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Negative impacts of petroleum coke as an energy source in the brick-making industryZagorka Radojević¹⁾, Milica Vidak Vasić^{*1)}¹⁾ Laboratory for Building Ceramics, Institute for Testing of Materials IMS, Bulevar Vojvode Mišića 43, 11000 Belgrade, Serbia

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ABSTRACT

The technical features of the issues caused by the brick industry's usage of petroleum coke as a fuel were identified in this study. The effects were evaluated in terms of the concentration of hazardous materials in petroleum coke, the CO₂, SO₂ and NO_x emissions in the flue gases, the corrosion of refractory materials in the furnace, the corrosion of pipelines and metal structures in the dryer and furnace, the deposition of sulfate scum on dry products, and the fixation of white scum on finished products. To assess the microstructure and composition of the regions of the samples exposed to flue gases and that inside the material, refractory brick samples from the furnace walls were examined under a microscope. The compressive stress of the part of the sample affected by the flue gas from the kiln is lowered by 37.3 %, which is caused by the agglomeration of sulfate salts and the presence of a high quantity of vanadium. It was determined that, regardless of potential energy savings, the sulfur concentration in petroleum coke must be below 5% if utilized as an energy source in the brick sector since there are suitable conditions for accelerated corrosion processes.

1 Introduction

Petroleum coke (petcoke) is an important commercial product known since the 1930s that is obtained in several refining processes from all types of oil (light or heavy crude oil) during the refining process. This kind of coke has drawn more attention as a fuel substitute over the past 30 years as a result of the decline in high-quality energy sources. After the distillation of heavy fractions of oil, petroleum coke is produced by cracking and carbonizing the residue leftover. The chemical composition of this energy source depends on the characteristics of the raw material (including its geological background) and the production process, but it contains carbon as its main constituent. Petroleum coke exists in two forms: raw coke, which is used as fuel, and calcined coke, which is used as a raw material in the production of aluminum, steel, glass, paper, paints, coatings, fertilizers, etc. High-quality coke contains low amounts of sulfur and heavy metals and is used to produce electrodes in the aluminum and steel industries. About 80% of the world's petroleum coke production is of poorer quality (higher contents of sulfur and heavy metals) and is utilized as a fuel in electricity generation, cement kilns, and other industries. Calcined petroleum coke is used by brick and glass manufacturers because it has a significantly lower ash content compared to other fuels while minimizing the presence of residual hydrocarbons (volatile matter) [1-4]. The ash from the burnt petroleum coke, however, mostly consists of heavy metals [5].

The Environmental Protection Agency (EPA) classifies petroleum coke as a highly stable product that is non-reactive in environmental conditions and has a low potential for health hazards. Petroleum coke is chemically inert and non-toxic (it does not chemically react with water nor dissolve in water, and it is not bioavailable, i.e., organisms cannot absorb it and it does not accumulate in the organism) [6,7]. The majority of petcoke toxicity evaluations conclude that it poses no risk to human health or the aquatic or terrestrial environment and that there are no known carcinogenic, reproductive, or developmental effects. The facilities for the storage and handling of petcoke must include dust management and appropriate permits for the storage of flammable material [1]. Petroleum coke averagely contains 90-95 % carbon and 3-6% sulfur; the other ingredients are hydrogen, oxygen, and nitrogen. Also, metals and organic compounds are present in traces [8]. The heavy metal content present in petcoke makes it potentially dangerous, both due to air release during combustion and to the local environment during storage. Petroleum coke is most often stored in open dumps, although studies have shown that the risk to human respiratory systems is no different from regular coal [1]. Significant amounts of fugitive dust from coke storage and handling operations pose a health risk. A particular problem is created by particles with a diameter of $\geq 10 \mu\text{m}$ (PM₁₀) because these can pass through the throat and nose and enter the lungs. When inhaled, these particles can affect the heart and lungs and cause serious health consequences. Petcoke is an extremely stable fuel, which

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means there is little risk of burning during transport. Due to its high carbon content, it releases up to 10% more CO₂ per unit of energy than ordinary coal when burned. This CO₂ footprint is higher than that of almost any other existing source of energy. Thus, increased pollution control during combustion is needed to remove the acid gas containing H₂S and CO₂, and/or sulfur recovery units [8].

