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Peculiarities of Firing Porous Clay Products With Burning Out Additive

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The paper considers the problems associated with firing of porous clay masonry units with large amounts of burning out additive. One of the major problems is the reduction of the pyrolysis products and CO in burnt gases as well as reducing density of the product. To solve the above problems, tests aimed at comparing the behaviour of various clay mixture in burning and determining the amounts of the released gases during this process were made. The use of expanded polystyrene was found to be most effective for reducing the weight of ceramic body. Based on the data obtained, the amount of the released CO per unit weight of the introduced burning out additive was calculated. When expanded polystyrene was added, the release of CO per one gram of the material was the highest; however, an absolute emission value was the smallest.

Keywords: porous clay masonry units, burning out additive, reduction of CO emissions.

INTRODUCTION

To reduce the density and thermal conductivity of clay masonry units, as well as the amount of fuel for their manufacture, porous products should be used. When the density of ceramic articles is 1800 kg/m^3, the density of porous products can reach 900 kg/m^3 – 1000 kg/m^3. Various kinds of burning out additives, e.g. peat, sawdust, wooden board grinding dust, coal, coke, etc. are used for pore-formation [1 – 4].

Burning of clay with large amounts of burning out additive has not been profoundly investigated yet [5]. Moreover, there is an additional problem associated with the increasing amount of CO in burnt gases harmful to the attending personnel. Besides, carbon monoxide causes greenhouse effect. The calculations show that 100 Mt CO have the same effect on warming of the climate as 5 Mt CH_4 [6].

The problem of reducing the amount of carbon monoxide released in burning clay masonry units is usually solved by replacing sawdust with other materials. Using petroleum coke [1] can reduce CO emission in the atmosphere at 400 °C to about 0.45 of its former value because this additive burns slower and at a higher temperature. However, peat or its mixture with sawdust are added in the quantity of about 15 % of the dry mass in clay masonry units manufacture because of their low cost. Peat starts burning in the air in clay masonry units at 250 °C, while losing about 43.3 % of its mass at 500 °C. However, 59.9 % of sawdust burns out at 380 °C [2].

A large amount of fuel in the mixture affects its rate of burning out in two ways. When the amount of fuel is increased, more oxygen should get into the mixture. This increases the time needed for fuel to burn out. However, when the porosity of the material increases, the rate of burning also increases. Dehydration of clay minerals retards the oxidation of the coke remained in the fuel because partial pressure of the water in the pores of the material is increased [7].

In the present investigation, the kinetics of burning of various materials used for pore-formation in ceramic body were studied in determining carbon monoxide emission and the effects of burning modifiers, oxidants [8] and fire retardants, on pyrolysis and burning.

EXPERIMENTAL

In the present work, the clay from Kertupis deposit, having the following composition: SiO_2 – 46.88 %, Al_2O_3 + TiO_2 – 16.08 % , Fe_2O_3 – 5.31 % , CaO – 10.36 %, MgO – 4.37 %, K_2O + Na_2O – 2.67 %, SO_3 – 0.19 %, L.o.i.- 14.09 %, was used. The burning out additive for pore-formation in clay mixtures consisted of wooden board grinding dust (WD) and fine expanded polystyrene (EP). Granulometric composition of these materials is given in Table 1. The salts KNO_3 and $Na_2B_4O_7$, modifying wood burning, were introduced as solutions by moistening and drying out pore-forming additives. The mass obtained from dry materials was moistened and cured for 72 hours. Then, cylinders which are about 40 mm height and having 30 mm diameter were formed. The specimens were dried for 48 hours under natural conditions and then placed into a drying oven at the temperature of 105 °C ±5 °C for 24 hours. The water adsorption was determined according to LST EN 771-1:2003, compressive strength – according to LST EN 772-1:2003. A concentration of burnt gases was determined by gas analyser TESTO 342-3.

The burning of clay specimen in the special gas tight furnace was studied, allowing for determining the variation of specimen weight accurate up to 0.005 g. In Fig. 1, a system used in the furnace for gas off take and uptake for analysis as well as the control and data recording system are presented. During the burning of the specimens, 4.0 ±0.2 l/h of gases were removed from the kiln. The rate of the temperature rise was constant in all cases, being automatically controlled and ranging from 50 °C to 300 °C – 3 h, and from 300 °C to 950 °C – 4 h.

Compositions of the mixtures used in the present investigation are given in Table 2.

