

**ANALYSIS OF CERAMICS THAT WORKED IN THE EROSIVE ENVIRONMENT
OF COMBUSTION FOR 100.000h AT 600-700°C AND THE STREAM SPEED 5 m/s.**

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Abstract

The structural analysis of the thermo-insulation brick and ceramic cover of the third boiler of the working Kaunas Powerstation was carried out. It has been determined that the brick whose thickness is ~63 mm after staying in the energetic boiler at high temperature (1200-1400 °C) around 98,985h demonstrates structural deposition. During the mentioned process that causes adequate alternations, the increase or decrease of the chemical elements in the parts and layers of the ceramic brick and its cover has been observed. It depends on the distribution of temperature within the volume of the brick.

Key words: ceramics, high temperature, thermo-insulation, structure, needle-shaped, brick

1. PROBLEM FORMULATION

When affected by high temperatures, many fire resistant demonstrate the zone deposition of the material. Such zone structures occur in the magnesium, cromomagnezium and forsteritium products, when they are put into the open-hearth, electrofusion and other types of furnaces [1]. In such furnaces the temperatures of the ceramic surface reach 1300-1500°C. The amounts of the combustion products in the volume of the furnace make 90-110 kg/h. At such temperatures the zones are formed in which certain properties of the ceramic material may be changed, do them. During beating the thermo stretchings may develop that may even deteriorate the structure of the material.

The formulation of the zones in the volume of the ceramic through which thermal flows pass may be influenced by the re-distribution of the easily fused components inside the material. In the mentioned case, most probably, the formation of the zones may be affected by the gas materials diffusing from the furnace environment that are, in their turn influenced by the different fields of temperature within the volume of the material. The experiments showed [2] that after 2 hours of testing at 1400°C, the material who composition is: $\text{Al}_2\text{O}_3 > 57,0 \%$; $\text{SiO}_2 < 39,0 \%$; $\text{Fe}_2\text{O}_3 < 1,0\%$; $\text{CaO} < 1,6\%$ acquire the strength by pressure 72 MPa. After 5 hours of testing it reaches 105-120 MPa. Thus, it may be claimed, that high temperature treatment affects the structure of a fire resistant as well as its strength.

In thermal aggregates, when the temperature is high, the fire resistant get into a direct contact with gas environment in which hard particles, dust, clinker elements, ore and hard products of erosion occur, at such conditions, the interaction between the high temperature environmemt wiyh the fire resistant takes place. The going on processes and their character determine the time of the fire resistant durability. In certain cases, the gas environment has a deteriorating effect on the timbering. For instance, under the blast-furnace contitions at low temperatures, carbon oxide operates as a deteriorator of the fireclay products, since carbon oxide is decomposed due to the following reaction:



During this reaction carbon soot is formed that is often distributed in the open pores of the materials surface. Due to their large volume the stretchings in the material's structure are formed. When reacting with iron combinations, carbon soot form FeC that has a considerably larger, volume than the volumes of the reacting materials the result of which is the interior mechanical stretchings that decrease the strength.

With time, the deterioration of the fire resistant caused by gas reactions and their thermo-insulation properties may considerably alter. It depends on the general porosity of the fire resistant and the number of the pores on the surface. Small pores whose size is close to the size of the free movement of gas molecules are especially fit for the reaction to take place. Therefore it is important to know the amount of such pores ($\sim 10^{-5}$ cm and smaller) in the tested surface of the fire resistant and in its mass.

Knowing that with the participation of the catalysis carbon soot is exuded from methane, ethane and other carbon hydrogen combinations it is possible to present the information to the system of the "Lithuanian Gas" that the average composition of natural gas is as follows: methane – 97,824%, ethane – 0,902%, propane – 0,254%, etc., [3]. Hence there is a potential for the dispersion of carbon soot in the gas environment of the furnace and in the flow of the combustion products. In case the process takes place on the surface of the fire resistant or within its volume, it is the catalyst that plays a very important role. It may be metal ferrum. However, carbon soot does not make the reason for the deterioration of the fire resistant. Its deterioration is related with the ferrous oxide reaching the metal condition and thus reacting with carbon monoxide and forming carbides and oxides. These final reaction's take place with the growth of the volumes of the material that may have an impact on the fire resistant.