Despite the environmental problems associated with the production and use of petroleum coke, it remains popular due to its cost-effectiveness. It is easily exported and is an attractive source of cheap fuel, especially for developing countries [1]. Notwithstanding the attention paid to the content of sulfur in liquid fuels, especially fuels for transoceanic ships [9], restrictions on manufactured solid fuels, including petroleum coke, have been introduced only in selected countries like Ireland [10] and Great Britain [11]. The sulfur level of coal products and manufactured solid fuels, including manufactured component biomass products, must be less than 2 wt.% on a dry ash-free basis, which is to be reduced to 1 wt.% by 2025 [10,11]. There are no regulations concerning the usage of petroleum coke in Serbia, as long as the flue gas composition is kept within the prescribed limits [12].

In this study, emphasis is given to the problems that petroleum coke causes in the brick industry, related to the wall of the kiln, metal pipes and installations, and the final appearance and quality of dry and fired products.

2 Methodology

In this research, an analysis of the possible negative impacts of using petroleum coke from Serbia with a higher sulfur content was performed.

The analysis included the determination of:

1. Content of harmful constituents in petroleum coke (*Chapter 3.1*),
2. Increases in SO₂ emission at the tunnel furnace emitter (*Chapter 3.2*),
3. Increased corrosion of refractory materials in the furnace at high temperatures (*Chapter 3.3*),
4. Increased corrosion of pipelines and metal structures in the dryer and furnace (*Chapter 3.4*),
5. Deposition of sulfate scum on the surface of dry products and fixation of white scum on fired products (*Chapter 3.5*).

The chemical composition of petroleum coke was determined by the method of energy dispersive X-ray fluorescence (XRF) using the Spectro Xepos device and adequate certified reference materials [13].

The emission of gases at the emitter of the tunnel furnace (without the use of an emission reduction system) was measured with the help of a flue gas analyzer (Environnement S.A., France, model MIR 9000 CLD). The detection limits of the device are for NO - 2000 ppm, NO₂- 200 ppm, NO_x- 2000 ppm, and SO₂ up to 2000 ppm.

Total organic carbon content was determined using Environnement S.A. of the Graphite 52M device, which contains a flame ionizing detector and measures range 0-10/100/1000/10000 ppm.

The quality of the refractory bricks from the wall of the ceiling of the tunnel furnace was tested by determining the resistance to the action of strong acids according to the standard SRPS B.D8.070:1981 [14]. The test was performed using sulfuric acid at boiling temperature for 6 hours. By measuring the mass of the sample before and after the test, the relative mass loss in percentage was determined.

The bulk density of the cut part of the samples is determined by measuring weight and dimensions. The compressive stress of refractory brick samples measuring 50x50x50 mm from the tunnel kiln ceiling is tested using a universal hydraulic machine by Alfred Amsler until the samples are completely crushed. Both results were gained from testing three samples.

Before microstructure analysis, samples were dried and evaporated using Au-Pd powder in a Fisons Instruments chamber. The surface micromorphology of the so-prepared samples was examined in a high vacuum using a JEOL JSM 5800 scanning microscope equipped with energy dispersive spectroscopy (SEM-EDS). The composition was determined using an Oxford Link Isis 300 with a SiLi X-ray detector calibrated using a Ni plate. The magnification employed was up to 500 μm.

