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ANALYSIS OF THE UTILIZATION OF WASTE CATALYSTS FROM CATALYTIC CRACKING REACTORS IN OIL INDUSTRY

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Abstract

This article covers the investigation of the catalyst waste (T.R.M 1 and T.R.M 2) produced in the reactor of oil catalytic cracking. The analysis of this waste was carried out. The properties of T.R.M 1 and T.R.M 2 were investigated and determined, the mineralogical analysis of catalyst waste was implemented, the analysis of thermal effects during the burning was performed. Catalyst waste materials investigated were used in a ceramic system (from 7 % to 20 % of the overall amount). It was identified that the optimal quantity of additive T.R.M 1 in formation mixes was 10%. With this amount of the additive, after the burning of formation mixes at 1050°C temperature, ceramic systems with the following properties were formed: total contraction - up to 6.5%, density of the system - larger than 1847 kg/m^3, compressive strength - larger than 13 MPa, water absorption - up to 11 %, and effective porosity - up to 21 %. The identified optimum quantity of additive T.R.M 2 in the formation mix was 20 %. The obtained ceramic systems have the following parameters: total contraction - less than 10 %, density - higher than 1852 kg/m^3, compressive strength - higher than 15 MPa, water absorption - less than 9 %, and effective porosity - lower than 17 %.

Key words: building ceramic, catalyst, oil waste, recycle

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1. Introduction

The progress of science and engineering during the last decades together with the increasing rate of industrial development lead to the accumulated large quantities of industrial and domestic waste. Particularly, large amounts of waste are produced in various industries, such as chemistry, building materials, metallurgy, as well as in the field of thermal energetics. Worldwide, significant attention is paid to waste management, utilisation and recycling. However, the implementation of waste management differs in various regions of the world, depending on economic development level in a particular country, the urbanisation level and the nature of an area. The main source of natural hydrocarbons on the Earth is oil. The main waste produced in oil industry is oil sludge and catalyst waste.

Oil sludge is created during the cleaning of sewage water. However, when automated equipment is employed for the sludge cleaning, sludge is not accumulated in the ponds, but recycled to oil, water and soil. After the separation in this equipment, oil is further returned for the recycling, water is drained to the sewage cleaning equipment, and soil is brought to

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a soil regeneration site. Modern oil industry factories use liquid catalytic cracking widely. A catalyst is applied in a catalytic cracking equipment to decompose the oil hydrocarbon molecules into smaller ones (Wu et al., 2003). The catalyst waste created in the cracking equipment is slightly ground. Waste particles mainly consist of the minerals Al_2O_3 and SiO_2, and are slightly contaminated with metal impurities, including heavy metals.

Approximately 400 000 tons of catalyst waste is created worldwide every year (Furimsky, 1996). In Lithuanian oil refinery company, approximately 200 tons of this waste is produced annually. On average, about 50 tons of catalyst waste is transported to the metallurgical companies, 90 tons of this waste is returned to the manufacturer, and approximately 60 tons are transported to the special dumps.

The general analysis of the catalyst waste utilised in the oil industry shows that some catalysts are assigned to the group of hazardous, while others – to the group of non-hazardous materials. The hazardous catalyst waste may contain larger quantities of two-valent nickel, cobalt oxides, four-valent molybdenum oxide, and molybdenum trioxide. Some of these materials cannot be heated at higher than 40°C or 60°C temperatures, because poisonous carbon nickel combinations, smoke with chlorine and hydrogen chloride can be formed during the burning. These hazardous materials must not be exposed to the moisture, carbon monoxide, strong acids, alkalis or oxidants. These materials are usually toxic and it is difficult to decompose them biologically. Although, in the natural conditions these materials are stable, they should not be exposed to the environment, but only reused or utilized. The isomerisation catalysts contain hydrocarbons and other residue materials. During the heating, the decomposition products may also be formed from the residue materials. The group of non-hazardous materials contains large amounts of aluminium and silica, some iron, titanium oxide, and the traces of rare alkaline oxides and earth alkaline metals (Aleknevicius, 2010).

In recent years, a lot of research is carried out on the utilisation of such catalyst waste as an additive for the grouts and concretes with Portland cement (Paya et al., 1999, Su et al., 2000; Su et al., 2001). It has been determined that catalyst waste is a filler aggregate increasing the compressive strength of composites with Portland cement (Chen et al., 2004, Paya et al., 2003; Pacewska et al., 2002, Pacewska et al., 2004;). Waste catalysts in lightweight concrete increase the density and the compressive strength (Maciulaitis et al., 2007). Applying the waste catalysts in cement composites, the cement hydrates, more heat is transmitted, and the exothermic effect occurs several hours earlier. The preformed investigations showed that the waste catalysts from oil industry can be applied during the manufacturing of ceramic products (Acchar et al., 2009, Escardino et al., 1995, Souza et al., 2004) and thermal resistant concretes (Stonys et al., 2008).