2. EXPERIMENTAL TESTS

In the gas environment of the energetic boiler, and in the flow of the combustion products not to mention the ceramic itself, vanadium is often found the combinations of which show the oxidation degree from +2 to +5. Its combinations with the oxidation degree +5 are of highest resistance that regarded as typical. The vanadium oxidation starts at 300°C and becomes intensive at 600-700°C, when the formed vanadium pentoxide is melting. At high temperatures vanadium reacts with many nonmetals there by forming carbides, nitrates, etc. The vanadium combinations are active catalysts [4].

The analysis of the thermo-insulation ceramics that operate in the energetic boilers was carried out on the basis of the samples of the fire resistant that were taken out of the wall of the third boiler used in the Kaunas Energy System Service after the exploitation which lasted for 98.985 h. The ceramic blocks of the thermo-insulation wall in the shape of standard bricks were investigated, described and later mechanically split to reach the deepest interior layers of the ceramic.

The picture of the split off piece of one brick is given in Figure 1. Consider:

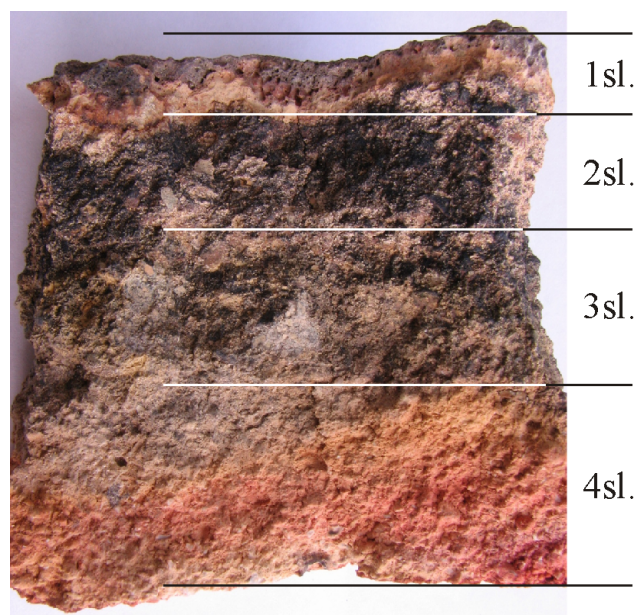


Fig. 1. The picture of the thermo-insulation ceramic brick structure in the split off transvenal part. The working time of the brick at high temperature is 98.985 h. in the wall of the third boiler. The temperature of the environment is 1200-1400°C.

The thermal flow enters the brick volume through the surface of the brick (Fig. 1), marked as Layer 1 the brick has four layers (Layer 2, Layer 3, Layer 4). Such division into layer allowed for the couvenieme of description.

When the ceramic bricks were laid into the boiler, their surface was covered with the ceramic mass. Consider Figure 2:

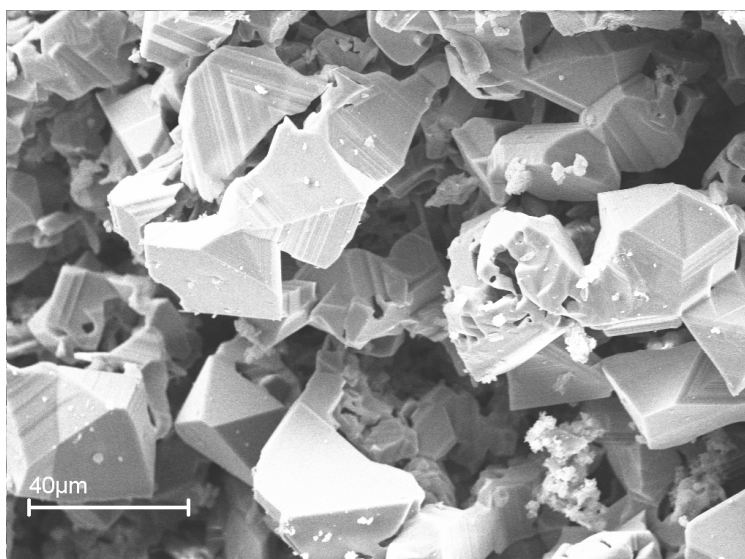


Fig. 2. The surface of the thermo-insulation ceramic brick cover that has a contact with the high temperature combustion products. The thicknes of the cover is ~10 mm.

