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The afterburning of carbon monoxide in natural gas combustion gases in the presence of catalytic ceramic coatings[☆]

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Abstract

Some more important types of environmental noxiousness connected with the emission of CO and other toxic gases have been characterized. Methods are detailed, which permit the reduction of pollutant emission from the burning processes, of which catalytic afterburning is emphasized.

The results of studies are reported, concerning the catalytic effect of ceramic coatings as plasma sprayed onto burning space containing surfaces on the variation of combustion gas parameters. The catalytic afterburning processes were carried out in tube furnaces by burning coke-oven gas, in bathroom-type water heaters where natural gas was burnt, and in a model chamber ended with combustion gas ducts filled with ceramic shapes having sprayed catalytic coatings. The obtained measurement results confirm the purposefulness of using the burning-process catalyzing coatings.

Keywords: afterburning, carbon monoxide, catalytic ceramic coatings, natural gas, combustion gases

1. Emission of carbon monoxide and other pollutants

In 1997, above 4 million tons of toxic waste gases were emitted in Poland, of which only 15% were neutralized. Losses due to pollutant emission to the atmosphere account for 17% of the national income [1]. The most burdensome pollutant sources are the commercial power engineering and the effects of the transport. About 14% of the territory of Poland (the Upper Silesian Industrial Region, the Legnica-Głogów Copper Region, and the city of Cracow) are the areas of environmental disaster, for which the burning of fuels is the main source of pollutants.

Admissible pollutants emissions have been established in Poland only for boilers, and their values are being automatically transferred onto industrial furnaces and municipal boiler furnaces. Also, there are no limits established for motorcar engine emissions.

Penalties for transgressing the admissible emissions cover merely 10% of the value of actual losses incurred by the national economy.

Carbon monoxide was one of the first burning products recognized as a pollutant, because of its highly toxic action. In addition to CO, the major pollutants include: hydrocarbons (CH), carbon soot (C_s), dusts, pitchy substances, NO_x, SO_2, and organic micro-particles.

According to the existing views, almost all elementary carbon from the fuel passes through the CO stage. For this reason, the efforts aim at accelerating

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its oxidation to CO instead of restricting its formation in the burning process. The mechanism of the elementary reactions of CO oxidation is well known, this not being true, however, for the mechanism of CO formation.

A substantial improvement in the negative environmental effect of coal burning processes will be possible to be achieved through:

- widespread implementation of the coal enrichment technology,
- introducing fluidized-bed furnaces into service,
- widespread implementation of low NO_x emission powdered-fuel burners,
- widespread implementation of combustion-gas SO_2 removal equipment.

The studies conducted by the authors within the catalyzing of combustion gas afterburning and the NO_x emission reducing processes may have a substantial contribution to the improvement of environmental conditions. They are conducted with consideration being paid to the needs of the industry including the power engineering and metallurgical industries, as well as the municipal economy and transport [2].

According to the catalysis process theory of, so called, active complex (refereed to as the transitory state theory), which claims that the collision of active particles occurs particularly easily on the walls that contain the burning space, and further that the reaction chains are the shorter the greater is the ratio of the wall-contained surface area to the reaction space volume, the surface development promotes the intensification of the processes. The problem boils down to selecting the coating types, the parameters of their spraying, and giving them the necessary wear resistance.

The plasma spraying of coatings from high-melting, high-hardness materials onto the walls of furnaces, boiler furnaces, heat exchangers and other industrial equipment gives the coatings the desirable properties of protective action on the (corrosive and erosive) wear processes of the sprayed equipment elements, and catalytic action on the chemical processes and forming of heat exchange processes by radiation and conduction. These coatings are sprayed on the walls containing the operating spaces of equipment, which are made of metals, ceramics, or other materials. They are applied on either new or, predominantly, (several times) used and partially worn elements without having to remove them from their place of operation.

2. Purposefulness of using catalysts

The action of catalysts involves the reduction of the activation energy of a particular reaction, which is reflected in the fact that in the presence of catalysts, reactions proceed at a rate increased by several times (at a constant temperature) or, which is also important particularly in combustion-gas ducts, at a lower temperature. In the presence of a catalyst, the activation energy is significantly lower than that of the non-catalyzed reaction.

The use of catalysts, on the other hand, does not affect the energy of the substrates and products of the reaction, and does not cause changes in the enthalpy and thermodynamic potential.

Commonly, metal-platinum or metal-palladium catalysts are used. Less frequently produced are catalysts of transition (IV period) metal oxides.

