102223 Vilnius, Lithuania*
[2]*Vilnius Gediminas Technical University, Thermal Insulation Institute, Linkmenų 28, LT-08217 Vilnius, Lithuania*

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Investigation of ceramic products is presented in the article. The catalyst waste from catalyst cracking reactor of "Mažeikių Nafta" may be utilised in building ceramics. The work contains description of catalyst characteristics and also presents physical mechanical properties of samples from fusible hydro clays, sand, crushed bricks and foaming mass that 5 %, 10 % and 20 % of catalyst waste. It was determined that the catalyst waste may be utilised in the building ceramics production, but the fragment burning temperature must be increased.
Keywords: oil waste, utilization of waste, catalyst waste, building ceramic, water absorption.

1. INTRODUCTION

Oil refinery is an important and strategic branch of industry. The oil refineries alone satisfy 42 % of EU energy needs and produce 95 % of fuel necessary for transport, yet processing huge amounts of crude oil the by-products – raw materials appear, that form during manufacture of the main production. These raw materials are ranked as a factor increasing emission of environmental pollution [1]. Currently oil refineries mostly produce mud and the used chemical materials: catalysts, acids, amines, etc.

According to the waste record data around 130 thousands tons of dangerous waste pile in Lithuania per year. A very important group of dangerous waste is the waste containing heavy metals [2]. The biggest part of the dangerous waste in Lithuania – approximately a half – forms in the oil refineries. For example Lithuanian oil refinery company AB "Mažeikių Nafta" uses more than 40 catalysts of different types. Plenty of these wastes having a possibility to be used as the secondary raw materials go to dumps; their quantities continually increase and occupy big areas enhancing the danger of secondary nature pollution.

Special attention has been recently devoted to the process of waste minimization, pollution prevention and self – sustainable development as applied to the materials field [3 – 5].

The used catalyst from catalyst cracking reactor of AB "Mažeikių Nafta" is used in the production of heat resistant concrete and is widely analysed in the works of Lithuanian researchers [2, 6 – 9]. Investigations on oil refinery catalyst wastes and their application possibilities in construction industry in the similar direction are also performed in other countries [10, 11].

The oil refinery wastes in Europe are used in production of cement clinker and asphalt concrete. It is determined, that catalyst waste may be utilised in building ceramics, however applying these materials to formation mix the burning parameters are affected; the materials in catalyst increase the burning temperature of ceramic body [12].

The authors [13, 14] state, that mixes of clay and oil refinery waste may be used in the manufacture of the main ceramic products (façade bricks, blocks, tiles), however the densification of products and the processes taking part during sintering were not fully analysed in these works.

In the work of researchers [15] the properties of products are analysed changing the quantity of oil waste from 5 % to 20 % and the highest burning temperature from 750 °C to 1150 °C, also the important morphological changes in ceramic bodies during burning are defined. It is determined that the most optimal amount of waste – 5 %, the subsequent increase in quantity influences the compressive strength of products negatively.

Aim of this work – to perform the analysis of catalyst waste (the used catalyst from AB "Mažeikių Nafta" catalyst cracking reactor), to evaluate the catalysts influence on physical-mechanical, structural properties and sintering of ceramic body and to determine the optimal burning temperature.

2. INVESTIGATION METHODOLOGY, RAW MATERIALS

Chemical compositions of the main raw material were determined by the classical methods of chemical analysis for silicate material (GOST 12642.08-81, GOST 2692.12-81, GOST 21216.1-81 and GOST 21216.4-81).

Density of burned ceramic samples was determined according to LST 1272-92 "Ceramics bricks. Specifications and other overall methods". Compressive strength was determined according to LST EN 772-1:2003.

Phase analysis of burned samples was carried out by X-ray diffraction. The diffraction meter DRON-2 (Russia) with Cu anti-cathode and Ni filter / Fe anti-cathode and Mn filter was used when $U = 30$ kV, $I_A = 8$ mA and rotation speed of the sample was $1° \text{ min}^{-1}$. X-ray diffraction patterns were registered on paper and decoded comparing with the data of PDC catalogues [16].

