Influence of Petroleum-Refining Waste / Product Contaminated Soil on Properties of Porous Ceramic Article

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During the refining of crude oil, among other wastes, soil contaminated with oil products is produced. This is a viscous mixture of soil, various oil products and water. Every year more and more of this waste is accumulated, because there is no appropriate means for its utilization. The possibility for use the petroleum product contaminated soil in the production of ceramic articles was investigated. Thermographic investigations have shown that heating up to 140 °C causes a loss in specimen mass by 54 %, while the endothermic effect at 120 °C, is due to the evapourization of water. The material burns intensively at 300 – 460 °C temperature. The mass weight losses are correspondingly 15.7 and 7.4 %. The thermographic investigation results show that waste burning occurs at higher temperatures, than for sawdust temperature. As a result, the CO emissions into the atmosphere are lower. The best results were achieved when this waste was added to the ceramic mass with sawdust at a ratio of 2:1.

Keywords: product contaminated soil, waste, sawdust, porous ceramic, CO emision.

INTRODUCTION

Various non-plastic materials and porous inorganic (perlite, vermiculite) porisizing additives or burning-out additives (wooden sawdust, polystyrene granules, etc.) are used for the production of porous ceramics [1 – 6].

These are most often used various grinded or milled solid organic combustable or porous materials. At present, various liquid combustable additives are being used. In the recent investigations a liquid chemical industries waste "Vuppor" as well as petroleum refining waste – petroleum coke are used [7, 8].

Porous inorganic porisizing additives are very expensive, e.g. one ton of porisized vermiculite costs about 550 euros. The use of cheap organic porisizing additives for ceramic mass emits large amounts of CO gases due to the low burning temperatures (320 – 500 °C) in tunnel furnace preheating zone.

Porisized wall blocks of various dimensions are manufactured in Lithuania with a mass density from 850 to 950 kg/m^3 with a heat conductivity coefficient from 0.092 to 0.2 m^2K/W. The necessary ceramic shiver porosity and density is obtained by adding up to 13 % (by mass) of wooden sawdust [9]. The sintering of such articles in tunnel furnaces causes CO concentration up to 11522 ppm or 14400 mg/m^3 in flue gases. The maximum admissible CO concentration is 4000 mg/m^3. The CO concentration in flue gases can be reduced by replacing part of the sawdust by other ceramic porisizing additives, which would burn-out in the sintering zone and achieve the required ceramic porosity.

During petroleum refining, among other wastes, soil contaminated with oil products is accumulated. This is a viscous mixture of soil, petroleum products and water. Up to several hundred tons of this waste accumulates every year. This could satisfy the yearly requirement for one technological production line, however, at present, there are no other satisfactory ways to utilize it.

The purpose of this investigation was to explore the possibility to use soil contaminated with petroleum products for the production of porisized ceramic articles.

EXPERIMENTAL

The following raw materials were used for the formation of specimens: Girininku deposit hydromicacious carbonate clay of the following chemical composition, %: SiO_2 – 47.2; $Al_2O_3 + TiO_2$ – 18.3; Fe_2O_3 – 7.1; MgO – 3.8; CaO – 7.1; K_2O – 2.9; Na_2O – 0.8; Kn – 12.1. Additives used were: sand, milled sintered brick chamotte, wooden sawdust, with a 37.5 % moisture content, soil contaminated with petroleum products, the moisture comtent was about 54 %. This is a thick soil, petroleum product and water mixture mass. Because of the high water content in this mass, three mixture variations were prepared for the experiments, i.e. when petroleum product contaminated soil radio with wooden sawdust was 1 : 1, 1 : 2 and 1 : 3. JSC "Roku keramika" porous wall block production mass was used for laboratory investigations by equivalently changing the sawdust with soil containing petroleum products and sawdust mixtures. The laboratory specimen formation mixture compositions are given in Table 1.

Cylindrical specimens (31 × 40 mm) were formed by hand. The specimens were dried and burnt in a muffle furnace with a 3 – 4 °C per minute rate incolase up to 960 °C and holding that temperature for 1 h. According to the specimens dimensions and mass, the ceramic shivers density was calculated. Water absorption was determined by placing the specimen in ambient temperature water for 48 h. The compressive strength was also determined. The most important porous ceramic articles effectiveness indices are a low shiver density and high water absorption. These were evaluated according to the results obtained by

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using the liquid burning-out additive “Vuppor” results for porisizing similar mineral and chemical composition clays [7], also by comparing them with porisized shiver properties and results obtained using burning-out additive emulsified petroleum coke (R1 specimen) and wood sawdust (E specimen).

