

STUDY OF THE TECHNOGENICAL RAW MATERIALS (CATALYST) OF THE OIL INDUSTRY AND POSSIBILITY TO UTILIZE THEM IN THE CONSTRUCTIONAL CERAMICS PRODUCTION

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Abstract. During the processing of the raw materials in the oil processing plants the by-products are created, such as mud, utilised chemical materials (acids, amines, catalyst). The technogenical raw materials, catalyst utilised in the reactor of the catalytic cracking, were selected for the study. These materials are regenerated in Lithuania partially, the major part remains in the plant area. After the study of the technogenical raw materials, mentioned above, their properties and the possibility to utilise them in the production of the long term constructional ceramics were determined.

Keywords: technogenical raw, catalyst waste, ceramics, structural parameters.

1. Introduction

Large amount of natural resources is used for the production of the building materials and their products. The part of these resources could be replaced by the secondary raw materials. It is evaluated that the utilisation of the secondary raw materials allows replacing 5 – 40 % of the natural resources by industrial waste. Power resources used for such production are also lowered up to 30 % because the industrial waste materials already have a technological state provided during the initial stage. Additionally, by utilising industrial waste it is possible to create new building products of high technical and economical rates.

Reprocessing of the waste, its secondary usage - this is the future of Lithuanian companies manufacturing the building materials. Nowadays, most of the country's companies will have to implement the practice related to waste limitation, recording, collection, sorting, marking, transporting, storage, secondary reprocessing, burring, decontamination or other processing. The most promising for the utilisation are waste materials that are easily reprocessable to the new products, and other waste materials are hazardous or difficult to reprocess due to the contamination by various chemical materials.

Level of the usage of waste materials in Lithuania is still very low. Comparing to other countries of European Union, we are behind a lot in the area of the disposal of waste materials. Mostly, waste materials, such as slag, ash, sawdust, paper, glass are subject to reprocessing. The analysis of the data provided in the references showed that the obstacle of the utilisation of waste materials is the legislative background, drawbacks of waste materials' utilisation strategy. Large companies that produce building materials and products do not want to use waste materials in their production line because it is related to the change of the technological cycle. Additionally, in such a case it would be necessary for the industrial companies to enlarge their production areas, storehouses of raw materials, procure and use more additional equipment, utilise a lot of other resources, carry out additional researches in order to change the production line. The preparation of waste materials for the technological cycle would require additional finances as well. Waste materials wasting companies are also unwilling to produce building materials and products out of waste materials because, despite the above mentioned reasons, it is not profitable to maintain the company that manufactures products of different profiles. There is very little amount of companies that would focus on the reprocessing of waste materials at very beginning, therefore, the largest part of waste materials are

transported to the dumps and only a small part is reprocessed to the building materials.

The information about the utilisation of waste materials for the production of building materials is not systematized, the methodology is not based theoretically.

According to the hazardous waste materials disposal program that is prepared according to the legal documents of European Union regulating the disposal of hazardous waste materials (Directive on Hazardous Waste 91/689/EEC, Directive on Waste 75/442/EEC, Directive on Hazardous Waste Incineration 94/67/EEC), three versions of the common technology for the usage of hazardous waste materials must be implemented in Lithuania: thermal stabilisation in ceramics, thermal stabilisation in cement, burning at high temperature [2].

Thermal stabilisation in ceramics could be implemented during the production of the following products of building ceramics: low porosity, sintered constructional masonry elements used for the façades.

Therefore, one of the industry branches, where technogenical waste materials could be utilised, is ceramics industry. The existing ceramics industry in Lithuania has a lot of problems related to the power resources and technology used. It is obvious that new attitude could help solving these problems. Waste materials of the industry could be used for the production of ceramics. This would help to implement the policy of the handling of waste materials carried out in Lithuania, and companies of the ceramics industry would get a new status. Reasonable distribution and usage of raw materials and power resources for the operated technological equipment would also lower the pollution of the environment. This forces to seek for the necessary resources used in the technologies, that do not produce waste, or for the preventive means to stop the pollution of the environment among the local natural resources and waste materials produced in local industries.

During the search of the technogenical raw material suitable for the utilisation, the attention was paid to the oil refinery and gas industry. This is important strategic branch of the industry [3]. Only oil refineries satisfy 42% of EU power needs and produce 95% of the fuel required for the transport. Considering the large amounts of raw material processed (700 million tonnes of oil in EU, Switzerland and Norway), oil refinery factories do not produce a lot of waste. Currently oil refineries mainly produce sludge, waste materials that are not typical for the refineries (domestic, building waste) and used chemical materials (for instance, acids, amines, catalysts).