*Corresponding author. Tel.: + 370-5-2745219; fax.: + 370-5-2745219.
E-mail address: *okizinievic@hotmail.com* (O. Kizinievič)

The fusible hydro-micaceous clay was selected for investigation (clay A). Granulometric composition of this clay was in following: amount of sand particles > 0.05 mm is from 0.09 % to 0.77 % amount of dust particles (0.05 - 0.005) mm is from 9.26 % to 21.39 %, and amount of clay particles < 0,005 mm fluctuates from 72.11 % to 96.04 %.

And the fusible devonian clay – B (Lithuania) was selected for the research [Clay B]. According to the chemical composition the clay B is semiacid, because the quantity of Al_2O_3 in the heated clay is 15.8 %, the clay belongs to the group with a big amount of colorific oxides as 6.42 % Fe_2O_3, has low dispersion and coarse carbonaceous insert ≥ 3 %, has lot of sand fraction, the amount of free quartz ranges 30 – 60 %. Chemical compositions of the clays are presented in the Table 1.

Table 1. Chemical compositions of the clay

Chemical composition, %	Raw material	
	Clay A	Clay B
SiO_2	47.6	66.33
Al_2O_3+TiO_2	17.79	15.8
Fe_2O_3	7.66	6.42
CaO	6.27	1.8
MgO	3.59	2.72
MnO	0.09	-
K_2O	4.49	1.63
Na_2O	0.55	-
L.o.l.	11.55	5.3

Non-plastic materials used in the work were: crushed bricks, Daugeliai sand. Crushed bricks of encaustic samples were passed through 2.5 mm sieve. Granularity modulus of Daugėliai sand 0.9, amount of dust and clay particles 0.6 %, the grading of the Daugeliai sand present in Table 2.

Table 2. Grading of the Daugeliai sand

Fraction	Grading [mass, %]	
	Part	Full
2.5	0.02	0.02
1.25	0.044	0.064
0.63	1.89	1.954
0.315	21.13	23.08
0.14	41.76	64.84
< 0.14	35.16	100

According to the manufacturer data the catalyst C (GP – 534, Russia) is composite granule scentless material, composed of aluminium, molybdenum, nickel, phosphorus, zirconium, natrium and other rare earth element oxides. Bulk density of the catalyst C ranges from 0.80 g/cm^3 to 1 g/cm^3; diameter of granules 1.3-1.5 mm. This catalyst is assigned to the type of dangerous catalysts. By the data of AB "Mažeikių Nafta" the CaO appears in the catalyst after use, the colour changes to brown – reddish (Fig. 1). Chemical composition of unburned operated catalyst is presented in Table 3.

Fig. 1. Picture of the catalyst previously been in service

Table 3. Chemical compositions of the catalyst

Chemical composition, %	Catalyst
Al_2O_3	68.85 – 85.25
NiO	2 – 4
MoO_3	10 – 13
P_2O_5	2 – 6
ZnO_2	0.1 – 4
Na_2O	0.15
Rare earth element oxides	0.5 – 4

The X-ray diffraction analysis of catalyst was made burning it at the temperature of 1000 °C and 1100 °C. The X-ray diffraction pattern of the catalyst burned at 1000 °C temperature has shown (Fig. 2) that there is identified γ Al_2O_3 (B). Increasing the temperature to 1100 °C (Fig. 3), γ Al_2O_3 proceeds to α Al_2O_3 (corundum) and identified: cristobalite form $AlPO_4$ – Kr , spinel – Sp , powellite – C.

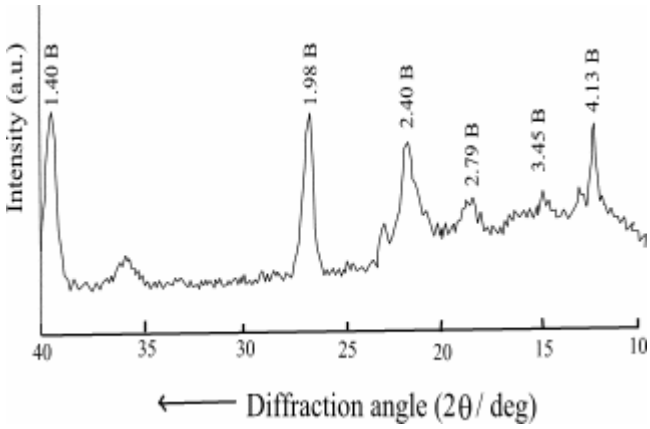

Fig. 2. X-ray diffraction pattern of the waste catalyst at burning temperature 1000 °C (notation index is presented in the text)

In order to determine the physical – mechanical properties, samples were made in a plastic formation way from the formation mixes presented in Table 4. The

additive of catalyst in the formation mix No.2 is applied non-milled.