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Table 1. Granulometric composition of the materials

No	Material	Material retained on sieve, %						
		5.0 mm	2.5 mm	1.25 mm	0.63 mm	0.315 mm	0.14 mm	<0.14 mm
1	Wooden board grinding dust		3.6	0.4	7.2	43.2	35.2	10.4
2	Fine expanded polystyrene	0	0	46.0	33.0	15.0	6.0	0

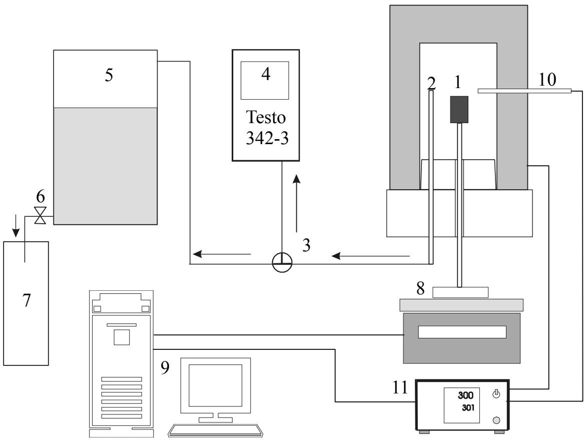

Fig. 1. A system of furnace control and gas off take: 1 – furnace muffle with a specimen, 2 – gas off take pipe, 3 – three-way valve, 4 – gas analyser, 5 – sealed water container, 6 – valve, 7 – measuring cylinder, 8 – scales, 9 – computer, 10 – thermocouple, 11 – temperature regulator

Table 2. Composition of mixtures

Composition No	The materials and its amount, %			Notes
	Clay	WD	EP	
1	100	–	–	–
2	90	10	–	–
3	90	10	–	WD treated by 20 % KNO_3 solution (1 g of WD – 0.4 g of KNO_3)
4	90	10	–	WD treated by 19 % $Na_2B_4O_7$ solution (1 g of WD – 0.365 g of $Na_2B_4O_7$)
5	96	–	4	–

RESULTS AND ANALYSIS

Physical and mechanical properties of fired specimens made of the ceramic mixtures which are given below were determined. The data obtained are presented in Table 3.

These data show that the density of ceramic body is most significantly reduced by EP additive (No 5). Though a small per cent of this material by weight was added, its volume was large because of low density. However, water adsorption remains in the same range as that of a commercial mixture (No 2). The addition of KNO_3 oxidator (No 3) increase water adsorption, while firing of the mixture was largely affected by sodium tetra borate (No 4). In this case, the highest contraction in firing was observed, when the specimen was fired only from the outside but its water adsorption remains high.

Table 3. Physical and mechanical properties of fired specimens

Composition No	Density, kg/m^3	Water adsorption, W_{48}, %	Compression strength, MPa
1	1768	19.0	35.2
2	1460	25.4	21.6
3	1420	30.2	19.2
4	1480	22.3	24.3
5	1110	27.5	13.1

The kinetics of weight variation of fired specimens was determined and are given in Fig. 2. Since the dimensions of the fired specimens matched the wall thickness of clay masonry units, the information about actual processes taking place during their firing was obtained. The data on the changes in weight of the fired specimens are provided in terms of the weight variation rate. Since the time of firing of the specimens makes only one-fourth of the time of clay masonry units fired in an actual kiln, the temperatures on the top of the curves experimentally obtained for the processes may be slightly higher.

The first peak of weight changing rate on all curves is associated with the removal of free moisture from the specimens. This takes place at the maximum temperature of 150 °C – 160 °C. The second peak is related to wood pyrolysis and the removal of gases at that time. It can be observed at various temperatures: at 290 °C for specimen No 2; at 262 °C for specimen No 3 and at 275 °C for specimen No 4. For a specimen No 5 with expanded polystyrene addition, this effect is longer, reaching the peak at 400 °C. The highest effect is observed in specimen No 3. In this case, the process is also accompanied by KNO_3 splitting and burning of organic materials. The addition of sodium tetra borate (No 4) also accelerates wood pyrolysis. Then, in the temperature range from 300 °C to 450 °C, slow burning of the remaining wood and expanded polystyrene particles takes place.

At 520 °C – 530 °C the highest increase of the rate of hydroxyl water removal from clay minerals can be observed in all specimens, while at the temperature from 600 °C to 880 °C the observed peaks of weight variation match decarbonising of $MgCO_3$ and $CaCO_3$.