The liquidation problem of the waste of oil refinement is one of the most important problems of ecology. These waste materials are transported to the dumps, the number of them increases by occupying large areas and this endangers of secondary pollution of the nature. According to the data provided by

Department of Polluted Territories and Waste of Ministry of Environment of Republic of Lithuania, 12 various names of catalyst waste materials were produced during the year 2000. Their total amount transported to the dumps was 200 tonnes. The utilization of these waste materials is very important, because there are heavy metal ions in the content of the catalyst [4].

In the research two technogenical raw materials are analysed, those are catalysts used in the reactor of the catalytic cracking, and the possibility to use these materials in the production of building ceramics is discussed.

2. Investigation methodology, raw materials

The fusible hydro – micous 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 Al₂O₃ in the heated clay is 15.8 %, the clay belongs to the group with a big amount of colorific oxides as 6.42 % Fe₂O₃, has low dispersion, is impured by coarse carbonaceous inserts ≥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 ₂ O ₃ +TiO ₂	17.79	15.8
Fe ₂ O ₃	7.66	6.42
CaO	6.27	1.8
MgO	3.59	2.72
MnO	0.09	-
K ₂ O	4.49	1.63
Na ₂ O	0.55	-
L.o.l.	11.55	5.3

Non – plastic materials used in the work are: crushed bricks, sand. Crushed bricks of encaustic samples were passed through 2.5 mm sieve. Granularity modulus of sand 0.9, amount of dust and clay particles 0.6 %.

Technogenical raw materials of the oil industry, used catalysts (further - additive CA and CB) in the reactor of the catalytic cracking are also used in the research.

Dosage of components was performed by mass. The samples were shaped in a plastic way. Mix was left for 3 – 5 days in the medium of (95±5) % relative humidity for moisture evenly spreading in the mix. After 3 – 5 days the laboratory samples were shaped into the dimensions 70×70×70 mm.

Materials mix compositions of ceramic samples are presented in Table 2.

Table 2. Composition of material mixes

Composition *, %	Formation mix			
	Clay mix	Non-plastic materials	CA	CB
1	80	10	10	-
2	70	10	20	-
3	76	17	7	-
4	80	-	-	20

The formed prefabs were dried at first under natural conditions in a laboratory, later they were dried the electric stone with temperature (105 ± 5) °C. The sample burning temperature were 1050 °C, 1100 °C. The burning time was 40 h, and exposure to the highest burning temperature was 4 h.

Density, water absorption of burned ceramic samples were determined according to LST EN 771 – 1+A1 Specification for masonry units – Part 1: Clay masonry units.

Water absorption of samples was determined to LST EN 771 – 1+A1, but after 72 hours, total open porosity and reserve of pore volume were determined according to applied the methodology [5].

Water absorption after 72 hours (%) is determined as:

$$W = \frac{m_1 - m_0}{m_0} \cdot 100 \%, \quad (1)$$

where m_0 – is the mass of sample dried up to the constant weight (g), m_1 – is the mass of sample saturated with water (g).

Parameter of total open porosity characterizes total open porosity space of ceramic sample in the aspect of macrostructure and microstructure. Total open porosity from the water absorption in the vacuum process (%) is:

$$W_R = \frac{m_2 - m_0}{V} \cdot 100 \%, \quad (2)$$

where m_0 - is the mass of sample dried up to the constant weight (g), m_2 – is the mass of samples saturated by the vacuum process in air (g), V – is the volume of samples with open pores (cm³).

Reserve of pore volume (4) 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.

$$R = \left(1 - \frac{W_e}{W_p}\right) \cdot 100 \%, \quad (4)$$

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 (%).

Phase analysis of burned samples was carried out by X-ray diffraction. The diffraction meter DRON-2 and DRON-7.

3. Experimental results

3.1 Analysis of the catalyst A (CA)

According to data the waste catalyst CA – composite granule scentless material, composed of aluminium, molybdenum, nickel, phosphorus, zirconium, natrium and other rare earth element oxides. Bulk density of the waste catalyst CA ranges from 0.80 g/cm³ to 1 g/cm³; diameter of granules 1.3-1.5 mm. This catalyst is assigned to the type of dangerous catalysts, the colour changes to brown – reddish (Fig. 1). Chemical composition of unburnt operated waste catalyst CA is presented in Table 3.