3 Results and Discussion

3.1 Harmful constituents in petroleum coke

A thorough chemical investigation was carried out to demonstrate the potential impact of petroleum coke ingredients in addition to sulfur. The potential of employing petroleum coke of lesser quality—the composition of which is displayed in Table 1—was taken into consideration to reduce manufacturing costs. The lower and upper calorific values of the examined coke were 7387 and 8311 kcal/mol, which makes it somewhat below the usual petcoke used in cement production [2], but is found satisfactorily in the production of clay bricks. The high loss on ignition value shows the main constituent is carbon. The harmful elements in the examined petroleum coke were sulfur, iron, nickel,

Table 1. Chemical composition of the petroleum coke

Investigated parameters	Petroleum coke
Loss on ignition at 1000°C, %	97.73
Ash content, %	2.27
The moisture content at 105°C, %	0.25
Total S, %	8.80
Fe, mg/kg	338.8
Ni, mg/kg	480.0
Co, mg/kg	3.8
Cu, mg/kg	8.1
Zn, mg/kg	8.0
As, mg/kg	0.3
Sr, mg/kg	2.5
Mo, mg/kg	0.92
Cd, mg/kg	17.4
Sn, mg/kg	3.1
Sb, mg/kg	8.6
Ba, mg/kg	64
Hg, mg/kg	<0.2
Pb, mg/kg	1.4
Bi, mg/kg	0.3
V, mg/kg	100.9
W, mg/kg	1.3

cadmium, and vanadium. The total content of sulfur was higher than previously reported in the literature [2,5], so the sample is considered a high-sulfur petcoke [15]. Such petroleum coke can also be useful in syngas production [16]. The proportion of nickel and iron was higher than the average literature data [17]. The catalytic action of metals like Fe, Co, Mo, V, etc. present in a solid fuel can have a significant impact on the combustion process [2], while the concentration of vanadium is considered the most significant [18].

3.2 Flue gases from the tunnel furnace

During the firing of clay, the following combustion products may occur: dust, nitrogen oxides and other nitrogen compounds, carbon monoxide and carbon dioxide, leachable organic compounds, metals and their compounds, chlorine and its compounds, and fluorine and its compounds. The processing of clay, its mixing, drying, and firing result in the creation of dust. Nitrogen oxides and nitrogen compounds occur mainly as a product of fuel combustion, where nitrogen binds with oxygen from the air at high temperatures. Carbon monoxide and carbon dioxide are produced as products of the combustion of organic matter in clay, especially at low oxygen content. The combustion of fossil fuels produces CO₂, which further reacts with elemental carbon to produce CO. Volatile organic compounds that can appear in the waste gas originate not only from the raw material but also from possibly used additives. Depending on the firing temperature, various organic compounds may appear (benzene, styrene, phenol, formaldehyde, etc.). The content of heavy metals in most raw materials is very low. Metal oxides that appear from pigments used to color ceramic products have a hard crystal structure, so they are stable even at high temperatures. The content of chlorine and its compounds in most clays is low. Hydrogen chloride emissions can occur during the decomposition of mineral salts at temperatures over 850 °C and organic compounds containing chloride at temperatures between 450 and 550 °C, as well as from water used for soaking clay, if it is rich in chlorides. Fluorine and its compounds are present in all raw materials for ceramic products, which is why they are found in waste gas. The hydrogen fluoride found in waste gas is produced by the decomposition of fluorosilicate.

Table 2 shows the results of this investigation confronting Serbian [12] and EU regulations [19] about flue gas composition. Serbian legislation refers to the emission limit value for existing plants for firing clay-based ceramic products, while the EU's directive is precise in the case of combustion facilities built before 2013 that use solid fuels. The allowances depend on the total rated thermal input that is divided into three groups (50-100, 100-300, and > 300 MW), while the maximum concentration of the waste gas allowed is lower in cases of higher energy input. According

to Serbian regulations, the only limits that exceed them are found in the case of total organic carbon, which is expected due to the composition of petcoke. When compared to the EU Directive, the results of SO₂ and total organic contents are revealed as problematic. Other flue gas constituents' mass flow, like HF, HCl, and benzene, was below 0.09 kg/h.

The brick factory where the tests were conducted uses petroleum coke containing 4.5 % of sulfur. The results of the emission test from the tunnel furnace (Table 2) show the concentration of SO₂ is 291.93mg/Nm³(mean value of three measurements). Applying a simple proportion, when using petroleum coke with 8.8% sulfur (considering that the calorific power of the fuel has not changed significantly), SO₂ emission at the tunnel furnace emitter of about 521.39mg/Nm³ can be expected, which is above the limit [12], so there is a risk of exceeding the permitted emission if filters are not used. The excess air in the furnace must be reduced to produce as little SO₃ as possible, especially if temperatures above 1200 °C are reached, which is rarely achieved in the brick-making industry [20]. Sulfates are formed at firing temperatures below 1200, which then remain on the surface of the product as white fixed stains. [21] (see Chapter 3.3).