The paper provides description of the experiments that were performed with the aim to analyse catalyst waste from oil industry in more detail and to apply this waste in the production of construction ceramics. The physical and mechanical properties, the selected structural parameters of the ceramic systems were identified; the quantitative chemical analysis of the washing out of heavy metals, and the X-ray diffraction analysis were implemented.

2. Materials and methods

Raw materials used in this investigation were clay (Clay 1 and Clay 2), non-plastic materials (crushed bricks and sand) from Lithuania, usually applied in the production of bricks, and catalyst waste from the catalytic cracking of oil industry (T.R.M 1 and T.R.M 2). During the preparation of samples, the powder of dry clay and the additives were mixed for 1 h. Then water was poured into the mixes in order to form the plastic formation mixtures (extrusion machine) with the humidity of 22-25□. The composition of the modelled formation mixes is presented in Table 1. Next, the formed samples (70 × 70 × 70 mm) were dried in a laboratory for 72 hours at (20±2) °C temperature; afterwards they were dried in an electric stove for 48 hours at (105 ± 5) °C. Finally, the dried samples were burnt out for 45 hours, keeping at the maximum 1050°C temperature for 4 hours. The catalysts were used in the oil industry at 550-700°C temperatures. The minimum amount of catalyst waste was selecyed according to the investigation results. Such amounts of the clay and concentration reducing additive are the most often used in the production of ceramic products in Lithuania. Chemical compositions of the main raw materials were determined by applying the classical methods of chemical analysis for silicate materials.

The density of the burnt ceramic samples was determined according to LST EN 772-13. Water absorption of the samples was determined according to LST EN 771-1. The compressive strength was determined according to LST EN 772-1:2003. The specific surface area was determined according to LST EN 196-6.

The parameters of effective and total open porosity, reserve of pore volume, relative wall thickness of pores and capillaries were determined according to the methodology (Mačiulaitis et al., 2007). Phase analysis of the burnt samples was carried out by implementing X-ray diffraction analysis (DRON-2, Cu anti-cathode, Ni filter / Co anti-cathode and Fe filter). Particles' size distribution was determined by "Cilas 1090" dry analyzer. The thermographic analysis was performed by derivatograph Q 1500 D. Microstructure analysis was carried out by using SEM „Quanta“ 250 with SE detector.

Reliability of making heavy metals non hazardous was tested by soaking samples (placed in the hermetically sealed desiccators) into 1 litre of acetic buffer solution with pH=4.0±0.1. The ion concentrations of iron, aluminium, zinc, nickel and phosphates in the solutions were determined by employing spectrophotometric methods according to the known methodology (Mickevičius, 1998).

Table 1. Composition of formation mixes

Formation mix	*Composition, %*					
	A	*B*	*C*	*D*	*E*	*F*
Clay 1	20	16	15	10	20	20
Clay 2	60	60	65	60	70	60
N.P.M	20	17	10	10	–	–
T.R.M. 1	–	7	10	20	–	–
T.R.M. 2	–	–	–	–	10	20

Note: N.P.M–Non-plastic materials (crushed bricks and sand), T.R.M 1 and T.R.M. 2–catalyst waste

3. Results and discussion

Catalyst waste of oil industry (T.R.M. 1) is a composite scentless material with the shape of granules (Fig. 1). Chemical composition of the catalyst waste T.R.M. 1 presented in Table 2.

Fig. 1. Picture of the catalyst waste (T.R.M 1) used earlier

After exploitation, the T.R.M 1 granules usually have brown-red colour, bulk density is 0.8-1.0 g/cm^3, the diameter of granules 1.3-1.5 mm. Before the utilisation T.R.M.1 catalyst granules were ground, the specific surface area of 170 m^2/kg was reached. The T.R.M 1 is assigned to the group of hazardous waste. T.R.M 1 contains toxic nickel oxide, which is considered as carcinogen of 1st category. Moreover, under the certain conditions it reacts with carbon monoxide and forms toxic gas Ni (CO)$_4$. After X-ray diffraction analysis of T.R.M. 1 (Fig. 2) the large amount of amorphous glass phase was observed. In addition, γ Al$_2$O$_3$ (0.413, 0.345, 0.279, 0.240, 0.198, 0.140 nm) was identified.