Fig 1. Picture of the catalyst previously been in service (×5 times)

Table 3. Chemical compositions of the catalyst CA

Chemical composition, %	Catalyst CA
Al ₂ O ₃	68.85 – 85.25
NiO	2 - 4
MoO ₃	10 - 13
P ₂ O ₅	2 - 6
ZnO ₂	0.1 - 4
Na ₂ O	0.15
Rare earth element oxides	0.5 - 4

After washing out this used catalyst, granules of three colours are seen (Fig. 2): white (Fig. 2, a), black (Fig. 2, b) and blue (Fig. 2, c) colours.

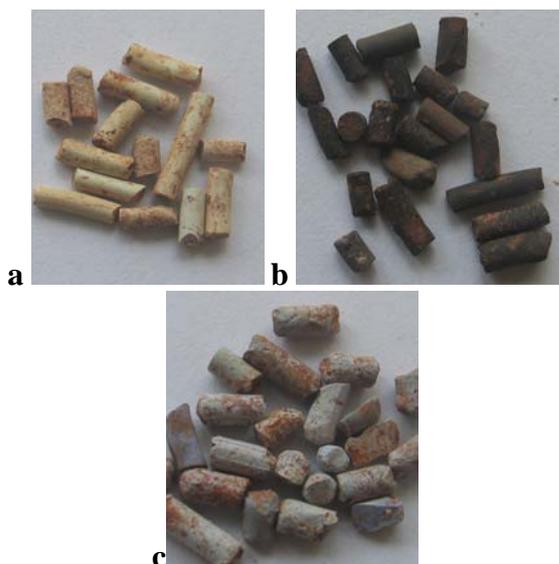


Fig 2. Washed, used, not burnt catalyst CA: a - white; b - black; c - blue colour (magnified by 2.5 times)

The X-ray analysis of the waste catalyst CA burned at 1000 °C temperature has shown (Fig. 3) that there is a big amount of amorphous phase in the catalyst, identified γ Al_2O_3 .

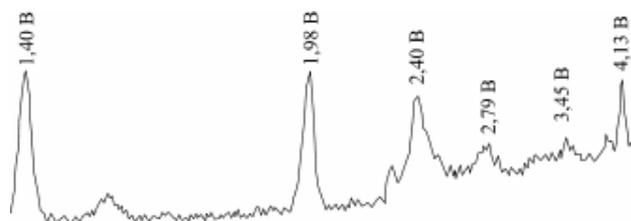


Fig 3. X – ray patterns (Å) of the waste catalyst CA at burned temperature 1000 °C (B - γ Al_2O_3)

The researches of the used catalyst CA and similar to it are widely carried out by the scientists of Korea and Singapore [6, 8]. These researchers have come to the conclusion that out of these technological raw materials, which consist of large amount of molybdenum oxide, it is possible to extract 99.4 % purity molybdenum oxide or use raw materials for the production of the ceramics products that have a commercial value.

3.2 Analysis of the catalyst B (CB)

The catalyst additive chemical composition is the following: 45 % of Al_2O_3 , 0,2-0,3 % of Na_2O , and the rest consists of ceolit ($(\text{SiO}_2)_{179}(\text{Al}_2\text{O}_3)_3 \cdot 25 \text{Al}_2\text{O}_3$. A part of Na is substituted by rare elements.

The ratio of oxides SiO_2 and Al_2O_3 in the catalyst makes 5.3. The relative surface of ceolit fluctuates from 80 cm^2/g to 240 cm^2/g . Changes of heating losses when catalyst is being heated at the

temperature of 1000°C amounts from 0 % to 6.7 %. The granulometric consistence of catalyst indicates that the largest part of the part of the catalyst consists from particles of average dispersion (Table 4).

Table 4. Grading of the waste catalyst CB

Fraction size, μm , residue on screen, %				
0-20	20-40	40-80	80-100	100-150
1	15	64	15	5

In the X-ray picture (Fig. 4) of the unburned, used catalyst, the zeolite identified by employing the known classification [9] belongs to the group of fozhazit $\text{Na}_2\text{Ca}[\text{Al}_2\text{Si}_4\text{O}_{12}]_2 \cdot 16\text{H}_2\text{O}$ (all peaks show the existence of this zeolite). According to the reference [10], the diffractometric analysis allows to determine zeolites in cases their amount exceeds 10 %.