Oxidation reactions occurring on oxide catalysts proceed in such a way that the compound which undergoes oxidation (CO, CH, or C_s) first reacts with the catalyst's surface oxygen to reduce the catalyst, and then the reoxidation of the previously reduced catalyst's surface occurs.

The above mentioned mechanism is particularly useful for the description of oxidation reactions occurring on catalysts as plasma sprayed from transition metal oxides (with an addition of high-melting metal-ceramic materials).

These catalysts are characterized by high surface development (5 time-increase in relation to the area resulting from the geometrical dimensions) due to the surface roughness of approximately 60 μm. The surface roughness of the catalysts promotes also increasing the rates of chemical reactions and heat absorption, which may lead to the reduction of the catalyst constructional dimensions.

3. Materials catalyzing the oxidation of hydrogen, carbon monoxide, and hydrocarbons

The catalytic action on the hydrogen oxidation processes is exhibited by platinum, palladium, and nickel (the latter being used for O_2-H_2 type fuel cells). The catalytic properties are also possessed by the oxides of the elements of Group IV of the periodic system, and particularly those of cobalt, copper, and nickel. The activation energy of H_2 oxidation in the presence of these oxides ranges from 45 to 100 kJ/mole, and the reaction order from 0.5 (Cr_2O_3) to 1 (Co_3O_4) [3]. Obviously, the most active are those oxides in the presence of which a 1-st order reaction occurs.

In the carbon monoxide oxidation process, a high activity is also shown by platinum and palladium. In the presence of these metals, 100% CO burning takes place in the oxygen atmosphere at as low a temperature as 470 K. The above mentioned oxides, i.e. those of Group IV of the periodic system, also catalyze CO oxidation, but a higher process temperature is required, and the process proceeds at a lower rate.

It has been found that during the catalytic burning of CO in the presence of nickel oxide oxygen adsorbs on the catalyst's surface thus forming O-ion which then reacts with the adsorbed CO. In Figure 1, the effects of the reaction-velocity constant logarithm, and the activities of the Group IV elements of the periodic system on the reaction course are shown for the reactions $H_2 + O_2$ and $CO_2 + O_2$.

The greatest activity is exhibited by the oxides of cobalt, copper, manganese, and nickel. The oxides of zinc, titanium, vanadium, and iron, on the other hand, are characterized by low catalytic activity [3].

CuO, NiO, and MnO_2 have found technical applications. For these oxides, the activation energy of CO oxidation (at a normal temperature) is 12.5 to 25 kJ/mole, and 62 to 110 kJ/mole at temperatures from 470 to 670 K. Also lanthanide-series oxides reduce the activation energy of the CO oxidation process, with the following order towards their decreasing activity: CeO_2, La_2O_3, Nd_2O_3, and Dy_2O_3.

In technology, CeO_2 is used in the form of a mixture with Al_2O_3 in the ratio of 3:4, which catalyzes the oxidation of CO already at the temperature of 475 K [3]; and it is worthy to be remembered that burning conducted at moderate temperatures favorably influences the NO_x content of combustion gas.