The differential thermal analysis of T.R.M. 1 (Fig. 3) showed that the first endothermic effect occurs at approximately 120°C temperature and is related to water evaporation. Second takes place at 840-860 °C temperature and is related to fusion and evaporation of MoO$_3$ oxides (Abdel-Rehim, 2004; Chychko et al., 2010). The total mass losses (after the heating up to 1000 C temperature) were 16.8 %. Prior to the application, this additive was ground in a disintegrator and passed through a 0.63 mm sieve.

Chemical composition of the catalyst waste 2 (T.R.M. 2) is provided in Table 2. Particles' size of T.R.M. 2 vary from 0.5 μm to 120 μm (Fig. 4); particles are spherical, specific surface area is 200 m^2/kg. SEM analysis of the catalyst waste T.R.M. 2 is presented in Fig. 5, which shows that powder material mainly contains spherical particles. The fractions of damaged particles are seen in SEM pictures. The surface of undamaged particles is uneven with small bumps. The colour of catalyst waste T.R.M. 2 is white. After X-ray diffraction analysis of T.R.M 2 the Y zeolite – faujasite (Na$_2$, Ca, Mg, K$_2$) O· Al$_2$O$_3$·4.5 SiO$_2$ 7 H$_2$O was identified. After the burning of the additive T.R.M 2 at higher than 1000 °C temperatures, the phase transition of zeolitic structure to mullite M (0.152, 0.221, 0.253, 0.269, 0.340, 0.541 nm) was observed. Another material identified – TiO$_2$ – anatase, with the most intensive peak of 0.350 nm, while other peaks – 0.166, 0.189 nm. The most intensive peak of spinnel (Šp) was 0.140 nm, the other peak – 0.198 nm. The peak for anorthite (A) was 0.324 nm. The amount of amorphous aluminium silicate phase had increased by one fifth compared to the X-ray diffraction pattern of unburned catalyst (Fig. 6).

Thermal analysis of catalyst waste T.R.M. 2 (Fig.7) shows, that the exothermic effect during the heating is related to the burning of the organic materials at 200°C temperature and the emission of volatile materials. T.R.M. 2 materials utilized contains up to 6.7 % of soaked oil refinement products that burn at 200ºC temperature when the T.R.M 2 is heated. Raw materials, used in this investigation, were clay (Clay 1 and Clay 2) from Lithuania. Clay is usually applied in bricks production. The chemical and granulometric composition of clays is presented in Table 3 and Table 4. The total contraction of the ceramic body formed from Clay 1/Clay 2 and burnt at 1000°C temperature was 8.4/10.3%, density – 1750/2080 kg/m^3, and water absorption – 14.8/7.4%. During X-ray analysis of Clay 1 and Clay 2 hidromica, kaolin, quartz, feldspar, dolomite, calcite were identified.

Table 2. Chemical composition of the catalyst waste (T.R.M 1 and T.R.M 2), in wt (%)

Catalyst waste	*Chemical composition, %*									
	SiO$_2$	*Al$_2$O$_3$*	*Fe$_2$O$_3$*	*MoO$_3$*	*TiO$_2$*	*NiO*	*P$_2$O$_5$*	*ZnO$_2$*	*Na$_2$O*	*La$_2$O$_3$*	*Rare earth element oxides*
T.R.M. 1	–	68.85-85.25	–	10-13	–	2–4	2–6	0.1-4	0.15	–	0.5-4
T.R.M. 2	55.15	40.94	0.90	–	1.48	–	0.11	–	–	1.41	–

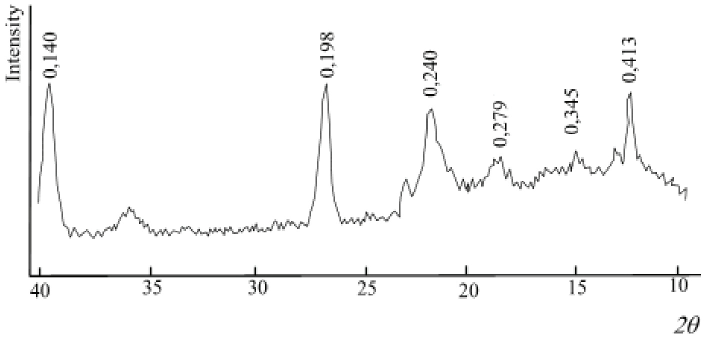


Fig. 2. X-ray diffraction patterns of the catalyst waste (T.R.M 1) burnt at 1000 °C. Peaks assigned γ Al_2O_3 are shown