The data on the changes in gas composition during the process of specimen firing are shown graphically in Fig. 3 – Fig. 6.

The tests have shown that the kinetics and intensity of CO emission in burning various compositions vary to a large extent. When the combustion addition is D, intense CO formation can be observed in the range of temperatures from 250 °C to 300 °C, while at the temperature, ranging

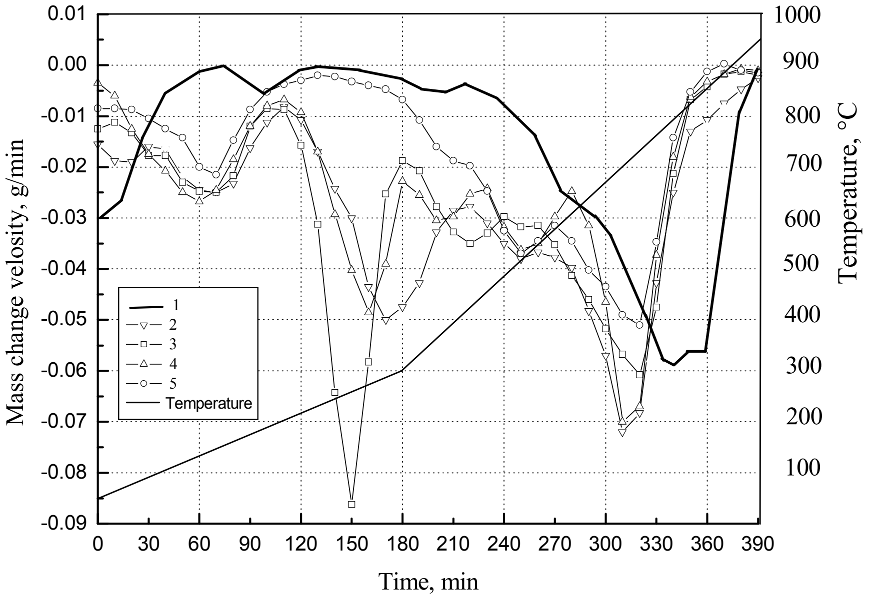

Fig. 2. The relationship between the specimen mass change rate, time and the temperature of firing. 1, 2, 3, 4, 5 – specimen composition numbers (according to Table 3)

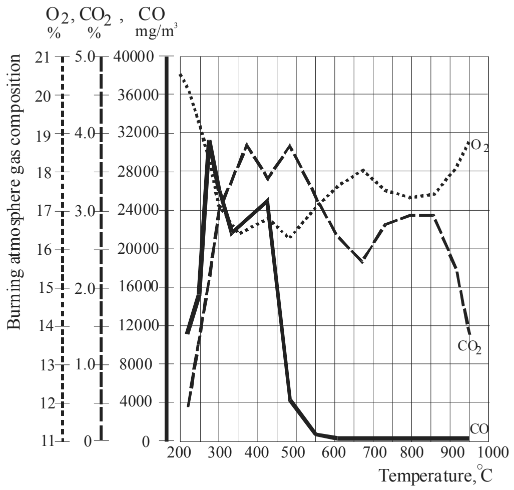

Fig 3. The relationship between gas composition and the firing temperature of specimen No 2

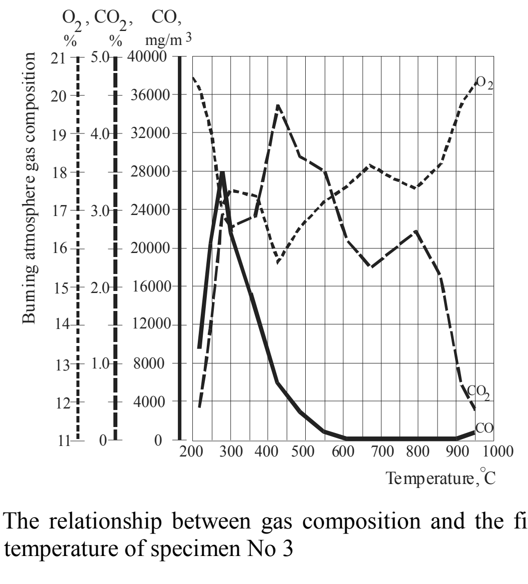

Fig 4. The relationship between gas composition and the firing temperature of specimen No 3

from 330 °C to 350 °C, it is not so rapid, intensifying only at a higher temperature of about 425 °C.