In the case of NO_x content (total nitrogen oxides expressed as NO₂), the plant meets the requirements of the current regulation, related to the emission limit values for new plants for the production of ceramic products by firing clay-based products in waste gas with a volume fraction of oxygen of 17 % [12]. The total volatile organic carbon content of the gas was unacceptably high. Additionally, the carbon in the exhaust gases does not only come from the fuel but also from the raw materials [12, 20]. The concentrations in the flue gas of a petroleum coke-heated tunnel kiln were lower than coal-fed kilns of different types reported in the literature [22]. However, the composition of the flue gases is also dependent on the mineralogical and chemical composition of clay, the chemical composition of the water used to produce the plastic mass, firing temperature, and possibly used additives to increase plasticity and porosity.

3.3 Corrosion of refractory bricks in the furnace ceiling

The quality of the refractory bricks from the wall of the ceiling of the tunnel furnace in Serbia was tested by determining the resistance to the action of strong acids according to the standard [14]. The mass loss of refractory bricks after the action of sulfuric acid according to the prescribed procedure is 3.55%, while the maximum permissible mass loss is 4%. It was concluded that refractory bricks met the demand for special-purpose products.

The petroleum coke constituents that have the greatest influence on corrosion processes (corrosion agents) are sulfur, nitrogen, vanadium, nickel, chlorine, potassium, and sodium. Sulfur and its compounds accelerate the corrosion processes of construction materials. Sulfur from petroleum

Table 2. Composition of the flue gases

Investigated parameters	Results	Maximum allowed in Serbia [12]	Maximum allowed in the EU [19]
Flue gas temperature	62.6 °C	/	/
Water vapor content	4.0 %	/	/
Dust	14.8 mg/Nm ³	20 mg/Nm ³	20-30 mg/Nm ³
Concentration of SO ₂	291.93mg/Nm ³	500 mg/Nm ³	200-400 mg/Nm ³
Concentration of NO _x	31.99mg/Nm ³	500 mg/Nm ³	200-300 mg/Nm ³
Total organic carbon content	22.43mg/Nm ³	50 mg/Nm ³	10 mg/Nm ³

coke turns into hydrogen sulfide during combustion in reducing local conditions, oxidizes into sulfur dioxide, or, in the presence of catalysts (vanadium pentoxide and iron oxide), turns into sulfur trioxide or sulfuric acid. Sulfur trioxide reacts with sodium and potassium compounds to form highly corrosive sulfates, low-melting pyrosulfates, and/or sulfuric acid. Sulfur compounds increase the corrosion rate of deposits containing vanadium and sodium [17, 23, 24].

The concentration of vanadium in the fuel is approximately 100.9 mg/kg, however, the deposit can contain over 80% of that amount (on the refractory walls of the furnace walls and ceiling and the walls of the wagon). It creates compounds with a low melting point when combined with other deposit components. Melted vanadium compounds create conditions for accelerated corrosion and swelling processes. At high temperatures, V_2O_4 and V_2O_5 combine with metal oxides to form solid solutions [17]. Bricks made of refractory material are destroyed by vanadium oxides at high temperatures. Molten V_2O_5 reacts with the refractory wall surface's oxide components at temperatures above 690 °C. It also causes slag to penetrate the material's pores, which lowers the melt's surface tension and viscosity. To reduce this effect (the formation of V_2O_5), it is recommended that the process be conducted without excess air. This will result in the production of far more refractory V_2O_3 and V_2O_4 , which will lessen the corrosion of refractory materials brought on by the presence of vanadium [17, 21]. The literature also describes one such issue that occurred when the ceiling in the tunnel furnace suffered severe damage (dropping off the wall at a length of 80 m) [25].