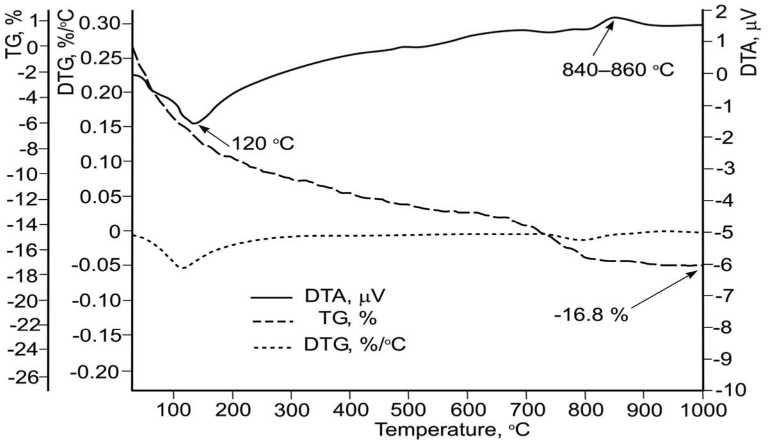
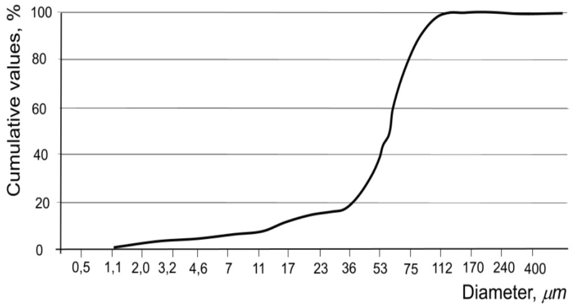


Fig. 3. T.R.M 1 thermogram: T – rate of temperature increase; TG – curve of mass change; DTG – differential curve of mass change; DTA – differential curve of thermal change



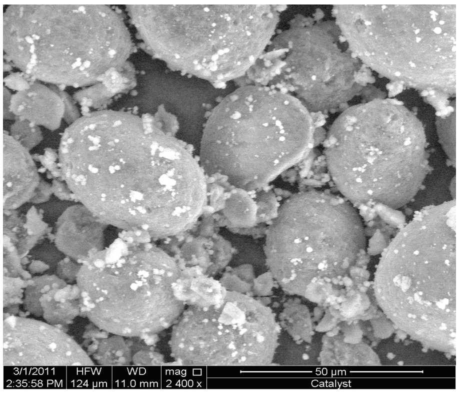


Fig. 4. Distribution of T.R.M. 2 particle sizes

Fig. 5. SEM images of catalyst waste T.R.M 2

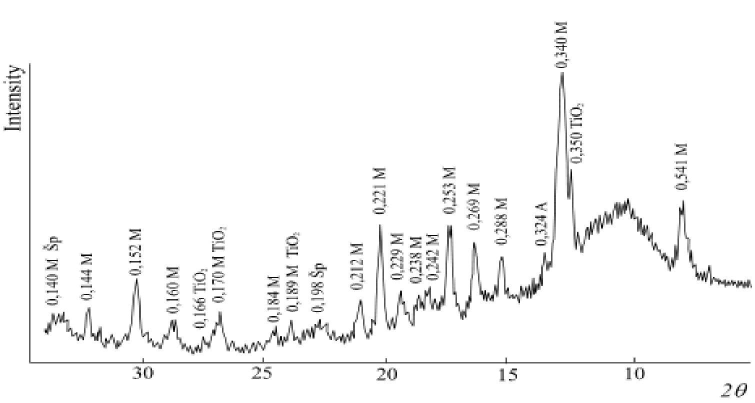


Fig. 6. X-ray diffraction pattern (nm) of catalyst waste of oil industry (T.R.M 2) burned at higher than 1000 °C temperature, (nm): M – mullite, TiO_2 – anatase, Šp – spinnel, A - anorthite (nm)

Non-plastic materials (N.P.M) used in the research were crushed bricks and sand. Crushed bricks of the burnt samples were passed through a 2.5 mm sieve. The granularity modulus of sand was 0.9 and the amount of dust and clay particles – 0.6%. During X-ray analysis of non-plastic materials the quartz and feldspar were identified. Results indicate that, after catalyst waste (T.R.M 1 and T.R.M 2) is added, the total contraction, water absorption and density increase, at the same time, compressive strength is reduced (Fig. 8 and Fig. 9). The values of density and compressive strength of the investigated ceramic systems are presented in Fig. 8 (a, b).