When the temperature rises up to 475 °C, the amount of CO is sharply decreased (Fig. 3). A similar effect can be observed when sawdust impregnated with sodium tetra borate is used (Fig. 5). However, CO emission is observed until the temperature of 660 °C is reached. When sawdust is impregnated with potassium nitrate, no second peak of CO concentration can be observed (Fig. 4). When expanded polystyrene is added, the relationship between CO formation and temperature is essentially different (Fig. 6) – the amount of CO is gradually increased in the temperature range from 200 °C to 480 °C and then is abruptly decreased.

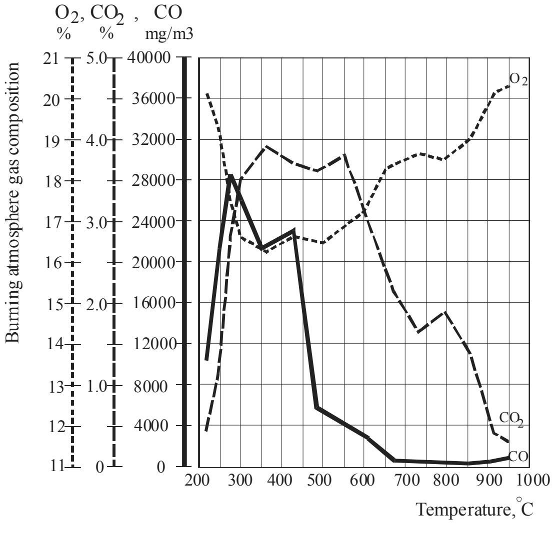

Fig 5. The relationship between gas composition and the firing temperature of specimen No 4

Since the air flow per kiln (≅4.0 l/h), as well as gas concentration and the reduction of the specimen weight during CO emission, are known, the amount of CO released was calculated per unit weight of the introduced combustion addition. The results obtained are given in Table 4.

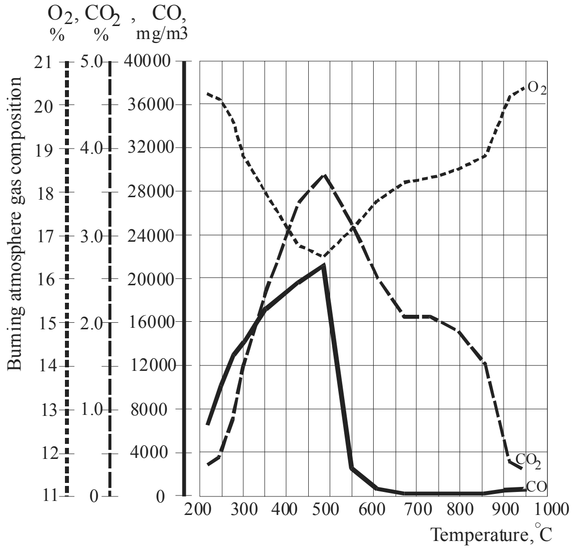

Fig 6. The relationship between gas composition and the firing temperature of specimen No 5

Table 4. Amount of CO released by 1 g of combustion addition

Composition No	Reduction of specimen weight, g (temperature range 217 °C – 610 °C)	The amount of the released CO, mg	CO amount released by 1 g of combustion addition, mg
2.	5.500	179.33	32.60
3.	5.925	140.30	23.68
4.	4.835	185.95	38.46
5.	2.655	138.92	52.32

As shown by the data obtained, the addition of KNO_3 decreases CO emission. The use of sodium tetra borate increases CO emission compared to specimen 2. When EP is added, CO emission per unit mass (1 g) is the highest, though the absolute value is the lowest. Moreover, the addition of EP is much more effective than WD in reducing the density of ceramic body.

CONCLUSIONS

The following conclusions can be drawn from the investigation:

1. Fine expanded polystyrene is an effective burning out additive used in manufacture of clay masonry units. The addition of 4 % of expanded polystyrene into the ceramic mixture decreases its density from 1768 kg/m^3 to 1110 kg/m^3.

2. The amount of CO released per unit weight of the introduced combustion addition was calculated. It was found to be equal to 32.6 mg/g for wood dust additive, 23.7 mg/g for wood dust impregnated with potassium nitrate, and 52.3 mg/g for expanded polystyrene. When expanded polystyrene is added, the largest amount of CO is released per one gram of its mass. However, the absolute value of emission from the product is the smallest in this case.

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