Images of refractory bricks removed from the ceiling of the tunnel kiln are displayed in Figure 1. The sample from the ceiling of the kiln is pale red in color. The lower part of the brick, which was directly exposed to smoke gases and water vapor, is greyish-yellow in height, ranging from 25 to 30 mm.

To determine the nature of brick corrosion in the lower part, the brick is divided into two positions:

- - Pale red part (without corrosion) - Position I (P I)
- - Greyish yellow part (with corrosion) – Position II (P II).

The average compressive stress on the 50x50x50 mm samples (Figures 1c and 1d, Table 3) determined on parts of the samples that were not directly influenced by the flue gas is 36.2, while the affected part showed 22.7 MPa (37.3% decrease). Bulk density decreased by 3.40%.

SEM-EDS analysis of deposits on a sample of refractory bricks removed from the furnace ceiling (Figure 2, Table 4) showed that sulfur, iron, and vanadium are deposited on the exposed surfaces of refractory materials but also penetrate the interior of the bricks. The proportion of sulfur in certain parts of the examined material was up to a maximum of 6.59% (Position I), while the vanadium content was detected up to 11.65% (Position II) in the spots not presented in Figure 2. Such high amounts of vanadium in bricks from the walls significantly lower the refractoriness of the $Al_2O_3-SiO_2$ system [21, 26]. Furthermore, the density of the deteriorated sample is detected to be lower than the initial one (Figure 2), which is consistent with the results gained through bulk density tests.

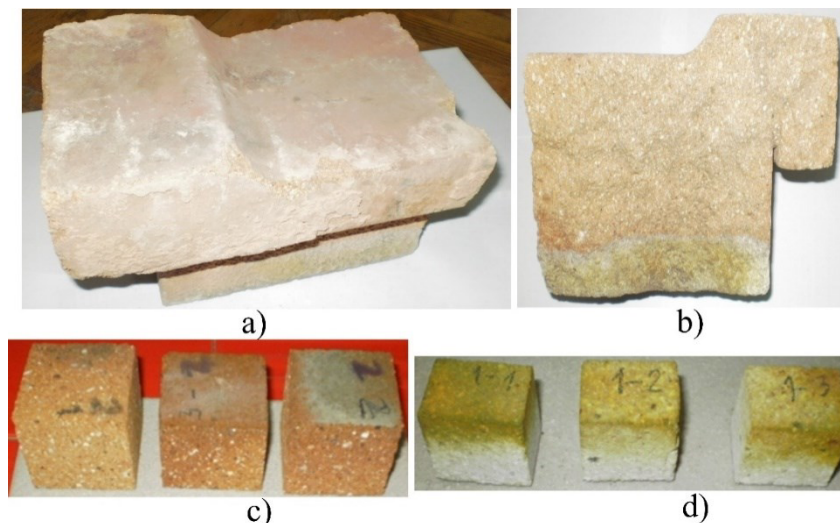


Figure 1. The visual appearance of the sample from the furnace wall: a) sample, b) section of the sample with the appearance of positions I and II, c) Position I, and d) Position II.

Table 3. Compressive stress of different parts of samples

	Compressive stress(MPa)		Bulk density (g/cm ³)	
	Position I	Position II	Position I	Position II
Test sample 1.	33.2	25.7	1.76	1.72
Test sample 2.	36.8	18.3	1.78	1.69
Test sample 3.	38.7	24.2	1.81	1.70
Average	36.2	22.7	1.76	1.70