It was determined, that the adding of the catalyst waste to the formation mixes decreases the density and compressive strength of ceramic systems. The density of ceramic system A was 1945 kg/m^3, and compressive strength – 17.3 MPa. After the application of the T.R.M 1 additive to the formation mixes, the average decrease of ceramic system density was 8%, and after the application of the T.R.M 2 additive – 4 %. Previous chemical analysis of T.R.M 1 and T.R.M 2 (Table 2) indicated that the main chemical components are Al_2O_3 and SiO_2. %.

Table 3. Chemical composition of clays, in wt (%)

Raw material	***Chemical composition, %***								
	SiO_2	***Al_2O_3+TiO_2***	***Fe_2O_3***	***CaO***	***MgO***	***MnO***	***K_2O***	***Na_2O***	***Loss on ignition***
Clay 1	47.6	17.79	7.66	6.27	3.59	0.09	4.49	0.55	11.55
Clay 2	66.33	15.8	6.42	1.8	2.72	–	1.63	–	5.3

Table 4. Granulometric composition of clays (%)

Raw material	***The amount of sand particles > 0.05 mm, %***	***The amount of dust particles (0.05-0.005) mm, %***	***The amount of clay particles < 0.005 mm, %***
Clay 1	0.09 – 0.77	9.26 – 21.39	72.11 – 96.04
Clay 2	23.93	34.03	42.04

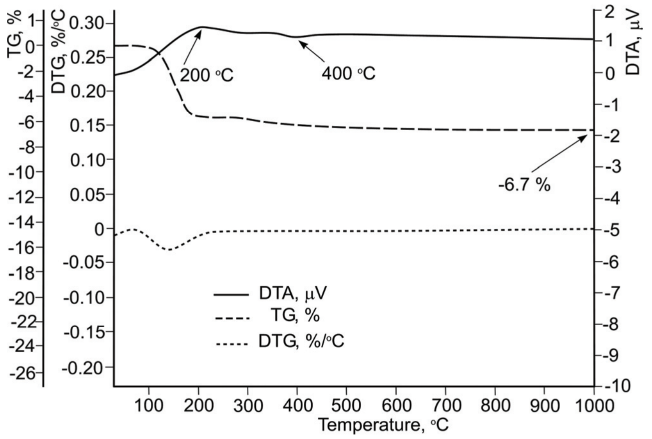
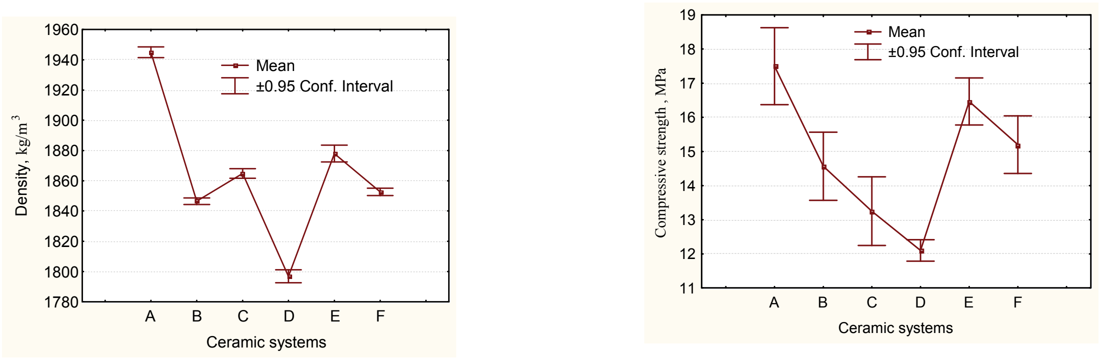


Fig. 7. T.M.R.2 thermograph: T – rate of temperature increase; TG – curve of mass change; DTG – differential curve of mass change; DTA – differential curve of thermal changes



(a) **(b)**

Fig. 8. Density (a) and compressive strength (b) of ceramic systems

It is assumed that the decrease of the density and compressive strength occured due to the fact that catalyst waste T.R.M 1 (which consists of the large amount of Al_2O_3, from 68% to 85%) did not fully reacted with the ceramic system, because of the insufficiently high burning temperature. Macrostructure analysis of the ceramic system D (Fig. 9) also confirms this assumption. T.R.M 2 additives contains large amount of SiO_2 (55%), which influences the ceramic system as concentration reducing additive.

When ceramic systems are burned at 1050°C temperature, the mass losses may reach even up to 18% due to the removal of organic impurities and moisture from the system and from the catalyst waste. This influences the contraction of ceramic system. The total contraction of the formed ceramic systems varies from 5.6 % to 9.8 % (Fig. 10 a).