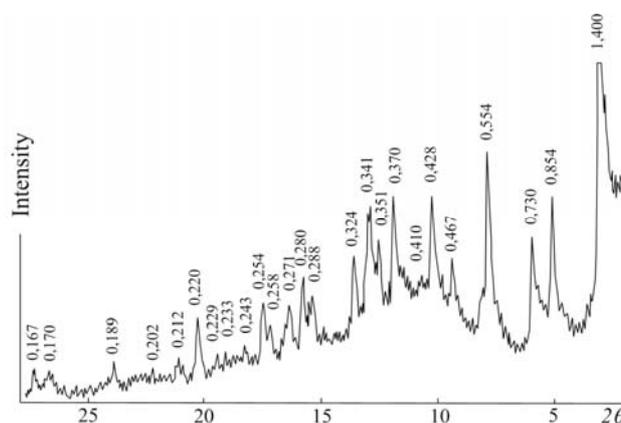


Fig 4. X – ray patterns (nm) of the waste catalyst CA

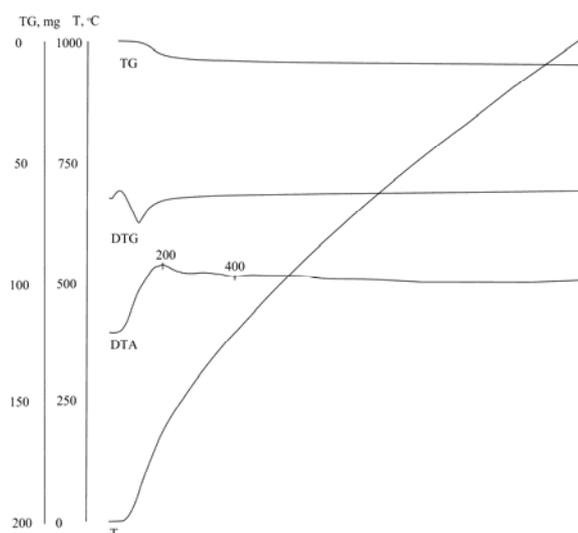


Fig 5. The thermograph of the used catalyst CB: T - ratio of the temperature increase; TG - volume variation curve; DTG - differential curve of volumes' variation; DTA - differential curve of thermal variations

When the thermal analysis of the used catalyst is carried out, the exothermic effect during the heating (Fig. 5) is related to the burning of the organic materials at the temperature of 200 °C and emission of the volatile materials.

The X-ray analysis of the waste catalyst CB burned at 1070 °C temperature has shown (Fig. 6) that there is a big amount of amorphous phase in the catalyst, identified mulite, anataze, spinel, anortite.

The burned CB additive is analysed by employing magnification of 350 times. As it can be seen (Fig. 7), granules with the fused surfaces dominate. Average dimensions of the granules ~ 70 µm. The colour of the burned granules - white. Determined loses of calefactory of the additive at the temperature of 1 070 °C – 0.86 %.

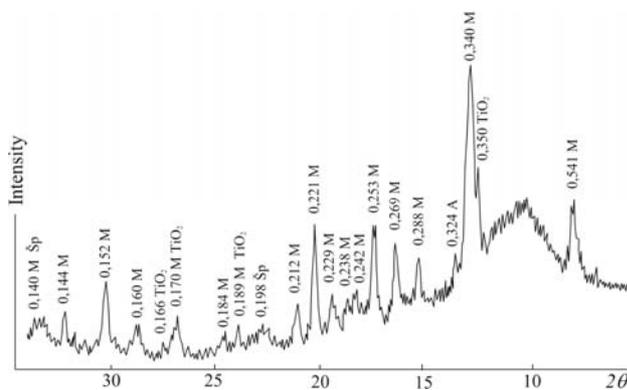


Fig 6. X – ray patterns (nm) of the waste catalyst CB at burning temperature 1070 °C (M – mulite; TiO₂ – anataze; Sp – spinel; A – anortite)

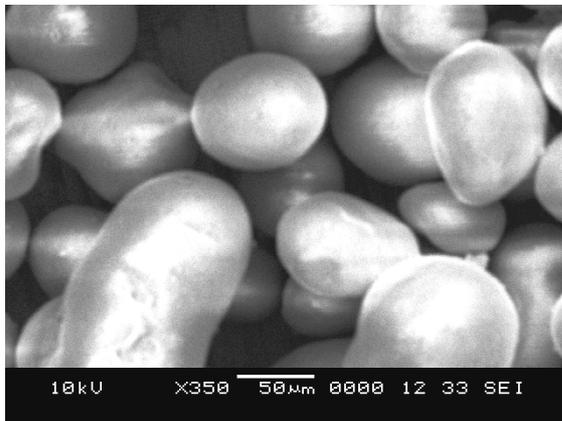


Fig. 7. The burned used catalyst CB at the temperature of 1070 °C (magnified by 350 times)

3.1 Analysis of formation mix

Dependence of density and volumetric freezing and thawing on the burning temperature present in the Fig. 8 and Fig. 9.

