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CLEANER PRODUCTION METHODS USING IN THE AIM TO REDUCE EMISSIONS TO THE ATMOSPHERE IN CERAMICS PRODUCTION TECHNOLOGICAL PROCESS

In the context of compliance with the requirements of the Council of the European Union Directive 96/61/EC (Directive on integrated pollution prevention and control) in ceramic technology, it is particularly important to ensure that air emissions are reduced. Gaseous compounds are released from raw materials during drying, calcination and firing, as well as during fuel combustion. A typical gaseous contaminant in ceramic technology is fluorine. The concentration of SOx (mainly SO₂) in flue gases is closely related to the sulfur content in the feedstock and in the fuel. In ceramic materials, sulfur can be present in the form of pyrite (FeS₂), gypsum, and other sulfates, as well as organic sulfur-containing compounds. In gaseous fuels, sulfur is practically absent, but its oxides are formed during the combustion of solid fuel and fuel oil. NOx is mainly released when the thermal "binding" of nitrogen and oxygen in the air supplied for combustion of the fuel. This reaction is facilitated by elevated temperatures (especially more than 1200 °C) and excess oxygen.

Also, the binding reaction can occur in the hot zone of the torch, even if the temperature in the furnace is below 1200 °C. When nitrogen compounds contained in fuels (usually solid and liquid) and organic additives are burned, NOX is formed at lower temperatures. Carbon monoxide (CO) is released by the combustion of organic substances present in ceramics, especially in conditions of lack of oxygen. Volatile organic substances can be present both directly in the raw material, and can be part of the material in the form of various auxiliary substances: binders, pore-forming agents, desiccants, adhesives, thermal and burn-out additives. At the initial stage of heat treatment, carbonation of organic compounds occurs, accompanied by the release of a wide range of volatile organic compounds. Emissions of heavy metals in the production of ceramics are formed mainly during the firing of glazed products. To prevent the emission of heavy metals from ceramic pigments and glazes, it is proposed to conduct firing of such products in a high-speed mode, in which heavy metals enter a strong crystal structure such as spinel or zircon, and the volatilization of components is minimized. Almost all clays contain fluoride. When the material is heated, hydrofluoric

acid is released. However, at low temperatures (500–700 °C) and the presence of water vapor, calcium fluoride is formed, which dramatically reduces the release of fluoride into the atmosphere. The decomposition of calcium fluoride is observed at temperatures above 900 °C, so the introduction of calcium-containing additives into raw materials and compliance with the firing and drying regime significantly affect the release of such a dangerous atmospheric pollutant as fluorine [1].

In order to reduce emissions of nitrogen oxides, sulfur, chlorine, fluorine and volatile organic compounds, it is recommended to use raw materials with a low content of these elements, which is not always possible in Belarus, and if there is access to other raw materials, transport costs increase. Introduction of calcium additives in the charge is possible in the production of bricks, ceramic pipes and glazed products, but it is not applicable in the production of refractories, i.e. for Belarus, which practically does not produce refractories, the introduction of this method is promising in most enterprises.

Main methods of process optimization according to the best available technologies approved in the EU [1-5]:

- optimization of the firing process;
- reduction of water vapor content in flue gases ;
- the post-combustion gases of the heating zone in a furnace;
- use of low-NOx burners;
- use of modern absorption systems for flue gas treatment.

Reducing the water vapor content in the flue gases can be achieved by using indirect heating of the furnace using gas emitter burners [5] or electric heating of the furnace. Modern equipment-roll-out hearth furnaces, roller furnaces [2, 3] – is very promising in the production of facing and floor tiles, tableware, decorative, sanitary products, technical ceramics, abrasives on an inorganic bond, but requires serious capital investments.

Afterburning of flue gases is provided by feeding them from the heating zone to the firing zone, where they are burned under the influence of high temperature. For this purpose, the part of the furnace where volatile organic compounds are released (the carbonation zone) must be separated from the rest of the furnace space, which is done using one or more sliding shutters or a special gas suction system. This technique makes it possible to significantly reduce the level of emissions of not only volatile organic compounds,but also carbon monoxide. The introduction of thermal afterburning when using a tunnel furnace as a simple countercurrent heat exchanger often creates difficulties during its operation and increases the associated costs. As a result, in recent years, enterprises, especially new ones, have become increasingly interested in systems for external afterburning of flue gases in thermosets and catalytic afterburning systems [5].

Horizontal cascade – type adsorbers, dry cleaning with bag and electric filters, and wet cleaning with nozzle and centrifugal scrubbers and Venturi scrubbers can be recommended as absorption units for flue gas cleaning [1, 4]. The table shows a comparative analysis of the technological and economic efficiency of various methods of cleaning waste gases [1, 5]:

Method	Horizontal cascade type adsorbers			Dry flue gas filtration		Wet flue gas cleaning	
Emission level			$SO_2 \ge 2500$ mg/m3 (n. o.)				
Absorber	CaCO ₃	Modified CaCO ₃	Modified CaCO ₃	Ca(OH)2	NaHCO ₃	Water / Ca(OH)2 or CaCO3	Caustic soda
Efficiency: HF	90 % (to 99 %)	to 99 %	to 99 %	80 to 96 %	>95%	92–99 %	98 %
SO ₂	8–20 %	43 to 85 %	30-43 %	7 to 80 %	98–99 %	20–98 %	90–98%
SO ₃	80 %	80-85 %	80-85 %	80–90 %	98–99 %	92–95 %	94-96 %
HC1	50 %	> 50 %	50 %	10-85 %	89 %	50 to 95 %	90–95 %
Dust	100 %	100 %	99 %	90–99 %	99 %	100 %	100 %
Excess sorbent ^A	2,5	2,5	2,5	1,35–2,00		1,01–2,00	
Water consumption (m ₃ / day) ^B	0	0	0	0		86–240	
Power consumption (kWh / day) ^B	641–864	864	864	1200– 2880		2352– 4824	
The sorbent cost (EUR/t)		99	99	104		30–100	
Capital investment (thousand euros) B, C ^{B,} C	228–278	692	692	766–1081		511–659	

Process parameters, efficiency, consumption level and costs for various flue gas treatment technologies

Note: A – the ratio between the amount of sorbent required in practice to ensure the required cleaning efficiency and calculated theoretically (based on the stoichiometry of the adsorption reaction);

B – according to the data of four typical enterprises;

C – installation Costs and overhead.

As the analysis of the table and approaches to the methodology of cleaner production of ceramics shows for Belarusian realities, the most applicable methods are the introduction of calcium additives in raw materials, optimization of combustion and firing processes, as well as, if possible, modernization of equipment in order to intensify fuel combustion and reduce energy and heat losses.

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