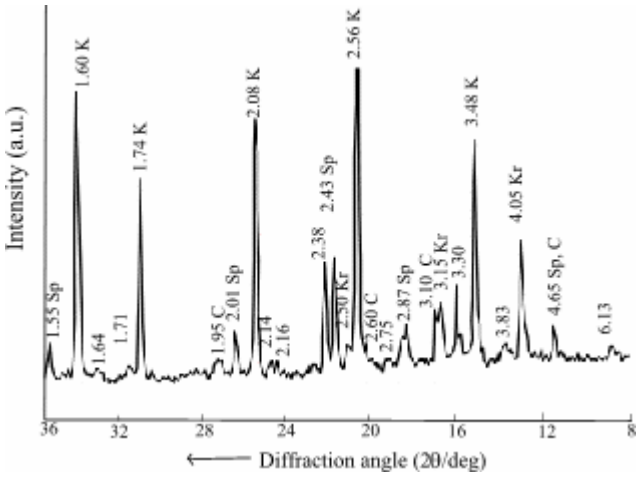

Fig. 3. X-ray diffraction pattern of the waste catalyst at burning temperature 1100 °C (notation index is presented in the text)

The laboratory samples were shaped into the dimensions $70 \times 70 \times 70$ mm. At first the prepared samples were dried in a laboratory under natural conditions, later they were left to dry for three days in the electric furnace under temperature from 100 °C to 110 °C.

Table 4. Composition of forming mixtures

No.	Formation mixtures compositions*, %
1	20 A; 60 B; 15 Ds; 5 Cb
2	80 A; 10 Ds; 5 Cb; 5 C
3	15 A; 65 B; 10 Ds; 10 C
4	10 A; 60 B; 5 Ds; 5 Cb; 20 C

* – see below; A – clay A; B – clay B; Ds – Daugeliai sand; Cb – crushed bricks; C – catalyst.

Dried samples were burned in the electric furnace with automatic regulator SNOL – 30/1300 (Lithuania) with accuracy of ±1 °C. The sample burning temperature was 1050 °C, 1100 °C, 1150 °C. The burning time was 40 h, and exposure to the highest burning temperature was 4 h.

Water absorption of samples after 72 hours and porosity were determined according to [17].

Reserve of pore volume (1) characterises the amount of reserve pores and capillaries, where water hardly penetrates. The larger the reserve of pore volume, the bigger usually is the frost resistance of ceramic body.

$$R = (1 - W_e / W_p) \cdot 100 , \quad (1)$$

where W_e is the effective porosity according to the water absorption after 72 h (%), W_p is the total open porosity according to the water absorption in the vacuum process (%).

3. EXPERIMENTAL RESULTS AND DISCUSSION

Dependence of density, compressive strength, soaking after 72 hours and reserve of pore space on the burning temperature are presented in Fig. 4 – 7 (where T1 – burning at 1050 °C temperature, T2 – burning at 1100 °C temperature, T3 – burning at 1150 °C temperature).

From the data presented in figures one can see that increasing the burning temperature of ceramic bodies to the highest, the densities of samples and compressive strengths increase, the water absorption decreases, i.e. the sintering processes intensifies, open effective and total porosity decrease.

Burning the ceramic body without the additive of catalyst already at the temperature of 1100 °C allows to obtain samples with the water absorption parameter less than 4 %, density exceeding 2000 kg/m^3. However the compressive strength of these samples is not sufficient (compressive strength is 19.88 MPa) as to be assigned as the sintered ceramic products. Analogous situation is while burning this body at the highest burning temperature (1150 °C).