At the highest burning temperature of 1050 °C and 1100 °C, when the amount of the used catalyst CA in the formation mass increases, the impregnation

of the samples increases, density decreases. The largest value of the pore volume rate, at the highest burning temperature 1 050 °C and 1100 °C, is reached when 7% of the used catalyst is added to the formation mass. When larger amount of catalyst CA is added, ratio of the pore volume decreases [11]. According to the structural characteristics, the optimal burning temperature for the production of the sintered long-lasting ceramics by using local clays and used catalyst CA in the ceramic mass is 1 100 °C, and the optimal amount of the technogenical raw material is 10%.

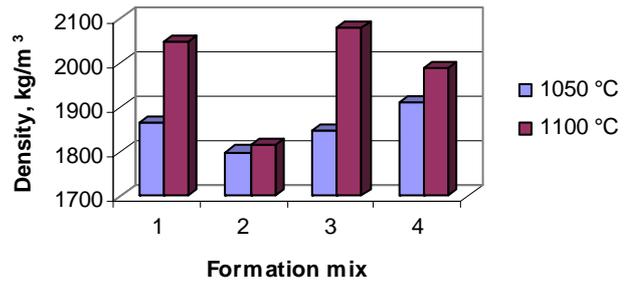


Fig 8. Dependence of density on the burning temperature

When used catalyst additive CB is used in the formation mass, already at the burning temperature of 1050 °C the ceramic body with the density of 1900 kg/m³ is created, and with the increase of the burning temperature, the density increases up to 1970 kg/m³. The samples are burned without any deformations.

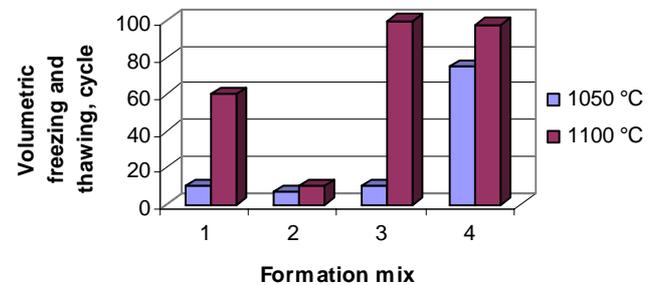


Fig. 9. Dependence of volumetric freezing and thawing on the burning temperature

Water absorption after 72 hours, total open porosity, reserve of pore space present in the Table. 4.

The impregnation of the ceramic body, burned at the temperature of 1100 °C by using additive CB, complies with the requirements applied for the sintered ceramics body (Table 4), and the reserve of pore volume reaches the maximal value (approximately 35 %).

When the amount of the used catalyst CA in the formation mass increases, its structural characteristics degenerate, and as it is known from [5], by using numeric values of the structural characteristics it is possible to estimate the durability of the ceramic

products according to frost resistance. This is confirmed by the analysis of the frost resistance carried out.

Table 4. Structure parameters of the formation mix

Structure parameters	Formation mix			
	Burning temperature, °C			
	1050°C			
	1	2	3	4
W, %	11.3	16.6	10.8	9.23
W _R , %	26.0	33.7	18.4	24.1
R, %	19.0	11.4	8.7	27.0
1100°C				
W, %	6.7	13.7	6.0	6.11
W _R , %	19.9	30.4	19.8	21.6
R, %	30.4	17.8	36.5	40.0

In case additives CA and CB are used, the frost resistance of the ceramic bodies, when volumetric frost resistance estimation method is applied, is approximately 100 cycles, this is the case when the amount of additive CA is 7 % or amount of additive CB is 20 %, and the highest burning temperature is 1100 °C.

In the X-ray picture 1 of the ceramic body with the additive CA the corundum peaks Kr (0.348, 0.256, 0.238, 0.209, 0.174, 0.161 nm) are identified. Their creation is determined by the reactions in the additive itself at the burning temperature, higher than 1000 °C. γ Al₂O₃ existing in the technogenical raw material is transformed to α Al₂O₃, i.e. corundum. The identification of the powellite's peaks is caused by the interaction of the MoO₃ existing in the technogenical raw material and CaO existing in the clay. During the reaction of CaO and MoO₃ oxides at the temperature of 800 °C, the binding of MoO₃ oxide is carried out, and due to this the powellite - CaMoO₄ peaks (0.310, 0.287, 0.193 nm) appear in the X-ray pictures.