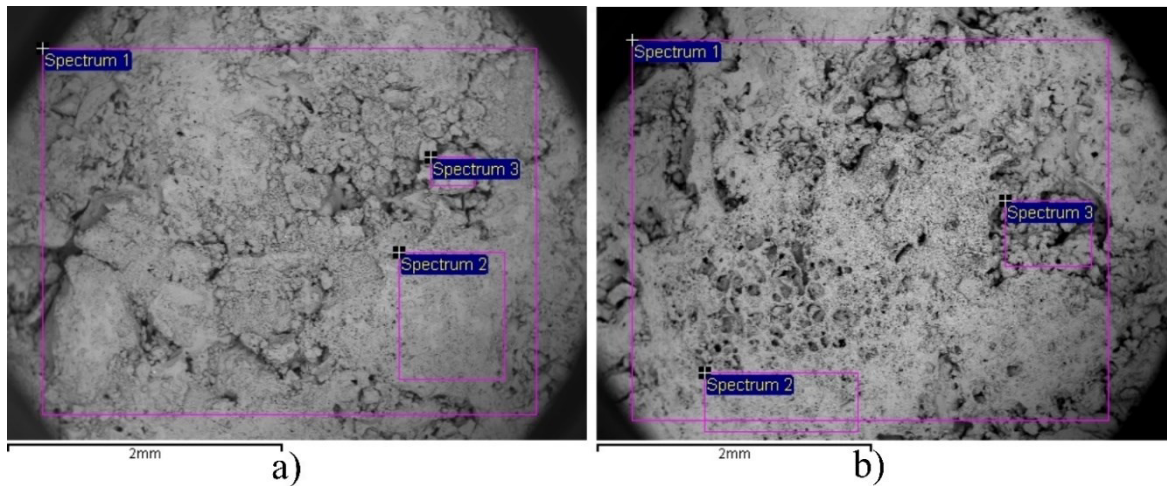


Figure 2. Microscopic appearance of the sample from the furnace wall: a) Position I, b) Position II.

According to the composition of the material itself, the presence of sodium and potassium is also evident (Table 4). All of the above confirms that there are conditions for accelerated corrosion processes. In addition, based on the difference in micromorphologies, it is observed that the discolored part of the sample (Position II) also contains

widened cracks and more pores as a result of the service life of the material. At increased magnification of that part of the material (Figure 3), micron-sized acicular crystals of primary mullite containing feldspars, quartz, and vanadium (Figure 3a) [26] and secondary mullite formed at temperatures above 1400 °C (Figure 3b) [27, 28] can be observed.

Table 4. Composition of refractory bricks from the walls of the tunnel kiln

Composition (%)	P I Spectrum 1	P I Spectrum 2	P I Spectrum 3	P II Spectrum 1	P II Spectrum 2	P II Spectrum 3
Na	0.66	0.37	0.51	0.70	0.60	1.45
Mg	0.32	0.33	0.45	0.80	0.52	0.54
Al	14.67	12.56	12.92	13.40	14.38	13.22
Si	26.78	25.68	20.36	25.26	25.12	27.54
P	0.00	0.00	0.00	0.00	0.00	0.00
S	1.59	3.66	6.59	0.65	0.46	0.30
Cl	0.00	0.19	0.00	0.00	0.00	0.00
K	2.04	1.92	1.81	2.65	1.34	3.63
Ca	2.38	3.69	6.28	1.07	0.67	1.29
Ti	0.31	0.68	0.25	0.56	0.41	0.45
V	0.00	0.00	0.00	4.93	6.00	1.92
Mn	0.00	0.00	0.00	0.00	0.00	0.00
Fe	2.58	1.83	2.14	1.81	1.83	1.69
Ni	0.00	0.00	0.00	0.00	0.00	0.00
O	48.68	49.09	48.69	48.17	48.69	47.99