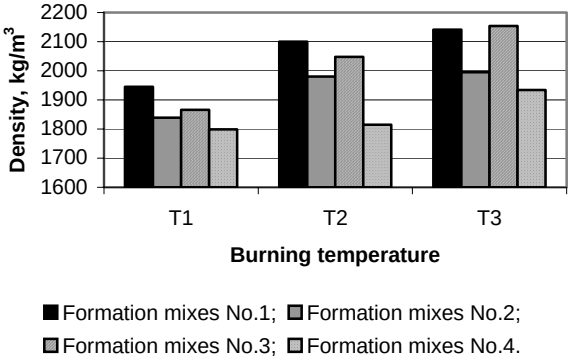

Fig. 4. Dependence of density on the burning temperature

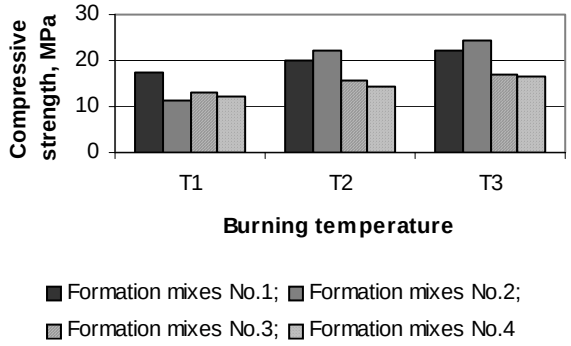

Fig. 5. Dependence of compressive strength on the burning temperature

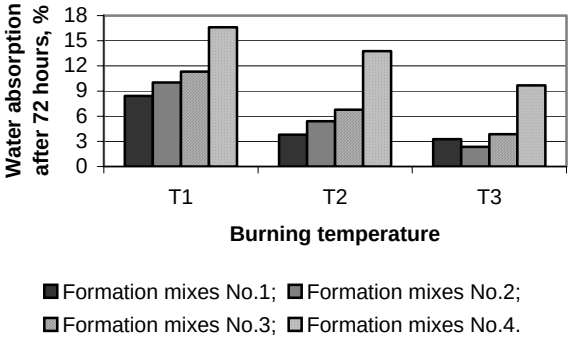

Fig. 6. Dependence of water absorption after 72 hours on the burning temperature

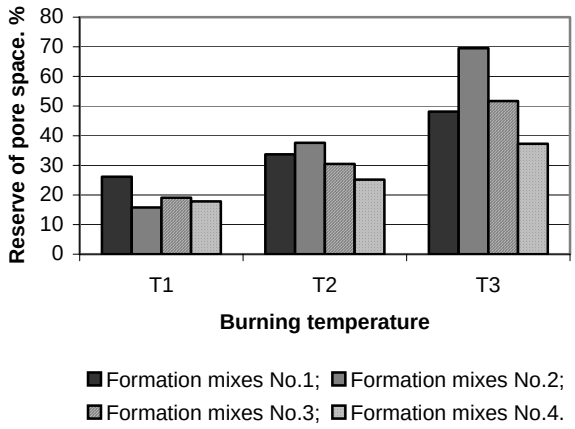

Fig. 7. Dependence of reserve of pore space the burning temperature

Applying milled catalyst additives in formation of mix and burning them at different burning temperatures allows to increase the water absorption, decrease compressive strengths and reserves of pore volume. Only the density and the reserve of pore volume of the ceramic body with 10 % of catalyst additive burned at the highest burning temperature are bigger than of the ceramic body without catalyst additive.

Water absorption of the ceramic body with 5 % of catalyst additive, burned at the highest burning temperature, is the smallest of the all investigated formation mixes, and the reserve of pore volume, indicating the potential increase in service frost resistance, is the biggest one, the compressive strength increases as well. This ceramic body after burning at the highest burning temperature is deep-brown, yet the catalyst does not fully fuse in it, only the catalyst surface slightly fused reacts with the other components of the mix (Fig. 8).

Fig. 8. Picture of the sample with non-milled catalyst after burning at 1150 °C temperature

It is seen that application of such catalyst waste to formation of mix influences the burning parameters. Materials existing in this catalyst waste increase the sintering temperature. This is justified by characteristics of ceramic bodies that show bigger water absorption comparing to the ceramic body without catalyst additive.

The X-ray diffraction patterns of sample of the ceramics body without of catalyst additive are presented in Fig. 9. The identified mineral are: quartz – Q (4.25, 3.35, 2.45, 2.28, 2.24, 2.13, 1.98, 1.82, 1.67, 1.54, 1.45, 1.38 Å), anorthite – A (4.04, 3.77, 3.21, 3.19 Å), hematite – He (3.71, 2.70, 2.52, 2.20, 1.84, 1.69, 1.48 Å), spinel – Sp (2.88, 2.03, 1.43 Å).