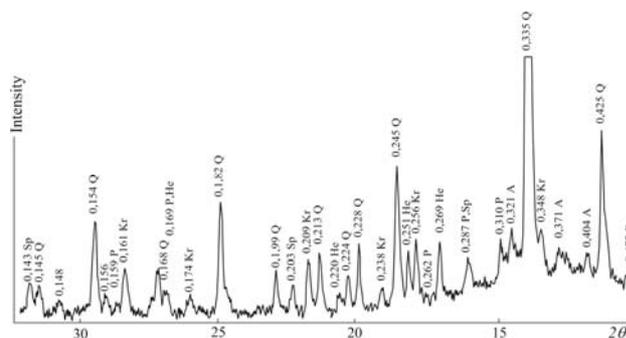


Fig 10. X – ray patterns (nm) of the formation mix No.1 at burning temperature 1100 °C (Q – quartz, A – anortite, Šp – spinel, Kr – corundum, He – haematite, P – povelate

Fig. 11 shows the X-ray picture of the 4-th burned ceramic body (burned at the temperature of 1100 °C). The main materials visible in this X-ray picture are: silica Q 0,425; 0,335; 0,245; 0,228; 0,224;

0,213; 0,198; 0,182; 0,167; 0,154; 0,138; 0,037 (nm), mullite M 0,544; 0,221 (nm), heamatite Fe₂O₃ 0,269; 0,251; 0,219; 0,1840; 1690; 145 (nm), spinel Šp 0,286; 0,202; 0,143 (nm), anortite A 0,404; 0,318 (nm), feldspar Lšp 0,324 nm.

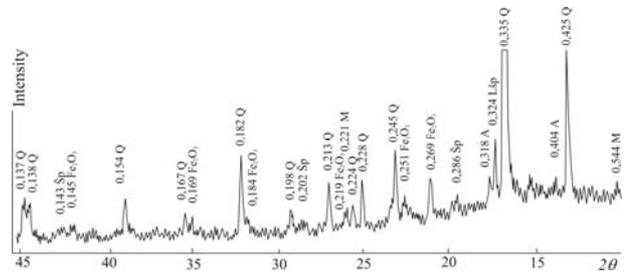


Fig 11. X – ray patterns (nm) of the formation mix No.4 at burning temperature 1100 °C (Q – quartz, M – mullite, A – anortite, Šp – spinel, He – haematite, Lšp – feldspar

4. Conclusions

The main part of the used catalyst CA consist of aluminium oxide, that transforms γ -Al₂O₃ modification to α -Al₂O₃ modification when heated at high temperature. In this used catalyst there is considerable amount of molybdenum and phosphorus oxide. The shape of the granules of the used catalyst is cylindrical, their diameter is 1.3–1.5 mm. When the catalyst is burned at the temperature of 1 000 °C, its shape does not change.

The used catalyst CB consists of up to 6.7% of soaked oil refinement products that burn at the temperature of 200 °C when the catalyst is heated.

Heavy metal ions and rare ground elements exist in the used catalyst CA and CB analysed. Due to these materials the amount of the used catalysts in the ceramic mass must be limited. It is advisable to admix only such amount of the used catalyst to the ceramic formation mass that could be thermally stabilised in the ceramics.

When catalyst additives CA and CB are used and in order to produce the durable sintered ceramic samples, it is necessary to increase the highest burning temperature, because from 45% to 85% of catalysts consist of Al₂O₃, which increases the sintering temperature of the ceramic body when added to the formation mass.

The samples produced from the formation mass, when used catalyst CB is used as an additive, are of dark brown, uniform colour, and when used catalyst CA is used - the colour is not homogeneous, the insertions of the light colour can be identified on the surface.

The frost resistance of the samples, produced by using 7% additive CA and 20% additive CB and burned at the temperature higher than 1100 °C, determined by implementing volumetric freezing and de freezing, is higher than 90 cycles, impregnation is lower than 6.

It is estimated that these technogenical raw materials can be used for the production of the frost resistive, sintered building ceramics products. These products can be burnt at the higher temperature than the ones produced from the low-melting clay by using typical additives. It is recommended to add up to 10% CA or 20% CB used catalyst.

Additionally, the usage of such technogenical raw materials would allow to reduce the amount of waste materials stored in the territory of oil refinery and would solve the usage problems of such raw materials.

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