Total contraction – is a decrease of the formed sample in volume during the drying and burning. The contraction magnitude determines how much size of the products, to be formed, should be larger in order to have necessary dimensions after the burning. The highest contraction was observed in the ceramic system F, which has the maximum amount of additive T.R.M 2 - 20

The smallest contraction was identified in the ceramic system B, which has the least amount (7 %) of T.R.M 1 additive, but it is has the largest amount (17 %) of the concentration reducing additives.

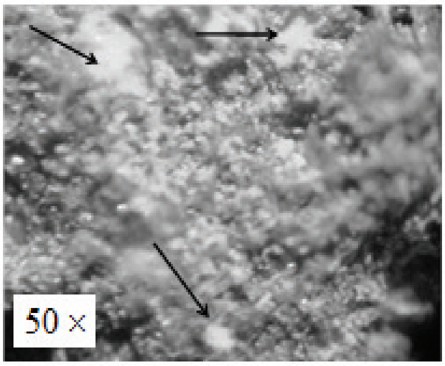


Fig. 9. Macrostructure of ceramic system D

Water absorption was higher for all burned ceramic systems with the T.R.M 1 or T.R.M 2 additives, comparing to the reference ceramic system A (Fig.10 b). After the introduction of 7 % of T.R.M 1 to the formation mix, water absorption of 10.8 % was identified, while after the adding of 20 % of T.R.M 1, water absorption increased up to 16.6 %. T.R.M 2 additive has less influence on water absorption of ceramic system. Even with the maximum 20 % of the additive, water absorption was not higher than 10 %.

The increase of water impregnation of ceramic body after the introduction of the additives T.R.M 1 and T.R.M 2 shows that the ceramic body has a lot of pores of various sizes, capillaries, as well as defective hollows linked to each other. The increase in total contraction and water absorption, as well as the decrease in density and compressive strength, after the introduction of catalyst waste, are the consequences of higher amount of Al_2O_3 and SiO_2 as it can be seen in Table 2 and Table 3. Temperature of 1050°C is not high enough for the formation of sufficient amount of the liquid phase (from Al_2O_3 and SiO_2) that could influence the thickening of ceramic body. This is an indication that the formation of a small amount of liquid phase does not contribute to the reduction of porosity. Due to the introduction of catalyst waste micro-cracks can be created. Values of effective porosity, total open porosity and reserve of pore volume are presented in Fig. 11.

The effective porosity of ceramic system ranges from 7% to 29%. The largest effective porosity was determined in the ceramic system D, which has the highest amount (20%) of T.R.M 1 additive. This is influenced by the large amount of MoO_3 in T.R.M 1, which fuses and evaporates at 800°C temperature (Abdel-Rehim, 2004; Chychko et al., 2010). The total open porosity of the obtained ceramic system ranges from 15% to 33%.

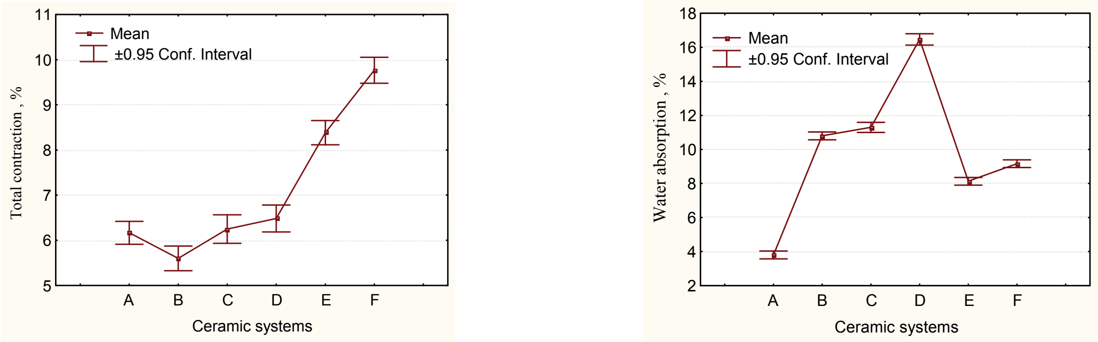
The ceramic system without catalyst waste had the smallest value of total open porosity. The reserve of pore volume characterises the part of ceramic system volume, which initially is not filled with water and is filled gradually afterwards. However, this is influenced by the existence of defects and sizes of pores and capillaries. With the increasing quantity of the catalyst waste in the formation mix, reserve of pore volume decreases significantly.

The smaller reserve of pore volume is obtained in the ceramic systems with the largest amounts of thinners to be used as concentration reducing additives and 7% of the T.R.M 1 additive.