From the X-ray analysis of the ceramic body with 5 % of catalyst additive burned at 1100 °C temperature (Fig. 10) it is seen that the main minerals are: quartz, hematite, comparing to the ceramic body without of catalyst additive the amount of anorthite increases – A, the peaks of diopside – D and corundum – K appear.

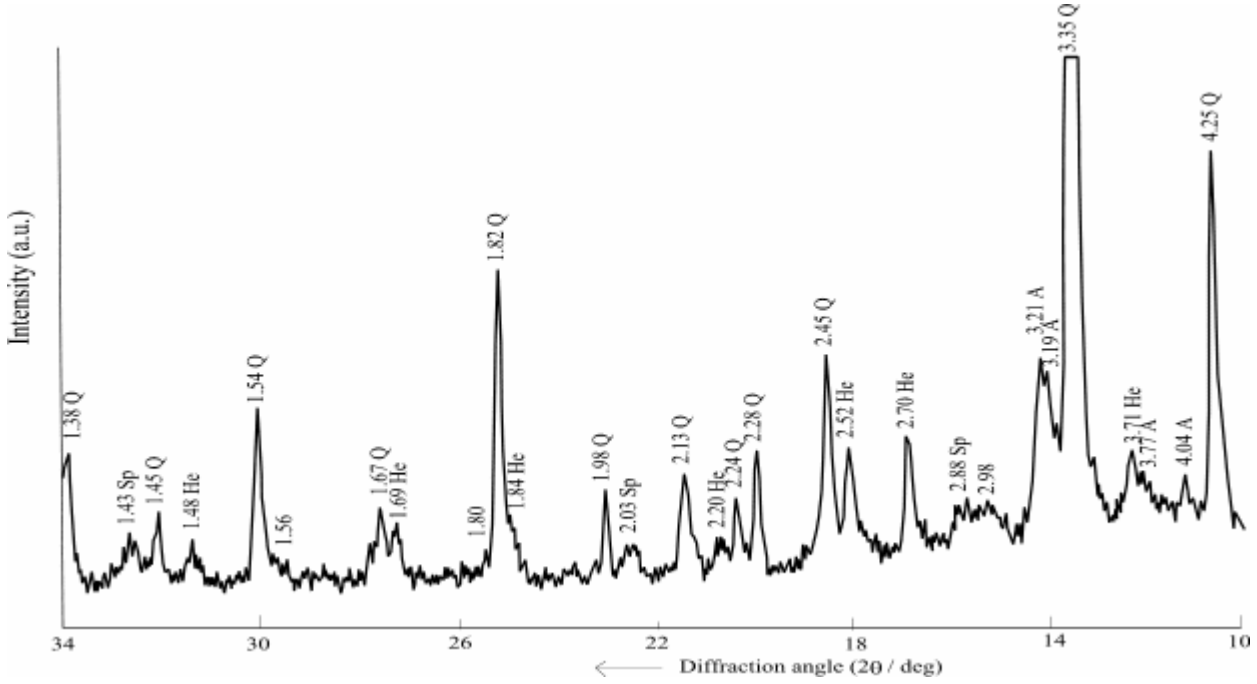

Fig. 9. X-ray diffraction pattern of samples of the ceramics body without of catalyst additives at burning temperature 1100 °C (notation index is presented in the text)