The temperature of the environment is 1200-1400°C

In Figure 2 the crystallites are observed on the separate surfaces of which the distinct edges are seen. It is the ceramic that was formed from the special ceramic cover of the surface when the boiler was operating and that had a direct contact with the interior environment of the boiler and the combustion products that were formed at high temperature. With the use of the electronic microscope SEM LEO EVO50 and the disperse spectrometer EDS Oxford Instrument, it was determined, that the thermo-insulation ceramic mass had undergone considerable alterations (see crystallized bodies shown in Figure 2). The crystals protecting the eroding surface and an entire system of the baked ceramic bodies that formed the porous ceramic covering the eroding surface grew on the surface of the samples through its direct contact with the high temperature flow of the combustion products (whose temperature is the highest and may reach 1200-1400°C). The composition of this material is as follows (mass %): Fe – 48,25; Al – 7,07; O – 26,97; Ni – 5,89; Mg – 3,35; and C – 3,27. The combinations that are found under the surface also include: Si – 1,28; Ca – 1,59; Ti – 1,04; and Cr – 1,19.

The analysis of the deeper layer of the cover surface (around 5 mm deep) showed, that the formed ceramic is a porous ceramic wall that well resists the thermal blows and does not undergo any considerable alterations (Figure 3). Only in some areas the bigger structural blocks were observed that consisted (mass %): Al – 17,54; Si – 18,42; Ca – 7,49; Na – 1,98 and O – 54,57. Meanwhile, the largest part of the ceramic mass consisted (mass %): Fe – 4,63; Ti – 1,38; K – 0,71; Ca – 5,79; Si – 19,92; Al – 19,27; Na – 1,31; and O – 46,99; Consider:

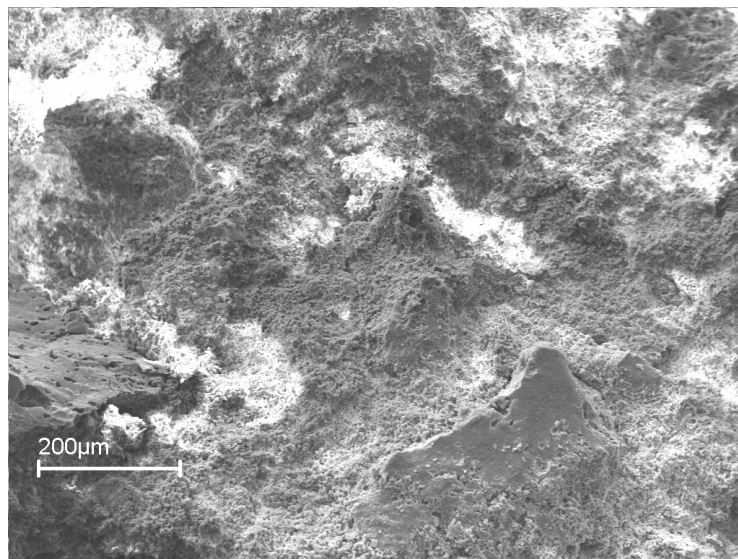


Fig. 3. The structure of the cover ceramic of the thermo-insulation ceramic brick.

Depth: ~5 mm from the eroding surface.

The temperature of the environment is 1200-1400°C.

It should be stressed that the good cohesion between the layer of the thermo-insulation cover and the surface of the ceramic brick testify to the high quality of the performed ceramic cover procedure.

The thermal flow coming from the heated environment of the boiler to the walls first passes through the cover of the thermo-insulation ceramic and then enters Layer 1 of the ceramic brick whose structure is presented in Figure 4. Layer 1 consists of many new bodies that were formed during the exploitation of the ceramic, such as the needle-shaped bars of various size of cross-section and of relatively large length. They are found in the pores of the ceramic and within the volumes of the cracks that appeared in the ceramic. Their chemical composition is characterized as follows (mass %):

Fe – 18,56; V – 25,91; Ti – 2,56; Si – 9,08; Al – 3,41; Na – 1,17 and O – 39,31. Meanwhile, the chemical structure of the formed crystals is characterized in the following way (mass %): Fe – 3,03; V – 45,94; Si – 6,93; Al – 3,22; Na – 2,21; and O – 38,66. These are the ceramic crystalline materials formed on the basis of vanadium that well operate under the high temperature conditions.