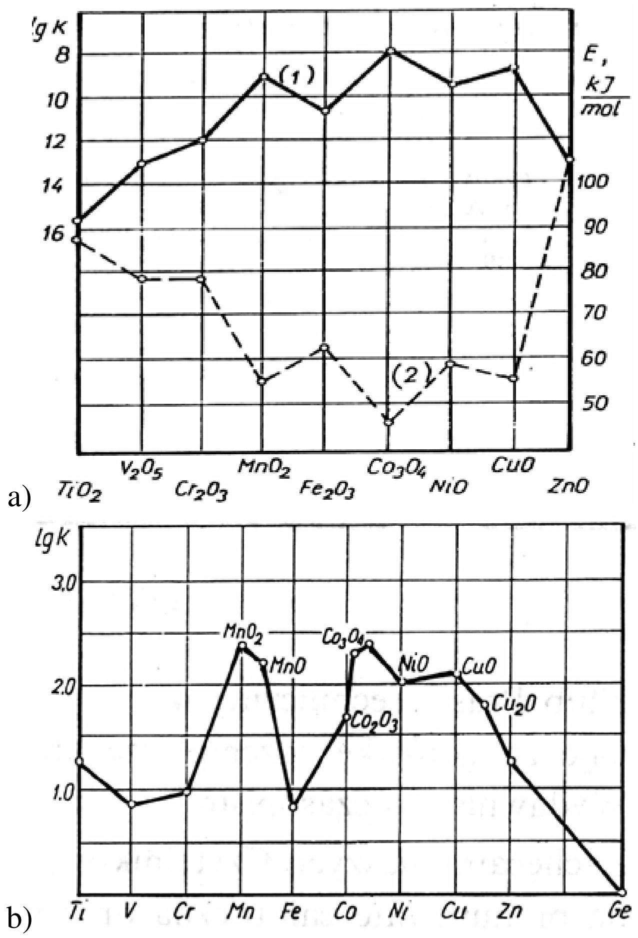

Figure 1: Variation of the reaction-velocity constant logarithm: a—variation of the reaction-velocity constant logarithm for the reaction $H_2 + O_2$ (1); and activation energy (2) for the IV period elements of the periodic system at the temperature of 325 K [1], b—variation of the catalytic activation logarithm of the IV period elements of the periodic system for the oxidation reaction $CO + O_2$ [1]

The oxidation of hydrocarbons is strongly influenced by the oxides of cobalt, nickel, and copper. Because of the symmetrical structure of, for example CH_4, its oxidation is a difficult process, and the greatest capability of catalyzing it has been shown by Co_3O_4, NiO, CuO, and MnO_2. Also, a great capability of oxidizing methane is possessed by the oxides of cerium and terbium [3].

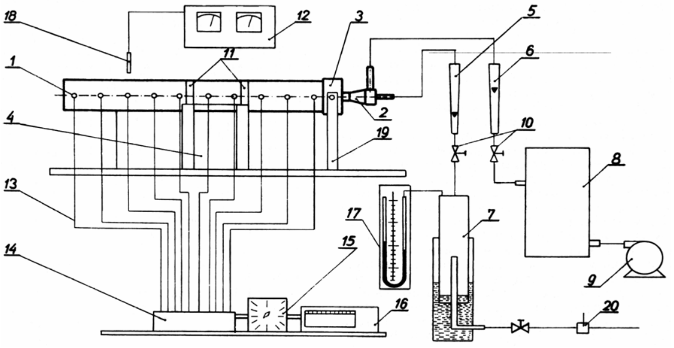

Figure 2: A schematic of the testing stand for measuring the parameters of the coke-oven gas burning process: 1—burning chamber, 2—burner, 3—burner hoop, 4—supporting construction, 5—gas rotameter, 6—air rotameter, 7—gas regulating vessel, 8—air tank, 9—fan, 10—rotameter valves, 11—clamp hoop, 12—combustion gas analyzer, 13—thermocouple, 14—thermostat, 15—thermocouple switch, 15—recorder, 17—U-tube, 18—gas sampling probe, 19—burner stand, 20—gas valve, G—gas, P—air

4. Studies on the effect of ceramic coatings on the catalyzing of coke-oven gas burning

Within the first part of the studies, the measurements of the distribution of CO and CO_2 contents and temperature on the length of several model tube-furnaces were carried out—Fig. 2.

The furnace was assembled of two halves of ceramic tubes, and coke-oven gas was burnt within it using a kinetic burner. Four completes of tubes were prepared for the tests. Three pieces of the above mentioned devices were sprayed with CeO_2 + Al_2O_3, K type, and M type coatings, respectively. The remaining (fourth) pieces were operated in the condition without a coating, and the obtained results made a reference for the parameter values obtained from operating the devices as sprayed with the coatings.

The effect of the used coatings on the values of the parameters studied was found to be diverse. The greatest desirable increase in the burning-characterizing parameters was obtained in the presence of the coating sprayed from the mixture of CeO_2 with aluminium oxide [2]. Thus, with an excess air of 1.05, an increase in the combustion gas temperature by 154 K along with a 0.8% drop in CO content were obtained in the burner-adjacent furnace zone, as against the values of the same parameters as obtained in the tube (of the model furnace) without a coating. In the end part of the furnace, an increase in the combustion gas temperature by 40 K was obtained, and the combustion-gas CO concentration decreased from 2.6% (in the furnace without a coating) down to 0.8% in the furnace with the CeO_2 coating.