X-ray diffraction analysis of the ceramic systems with T.R.M 1 additive helped us to identify the following phases: quartz, hematite, anorthite, spinnel, corundum, and powellite. X-ray diffraction patterns of the ceramic system C are shown in Fig.12.

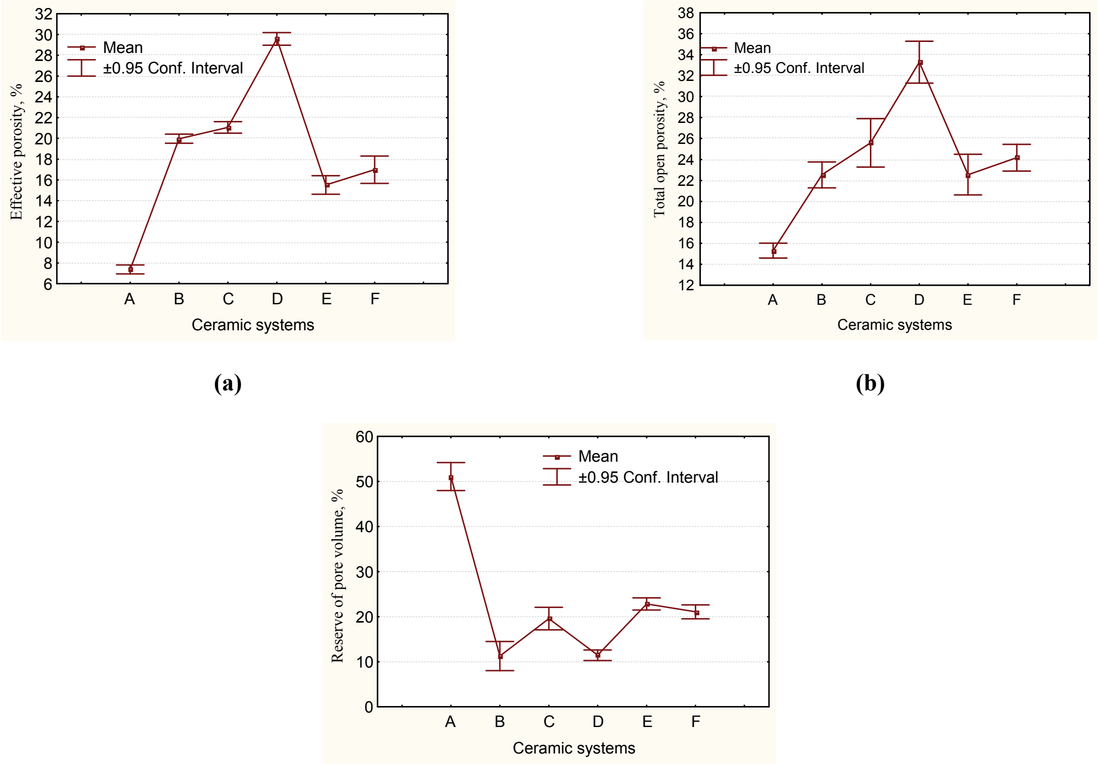
The corundum peaks are influenced by the reactions in the additive itself when the burning temperature is higher than 1000 °C. γ Al_2O_3 in catalyst waste is transferred to α Al_2O_3, i.e. corundum. The peaks of powellite are affected by the reaction of MoO_3 in the catalyst waste and CaO in clay. The oxides of CaO and MoO_3 react at the approximate 800°C temperature, the binding of MoO_3 occurs and the powellite $CaMoO_4$ peaks (0.310, 0.287, 0.193 nm) appear in the X-ray diffraction patterns.

After X-ray diffraction analysis of the ceramic systems with T.R.M 2 additive, the following phases were identified: quartz, mullite, hematite, spinnel, anorthite, and feldspar. X-ray diffraction patterns of the ceramic system F are presented in Fig.13.



(a) **(b)**

Fig. 10. Total contraction (a) and water absorption (b) of ceramic systems



(a) **(b)**

(c)

Fig. 11. Effective porosity (a), total open porosity (b) and reserve of pore volume (c) of ceramic systems