Table 1. Laboratory specimen formation mixture compositions

Specimen marking	Formation mixture composition, %
RO	Without burning Roku deposit clay – 80.4 %; sand – 9.3 %; milled sintered brick chamotte – 10,3 %
R	Production porisized blocks: Roku deposit clay – 75 %; sand – 8 %; milled sintered chamotte – 9 %; sawdust – 8 %.
R1	Roku deposit clay – 75 %; sand – 8 %; milled sintered brick chamotte – 9 %; sawdust – 4 %; petroleum coke emulsion with 5 % heavy fuel oil addition – 4 %.
R2	Roku deposit clay – 70 %; sand – 8 %; milled sintered brick chamotte – 9 %; sawdust – 4 %; soil contaminated with petroleum products and sawdust mixture (1:1) – 13 %.
R3	Roku deposit clay – 70 %; sand – 8 %; milled sintered brick chamotte – 9 %; soil contaminated with petroleums products and sawdust mixture (2:1) – 13 %
R4	Roku deposit clay – 70 %; sand – 8 %; milled sintered brick chamotte – 9 %; soil contaminated with petroleum products and sawdust mixture (3:1) – 13 %.

Thermographic investigations were conducted on a Q-1500 derivatograph. The inert material was corundum (temperature increase rate 10 °C/min). X-ray diffraction analysis of burnt specimens was performed by using a X-ray diffractometer DRON-1 with Co anode and Fe filter.

RESULTS AND DISCUSSIONS

Thermographical investigations of soil contaminated with petroleum productions (Fig. 1) have shown that the specimen mass loss reaches 54 % in the 20 – 140 °C temperature interval, while the endothermic effect at 120 °C is due to water vapour. The material burns most intensively at 300 °C and 460 °C temperatures. The mass losses are 15.7 % and 7.4 % correspondingly.

The preformed thermographical investigation results show that the burning – out of this waste material occurs at a higher temperature than wooden sawdust. This is the main reason for which this waste material could be utilized by including it into the ceramic mass mixture with sawdust.

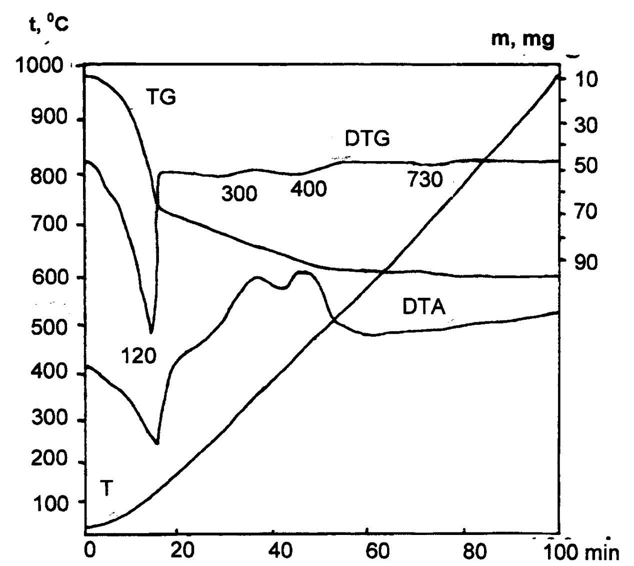

Fig. 1. Thermogram of soil contaminated with petroleum products. T – destruction temperature rate, TG – mass change curve, DTG – mass rate variation curve, DTA – heat change curve

Table 2. Porisized shiver properties, using “burning-out“ additives: soil contaminated with petroleum products, petroleum coke emulsion, “Vuppor”", sawdust and liquid additives

Physical-mechanical properties	Soil contaminated with petroleum products and petroleum coke emulsion additive amount % based on dry solids						“Vuppor“ additive amount, mass % based on dry solids			
	Specimen index									
	R0	R	R1	R2	R3	R4	0	1	3	5
JSC “Rokų keramika” production clay mass without additives	0									
Amount of soil contaminated with petroleum products	–	–	–	13.0	13	13		–	–	–
25 % Petroleum coke water emulsion with 5 % heavy fuel oil mass	–	–	4.0	–	–	–	–	–	–	–
Formation mass humidity, %	25.0	24.1	23.8	25.6	25.1	24.3	29.2	37.3	45.2	50.0
Specimen drying contractions, %	-	–	–	–	–	–	–8.1	–8.6	–9.4	–10.7
Specimen drying contractions, %	5.9	7.2	6.3	5.4	6.4	5.9	–	–	–	–
Specimen deformations during burning, %	–	–	–	–	–	–	–0.2	–0.9	–1.6	–2.0
Volume specimen contraction during burning, %	1.8	–	4.6	3.5	2.9	0.5	–	–	–	–
Mass losses, %	9.5	6.5	20.0	17.4	16.5	15.7	11.8	12.1	13.6	15.3
Water absorption, %	17.7	21.9	31.2	32.0	35.3	33.3	19.1	21.4	26.7	31.0
Ceramic shiver density after burning, kg/m^3	1792	1522	1348	1340	1365	1410	1707	1678	1554	1477
Burnt specimen compressive strength, MPa	39.6	15.0	8.5	6.1	11.1	8.4	65.1	38.0	23.8	16.0
Water capillary height increase, mm/h	26.0	27.0	27.5	36.0	40.0	51.0	18	36	65	86

Laboratory specimens with 13 % soil contaminated with petroleum products and wooden sawdust mixture additive (Table 1) were burnt at a maximum 980 °C temperature and then the obtained porisized shiver's properties were investigated. The obtained results are given in Table 2.