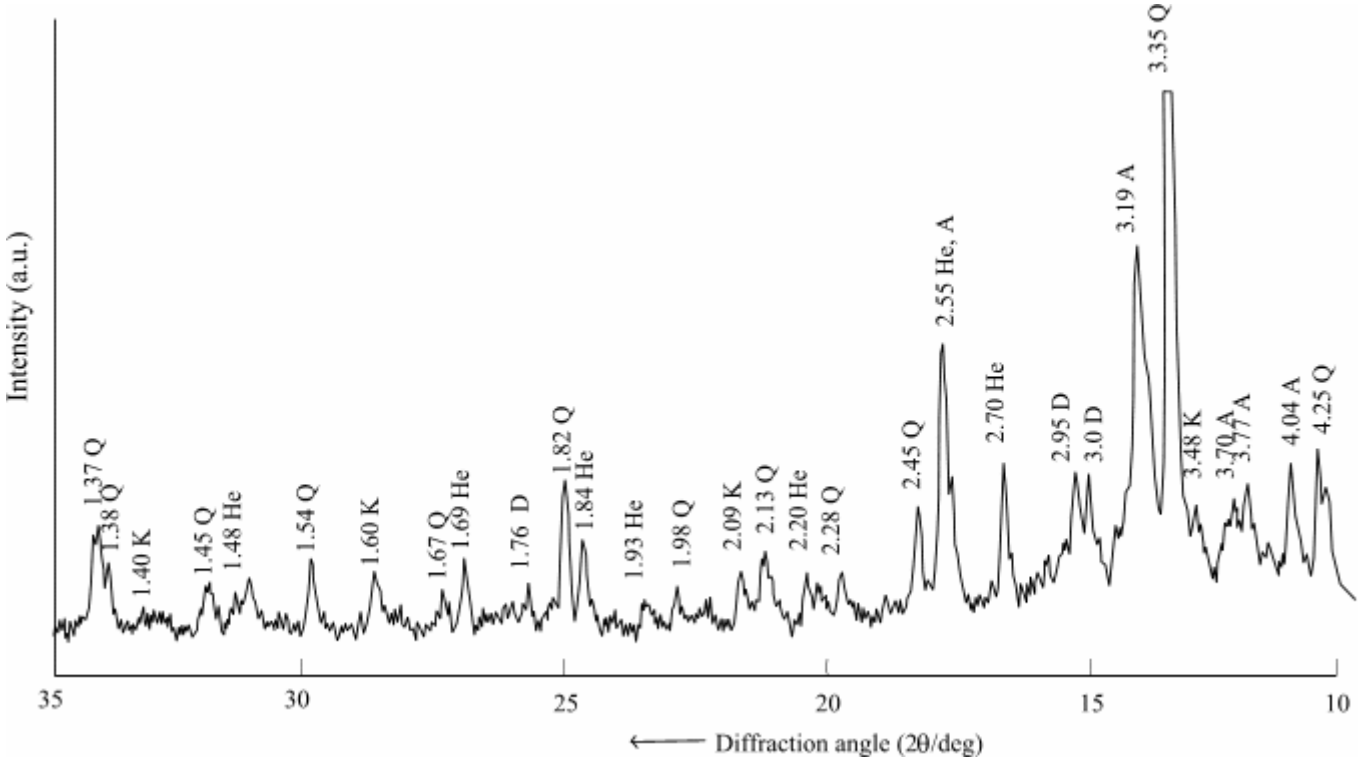

Fig. 10. X-ray diffraction pattern of examples of the ceramics body with 5 % of catalyst additives at burning temperature 1100 °C (notation index is presented in the text)