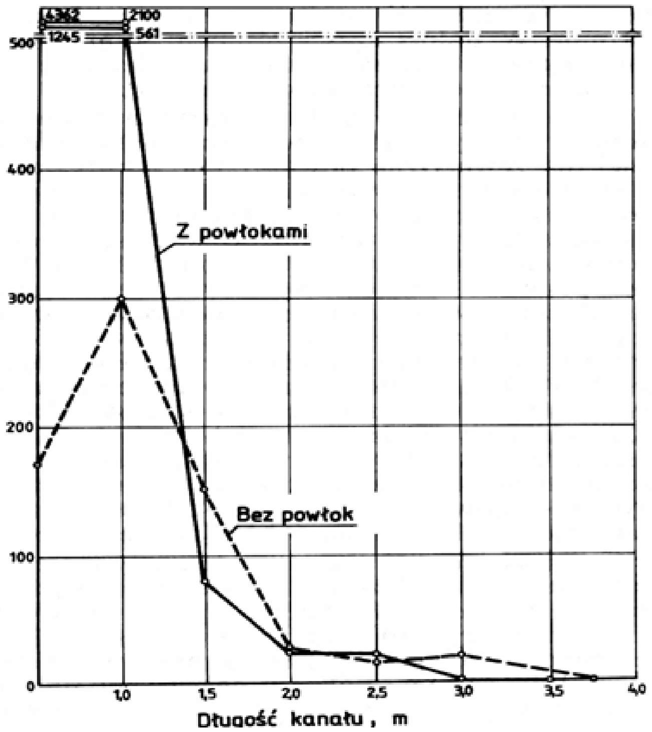

Figure 4: Variation of the combustion gas CO content on the length of the natural gas-fired model furnace

In the cases of coke-oven gas burning in the furnaces whose outer surfaces had been sprayed with the remaining coating types, smaller values of the temperature and CO and CO_2 concentration changes were obtained. The least advantageous changes occurred in the presence of the coating sprayed from the M type oxide mixture – Fig. 3.

5. Studies on the effect of ceramic coatings on the parameters of combustion gas formed from natural gas

The results of Stage II of the studies cover the parameter values of combustion gas formed in the absence of catalytic coatings, both on the internal furnace walls and on the coils. It results from the presented data – dotted lines in Fig. 4—that a little significant decrease in the combustion gas CO content was obtained on the duct length of approximately 4 m.