CO amount emissions into the atmosphere, depending in the heating temperature are shown in Fig. 2.

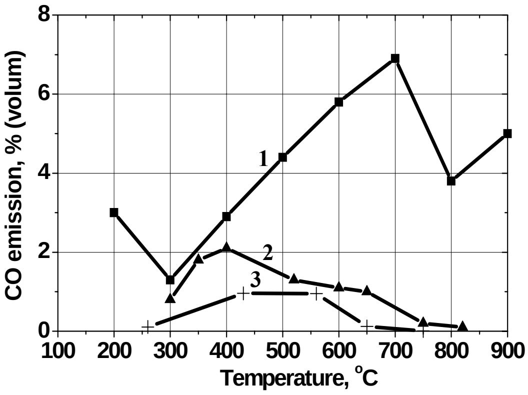

Fig. 2. Dependence of CO gas emission on temperature of specimens R are heated in a hermetic furnace (1), with air feeding (2) and specimen R1 (3)

Properties of ceramics obtained using soil contaminated with petroleum products (specimens R2, R3, R4) were compared with ceramic properties data obtained using petroleum coke emulsions (R1), sawdust (R) and "Vuppor" additives. The porisized ceramic quality was evaluated according to the shiver's density, water absorption and compressive strength.

The density, water absorption compressive strength values were as follows: using R2 mixture – 1340 kg/m^3; 39.0 %; 6.1 MPa. In the case of R3 – 1356 kg/m^3; 35.3 %; 11.1 MPa, while for R4 – 1410 kg/m^3; 33.3 %, 8.4 MPa. The best results were obtained when a mixture soil contaminated with petroleum products and sawdust at a ratio of 2:1 (R3) was used in the ceramic mass. The porosity values for ceramics with soil contaminated additive are close to that for petroleum coke modified ceramics.

The porosity of ceramics prepared by using these additives is higher then those achieved for sawdust or "Vuppor" additives, however the compressive strength values are lower then for ceramics with "Vuppor" additive. However the reached strength values fulfill all the requirements for porous ceramics (Ceramic blocks, LST 1270-92).

As we can see the CO emission at the furnace zone into the atmosphere is ~3 times lower when the soil contaminated with petroleum products (as well as petroleum coke emulsion) is used in place of sawdust.

X-ray diffraction analysis of burnt specimens was also conducted. X-ray patterns of the specimens without "burning-out" additives (R0) and specimens with soil contaminated with petroleum products (R3) are presented in Fig. 3. The same minerals, quartz (Q), fieldspar (Fš), diopside (D), hematite (H) were found in both patterns, however the peak intensivity was higher in the specimens containing soil contaminated with petroleum products.

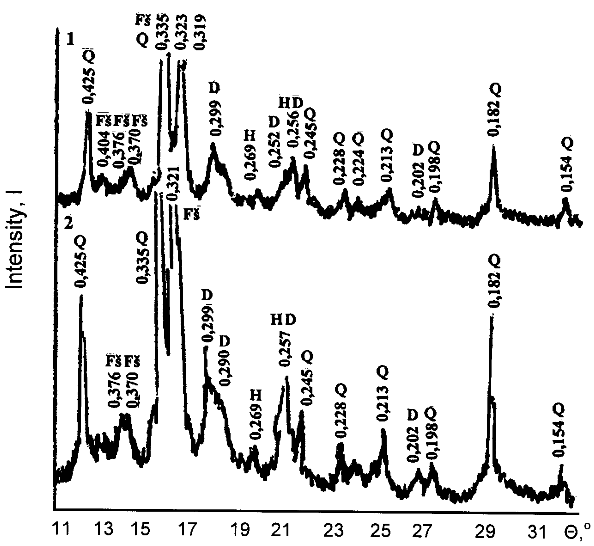

Fig. 3. X-ray diffraction patterns of porous ceramic specimen RO (1) and R3 (2). Q – quartz, Fš – fieldspar, D – diopside, H – hematite, DH – overlap of hematite and diopside peaks

CONCLUSIONS

1. The possibility of utilization of soil contaminated with petroleum products in porous ceramic production was demonstrated;
2. The petroleum products present in soil burn-out at higher temperatures then wooden sawdust, so the CO emissions into the atmosphere are lower;
3. The best ceramic shiver density, water absorption values were achieved using soil contaminated with petroleum products additive in comparison to the other investigated "burning-out" additives.

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