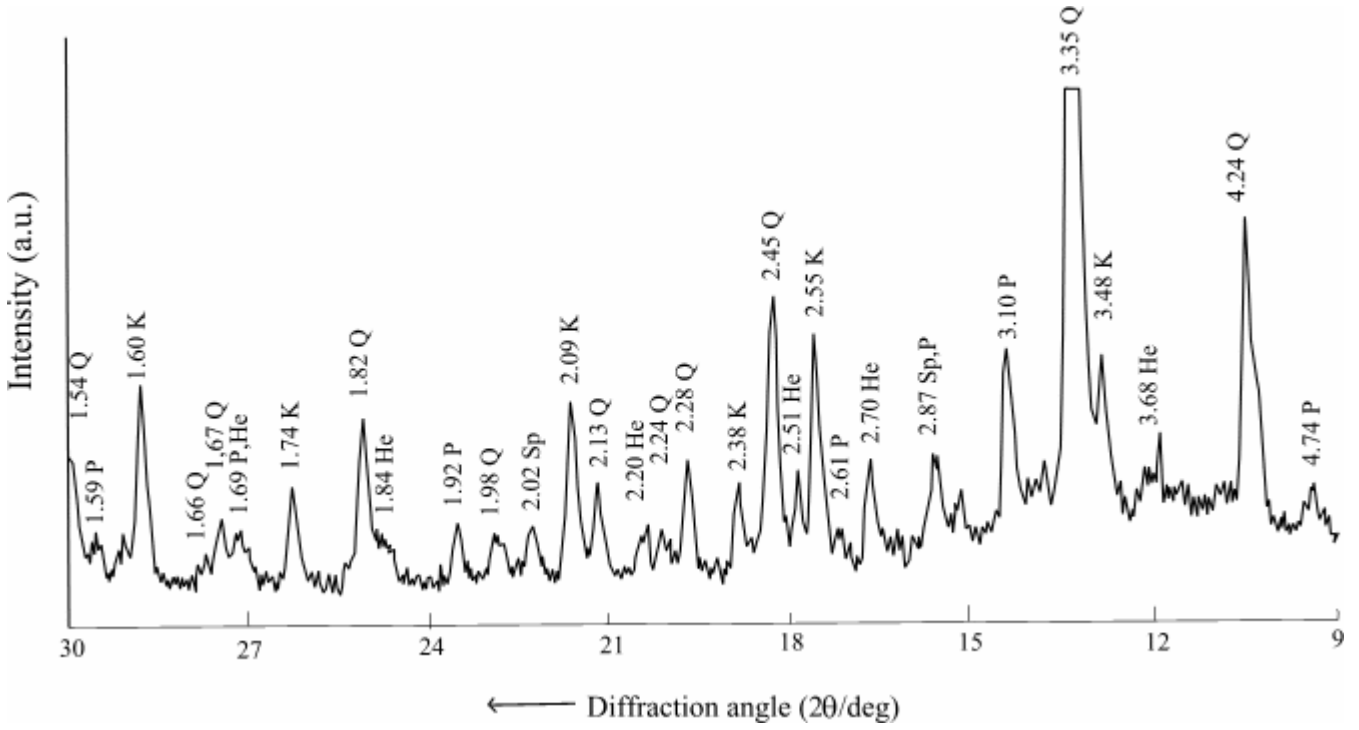

Fig. 11. X-ray diffraction pattern of examples of the ceramics body with 20 % of catalyst additives at burning temperature 1100 °C (notation index is presented in the text)

The X-ray diffraction analysis of the ceramic body with the maximum additive of milled catalyst – 20 % has shown (Fig. 11), that besides the main minerals – quartz, hematite and spinel, also powellite and corundum appears which peaks are more intensive than far the ceramic body with non-milled 5 % of catalyst additive powellite forms during reaction of calcium oxides existing in clay. Calcium oxides appear in the catalyst after use in catalyst cracking reactor and the molybdenum oxide in the catalyst. The X-ray diffraction patter of the ceramic body with 10 % of catalyst additives is similar to the one of the ceramic body with 20 % of catalyst additives sample, yet the intensities

of corundum and powellite peaks are smaller, this may be explained by the twice smaller amount of catalyst in the formation mix. The anorthite peaks in this ceramic body remain unchanged as well as in the ceramic body with 20 % of catalyst additives.

4. CONCLUSIONS

Catalyst waste may be utilised in the building ceramics production. It is used as an additive in the formation mix of A and B clays, sand and crushed bricks. Clay A is selected as having a large amount of CaO necessary for neutralisation of MoO_3 being in catalyst.

About 10 % of milled catalyst may be applied to the formation mix, the bigger (20 %) amount of catalyst in formation mix has negative influence on the physical-mechanical properties of ceramic body, even burning the ceramic body at the highest burning temperature.

According to X-ray diffraction analysis the active Al_2O_3 being in catalyst practically does not react with SiO_2 and does not form mulitte. Increasing the amount of milled catalyst in the formation mix, the decrease of anorthite peaks takes place, the diopside peaks vanish and the intensities of corundum and powellite peaks increase.

Properties of ceramic body with non-milled catalyst additive burned at 1150 °C temperature are the best, however the additive of catalyst waste material has not fully fused. The X-ray diffraction analysis of ceramic body has shown that during burning the anortite peaks increase, powellite does not form at all, and the intensities of corundum peaks are signally smaller comparing to the bodies with milled catalyst additive. We suppose that sustention of formation mix at the highest burning temperature should be increased in order the catalyst granules would completely fuse and react with other mix components.

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