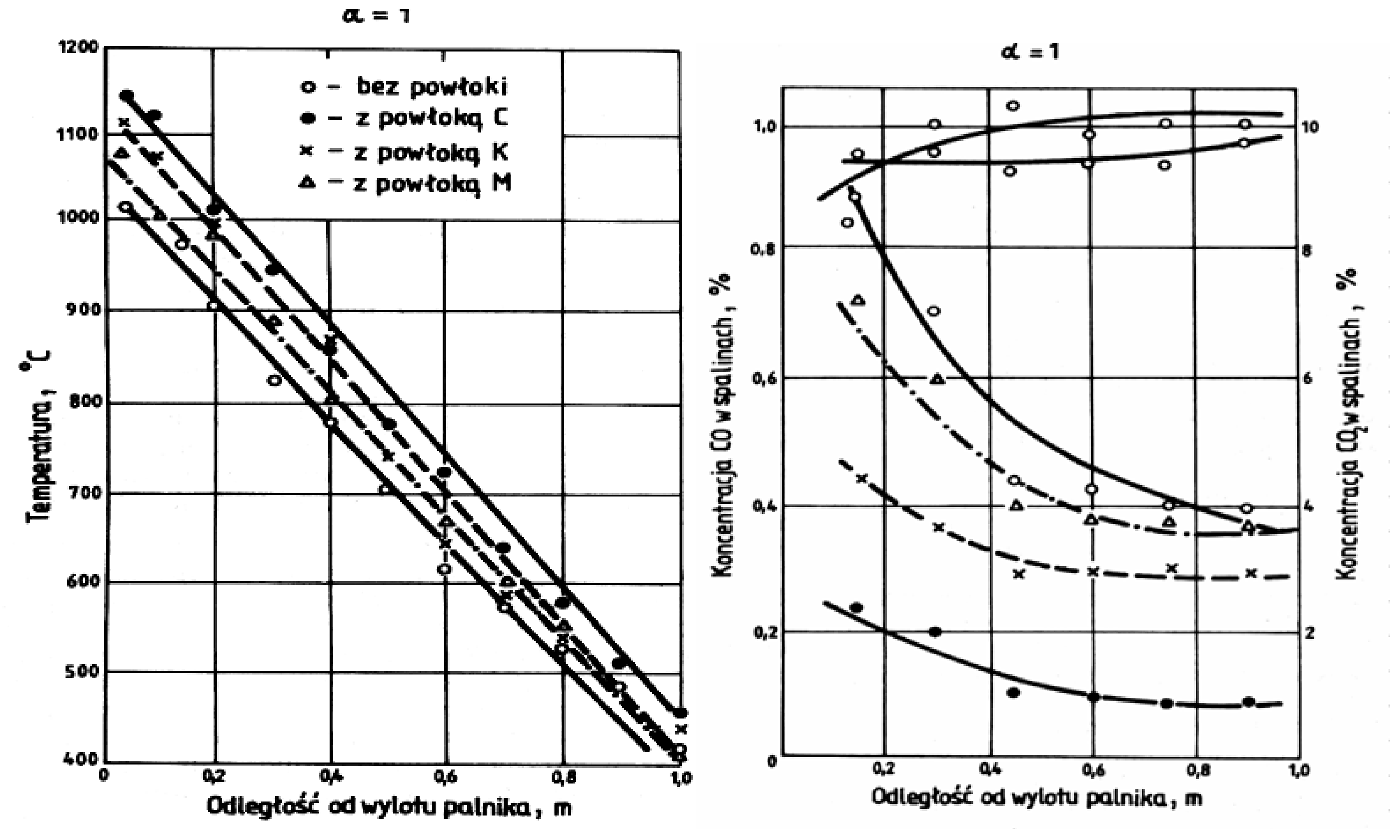

Figure 3: Temperature and CO and CO_2 concentration distribution in the combustion gas in the model tube furnace

In spite of the fact that efforts to maintain a constant ratio of the fuel, and thus also that of the combustion gas, in the tests were unsuccessful, a clear effect of the coating on the values of the parameters tested was obtained, which is indicated by the solid line in Fig. 4.

In the presence of the catalytic coating, the drop in the combustion gas CO content was approximately 15 times greater than that in the duct without a coating. In the third part of Stage II of the studies, the combustion gas was generated in a 3.5 metre-long ceramic chamber with a diameter of 0.6 m—Fig. 5. After flowing out of the chamber, the combustion gas stream was passed into a 1.5-metre high ceramic duct with an internal diameter of 180 mm. The duct was packed with ceramic shapes covered with the K type coating.

At the inlet to the ducts, the combustion gas contained several hundred p.p.m. of CO and about 200 ppm of NO_x (Table 1). At the duct outlet, on the other hand, i.e. downstream the catalyst, the CO content was only a few p.p.m. above 10; whereas the NO_x content was less than 1/3 of the initial content of this constituent. These results relate to the constituent contents of the combustion gas generated from natural gas. Studies are under way on the catalytic effect of other types of coating on the CO and NO_x changes both in liquid fuel-derived combustion gases and in combustion gases generated from natural gas.

6. Summary

1. The measurement results obtained from all stages of the studies have shown the purposefulness of spraying catalytic coatings onto burning space-containing surfaces, because they enable:
    - temperature increase in the burning space,
    - drop in the combustion-gas CO concentration,
2. The measurement results of the parameters values that characterize gaseous fuel burning in the presence of the catalytic coatings used

Table 1: Catalytic effect of the ceramic coating on the parameters of natural gas-derived combustion gas

Parameters		Concentration of CO and NO_x		
Combustion gas constituent	Unit	Upstream the Catalyst	Downstream the Catalyst	Conversion Degree
NO_x	ppm	198	73	63%
CO	ppm	57	0.0	100%

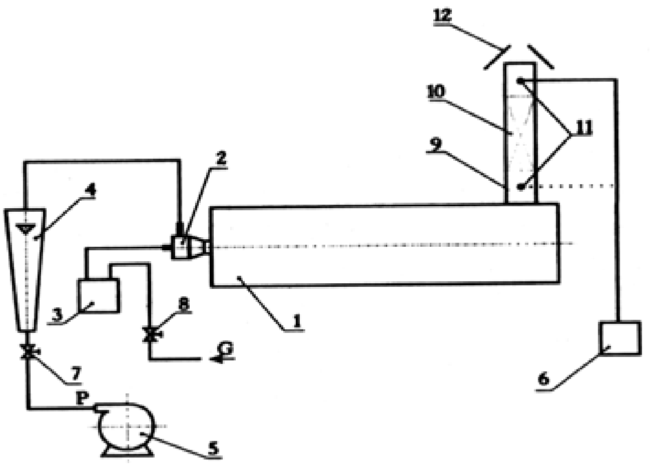

Figure 5: A schematic of the testing stand for the studies of the catalytic effect of the ceramic coating on the parameters of natural gas-derived combustion gas: 1—ceramic chamber, 2—burner, 3—gas meter, 4—air rotameter, 5—air fan, 6—PEMAC 3000 gas analyzer with a measuring probe, 7—air valve, 8—gas valve, 9—combustion gas duct, 10—catalytic system, 11—measurement points, 12—gas exhaust, G—gas, P—air

have shown the usefulness the CeO_2 and Al_2O_2 mixture-based and the K type coatings for those purposes.

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