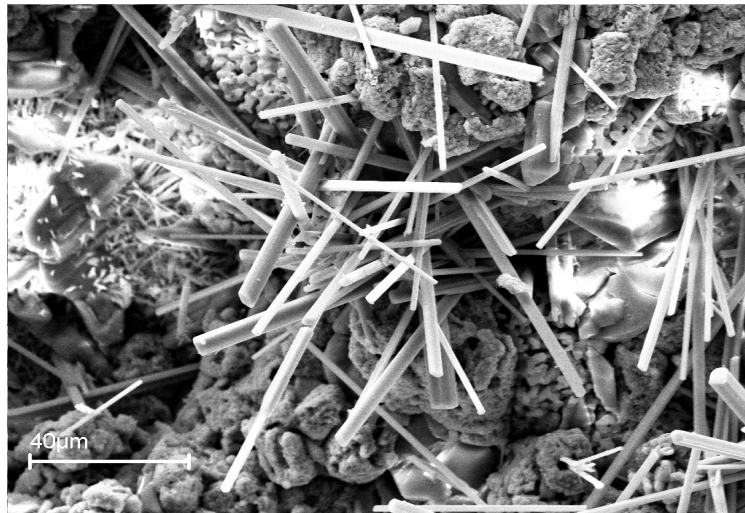


Fig. 4. The structure of the first layer of the thermo- insulation ceramic brick
(the split off surface). Depth: ~5 mm from the eroding surface.

When passing through the layers of the ceramic the heat flow is constantly decreasing thus losing some amount of its energy that is given to heat the ceramic. The analysis of Layer 2 of the ceramic brick (Fig. 5) also laid to the discovery of its specific ceramic structure that differs from the above described structures of the tested ceramic brick. The grains on the surface of the second layer resemble the shells of the opening buds that are double. Their chemical characteristics is described as follows (mass %): Fe – 2,13; V – 1,25; Ti – 0,52; Si – 13,00; Al – 34,54; Na – 0,76; and O – 47,80.

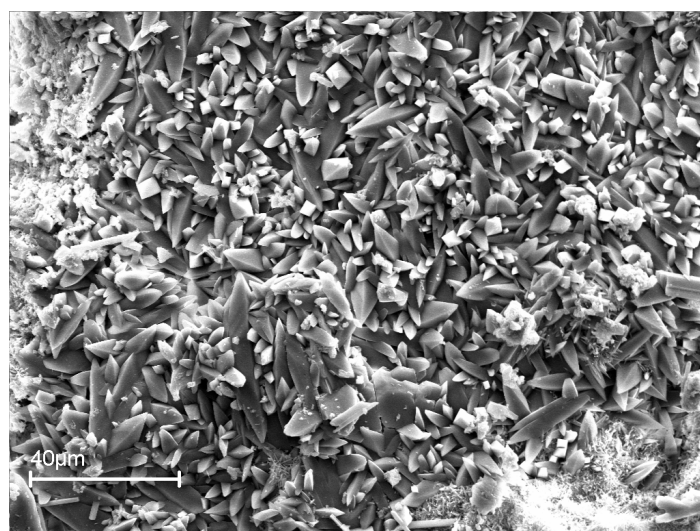


Fig. 5. The structure of the second layer of the thermo-insulation ceramic brick
(the split off surface). Depth: ~20 mm from the eroding surface.

In the discussed Layer 2, vanadium is accumulated in the new bodies whose chemical characteristics may be expressed in the following way (mass %): V – 46,22; Si – 9,82; Al – 2,46; Na – 2,62; and O – 38,88.

The ceramic formed in Layer 3 of the thermo-insulation ceramic brick (Fig. 6) is characterized by those elements (mass %): V – 5,89; Fe – 2,94; Ti – 0,79; Mg – 0,61; Al – 16,49; Si – 18,42; Na – 1,98; S – 1,14; K – 1,24; and O – 50,49. Meanwhile, the composition of the new bodies of the third thermo-insulation layer markedly differs from that of the second layer. Consider (mass %): V – 16,86; Fe – 1,99; Al – 10,50; Si – 15,66; Na – 2,66; S – 0,66; K – 0,90; and O – 50,74. Here the new bodies consist of a considerably smaller amount of vanadium and iron, and a larger amount of silicon, aluminium and natrium. In the new bodies formed in this layer sulphur and potassium have been discovered.