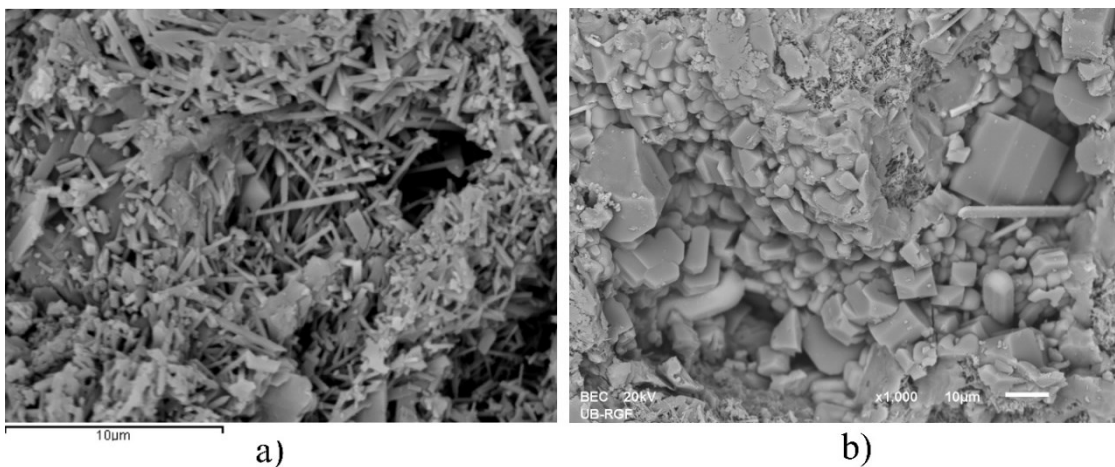


Figure 3. Microscopic appearance of the sample from the furnace wall (Position II): a) Crystals of primary mullite containing vanadium, b) Crystals of secondary mullite.

3.4 Corrosion of pipelines and metal structures in the dryer and furnace

Increased corrosion of pipelines and metal structures on the furnace and dryer is caused by the presence of sulfur oxides. In contact with water vapor, these compounds condense at lower temperatures and form acids (sulfuric and sulfurous), which affect the intense corrosion of metal structures. Any increase in sulfur concentration causes corrosion to grow noticeably, and there is a risk of rapid deterioration of metal pipelines and structures. Vanadium can also act as a catalyst to combine with sulfur from petroleum coke and generate a corrosive sulfate, which can seriously harm alloys at high temperatures [17, 29]. Moreover, the presence of CaO in petroleum coke causes the agglomeration of CaSO₄ under high-temperature circumstances, severely damaging the metal components [30].

3.5 Deposition of sulfate scum on the products

The dryer scum is formed if products enter the kiln with residual moisture that is suddenly released in the heating zone. For this to happen, the necessary conditions are that there is a certain amount of sulfur in the flue gases (usually waste heat from the kiln) and a low temperature of the flue gases. This way, sulfurous and sulfuric acids form salt scum with water on the external (free) surfaces of the products. Moreover, soluble salts present in raw materials can be driven off to the surface with water while drying, and thus again, sulfate scums are formed and bound (fixed) to the surface of products. The negative effects caused by these salts can be prevented by adding BaCO₃ to the raw materials, and the products must be sufficiently dried before reaching the heating zone in the kiln.

These drying-related salts typically become apparent only after firing. Kiln scum develops by a similar mechanism during the firing process and is mainly caused by the sulfurous gas in the kiln [31, 32].

Thus, when using petroleum coke as an energy source in the brick kiln, the increased content of sulfur significantly

risks the appearance of sulfate scum and, thus, a poor appearance of the finished product (Figure 4). Depositing is possible in the dryer and the heating zone of the kiln. The strength of the scum spots varies, and the "coloring" is more intense as a result of the products being stacked at the wagons and having differently exposed surfaces to the atmosphere in the kiln (flue gases).

Sulfate scum on the produced blocks is mainly the aesthetic problem that affects their poor placement on the market. Besides, since those sulfates are water-soluble, they may react with mortar during the construction phase and deplete their binding properties [33].

4 Conclusions

The impact of petroleum coke with a higher sulfur content was investigated concerning SO₂ emission from the furnace, corrosion of the furnace walls, metal pipes, and structures in the dryer and tunnel furnace. Moreover, the appearance of dried and fired products caused by sulfate scum was discussed. This investigation was the first of its kind available in the literature.

Due to numerous adverse effects, it is not advised to use petroleum coke with a high sulfur content (over 5%) as a fuel in tunnel kilns for the manufacture of ceramic bricks. The increased content of sulfur negatively affects the dryer, kiln, and final products and requires the use of flue gas filters. In the study, only the technical aspects of the negative impacts of the high sulfur content in petroleum coke were analyzed, while the health aspects were not considered.

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Figure 4. Macroscopic appearance of the samples containing sulfate scum

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