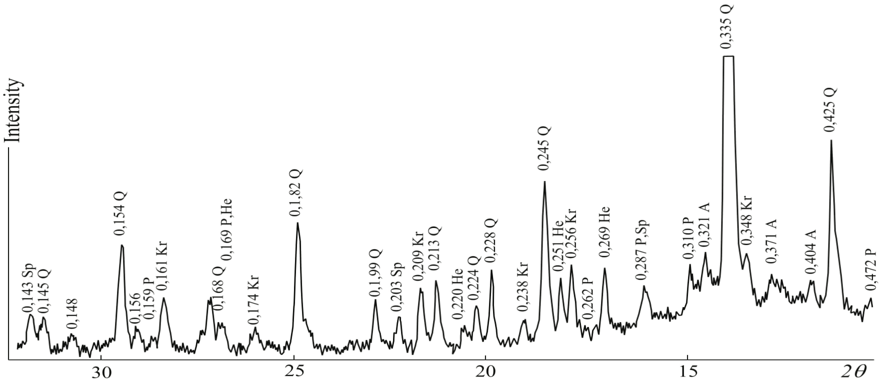


Fig. 12. X-ray diffraction patterns (nm) of the ceramic systems C (Q –quartz, A – anorthite, Sp – spinel, Kr – corundum, He – hematite, P – powellite)

The existence of amorphous glass phase and spinnel in the ceramic system shows, that the thermodynamic equilibrium was not reached during the burning. The newly formed phases were: hematite He (0.371, 0.270, 0.252, 0.220, 0.184, 0.169, 0.148 nm), anorthite-albite A (0.404, 0.307, 0.321, 0.319 nm), and mullite M (0.544, 0.221 nm). The occurrence of mullite in the ceramic system is influenced by the phase transition of zeolite structure at the temperature higher than 1000°C. Chemical composition of the used T.R.M 1 (Table 2) showed, that the additive had heavy metal impurities. The results of the quantitative chemical analysis of metal washout from the ceramic system D with 20 % of the T.R.M 1 additive are provided in Fig. 14. However, it should be emphasized that the conditions of experiments are significantly more aggressive than the natural ones. Firstly, under the natural conditions the rainfall rarely has pH equal to 4.0, the natural rainfall features substantially lower acidity. Secondly, under the natural conditions there is no constant contact of liquid with ceramic products. Therefore it can be assumed that the rate of metal washout under the natural conditions would be at least 10 times smaller than the one under the experimental conditions.

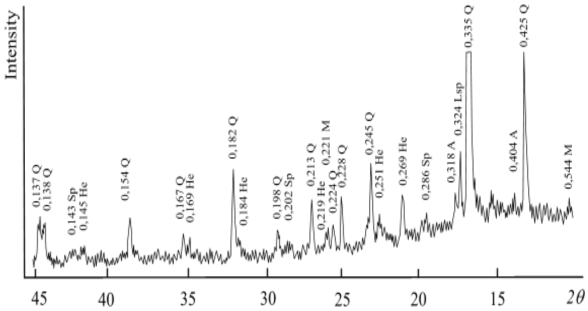


Fig. 13. X-ray diffraction patterns (nm) of the ceramic systems E (Q –quartz, M – mullite, A – anorthite, Sp – spinel, He – hematite, Lsp – feldspar)

In our case, when heavy metal washout is decreased by 10 times, the results show that the amounts of heavy metal washout of the ceramic system with the highest quantity of T.R.M 1 additive do not exceed the applicable norms (HN 105:2004).

Therefore, it can be assumed that ions of the heavy metals in the samples have strong bonds in the ceramic body and can be washed out from the ceramic body only during the influence of aggressive acids only. The results obtained during the investigation of the washout of heavy metal ions allow us to conclude that the burning temperature of 1050 °C is sufficient to bind the heavy metal ions in the ceramic system.

4. Conclusion

In the oil industry, the main components of catalyst waste of the reactor of catalytic cracking are Al_2O_3 and SiO_2. Currently this waste is not applied in the production of building materials widely.

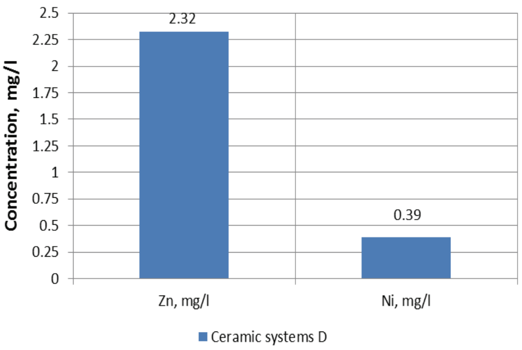


Fig. 14. Quantitative chemical analysis of metal washout from ceramic system with T.R.M 1 additive

Analysis of the catalyst waste of the reactor of catalytic cracking in oil industry (T.R.M 1 and T.R.M 2) and clays showed that these waste materials can be applied in the production of ceramic products in limited quantities.

The analysis showed that the amounts of the material, washed out from the ceramic system with T.R.M 1 additive, containing heavy metal ions, do not exceed the allowable limits. Thus the temperature of 1050 °C is sufficient to bind these materials in the ceramic system.

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