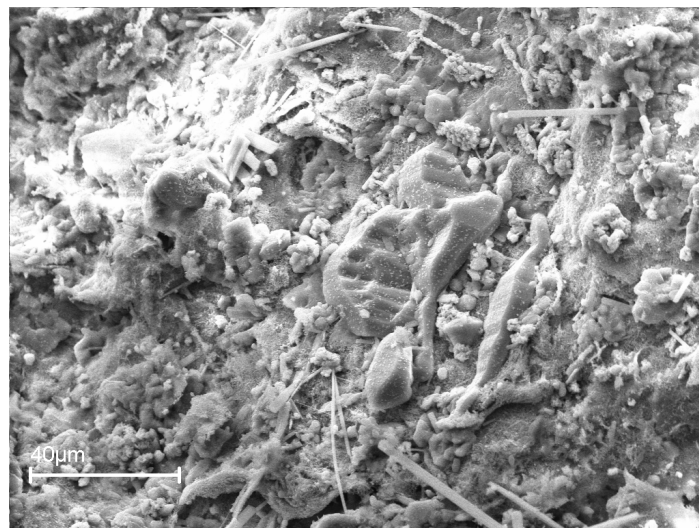


Fig. 6. The structure of the third layer of the thermo-insulation ceramic brick (the split off surface). Depth: ~35 mm from the eroding surface.

Layer 4 of the thermo- insulation ceramic brick (Fig. 7) demonstrates a considerable number of the low temperature ceramic characteristics. In its structure, the formation of natrium combinations have been observed in the shape of separate balls that are scattered across the observed area. These are the combinations of natrium, sulphur and oxygen. The composition of such a material is as follows (mass %): Na – 25,98; S – 21,76; O – 46,09; Si – 0,72; Al – 0,70; Mg – 4,74. Among the mentioned elements the ceramic mass includes (mass %): Fe – 1,16; Ti – 0,45; S – 0,31; Si – 24,43; AL – 19,67; Na – 0,70; O – 53,29.

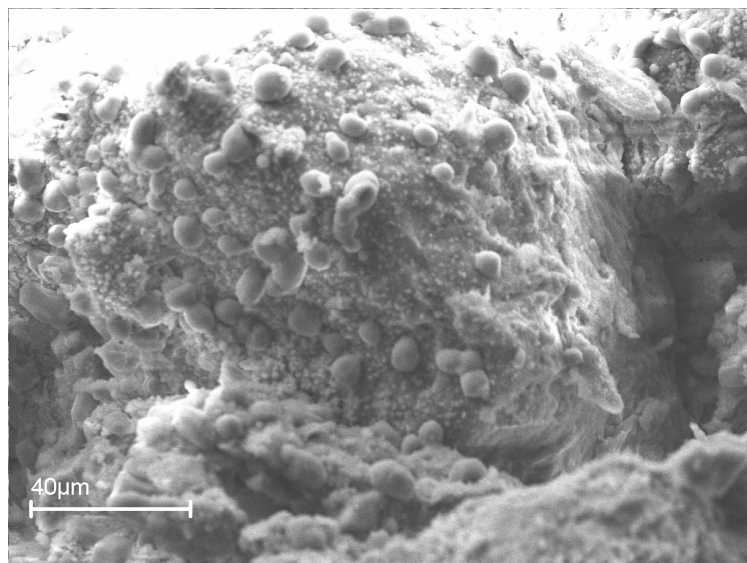


Fig. 7. The structure of the fourth layer of the thermo-insulation ceramic brick
(the split off surface). Depth: ~55 mm from the eroding surface
(the thickness of the brick is ~63 mm).

3. CONCLUSION

The process of the analysis of the thermo-insulation ceramic and its ceramic cover of the Kaunas Power station's third boiler has been started. The tests showed that the ceramic brick taken out of the thermo-insulation ceramic wall, whose thickness was ~6 mm, after its exploitation in the energetic boiler at high-temperature (1200-1400°C) for around 98.985 h obtained structural deposition. During such alterations the increase or decrease of the chemical elements has been observed in some parts and layers of the ceramic brick in relation to temperature by which the discussed layer was affected.

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