Review of technologies for suppressing emissions of benzo(a)pyrene at energy enterprises

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Abstract. Power engineering enterprises have a great impact on the environment. Flue gas emissions contain solid ash particles, sulfur oxides SO_2, SO_3, nitrogen oxides NOx, carbon monoxide CO (monoxide) CH hydrocarbons; in some cases, there may be a danger of radiation contamination, but the most dangerous substance emitted into the atmosphere is benzo(a)pyrene $C_{20}H_{12}$, which has a negative effect on human health. Polycyclic aromatic hydrocarbons (PAH), including benzo(a)pyrene contained in flue gas emissions from energy enterprises, have a serious impact on human health. Taking measures to suppress other harmful emissions from thermal power plants (nitrogen oxides and sulfur oxides) can increase the content of benzo(a)pyrene, which poses a serious problem for modern researchers. As part of this study, various technologies for suppressing benzo(a)pyrene emissions at energy enterprises were considered. The main disadvantages of the described methods are highlighted. The possible danger of increasing benzo(a)pyrene emissions when trying to suppress other emissions is noted.

1. Introduction
Air quality has a direct impact on human health, especially those living in a large city. First of all, air pollution affects the respiratory system. So, in 2018, an increase in the incidence of cancer was noted in the Trans-Baikal Territory. In the Aginsky district, growth was 1.76 times, in Chita - 1.21, in Petrovsk-Zabaykalsky - 1.24, in Ulyotovsky, Shelopuginsky and Shilkinsky - 1.1. Moreover, according to the analysis of the regional Rospotrebnadzor, in the list of incidence of oncology in the period from 2011 to 2015, the first place was occupied by cancer of the trachea, bronchus and lung. [11]

In 2018, Chita was included in the list of cities with the dirtiest air. The substance that caused the high pollution was benzo(a)pyrene, the vast majority of the emissions of which accounted for by numerous energy enterprises - the Chita TPP-1 and the Chita TPP-2, as well as a number of boiler houses that also operate on coal. [1-18]

Polycyclic aromatic hydrocarbons (PAH), including benzo(a)pyrene, are widespread in all areas of the environment, formed during the combustion of fuel.

Benzo(a)pyrene ($C_{20}H_{12}$) (Fig. 1) - an aromatic compound, a representative of the polycyclic hydrocarbon family, which is formed during the combustion of hydrocarbon fuels - causes a high level of atmospheric pollution (to a lesser extent during gaseous combustion). Benzo(a)pyrene is one of the most toxic combustion products belonging to the group of polycyclic aromatic hydrocarbons. This is a

substance of the first hazard class, with an extremely high level of hazardous effects on the environment and human health (there is a high carcinogenicity in contact with benzo(a)pyrene). In addition to the special danger, benzo(a)pyrene is chemically and thermally stable, and when it enters the body it can accumulate. At the same time, the mechanism of PAH occurrence during fuel combustion has not been sufficiently studied to date. [12]

2. Materials and Methods

In addition to the particular danger, benzo(a)pyrene is widespread, chemically and thermally stable, but it is fat-soluble, and when it enters the body it can accumulate.
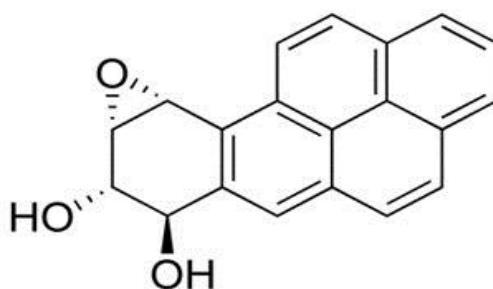

Figure 1. Chemical formula of benzo(a)pyrene.

The presence of benzo(a)pyrene in the emissions of the CHPP poses a rather serious complex problem of minimizing harmful emissions in flue gases, among the ways to solve which it can be indicated:

- Introduction of energy-saving technologies for heat consumers (including control and metering devices);
- Decrease in heat losses in networks;
- Optimization of boiler operation modes [18];
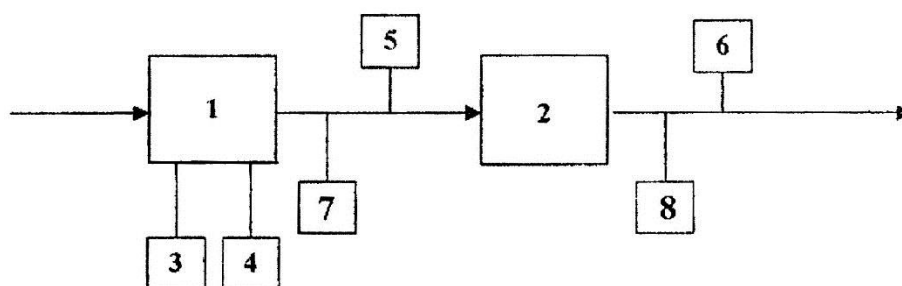- Improving the collection efficiency of fly ash (including finely divided fractions).

Figure 2. The method of purification of gas emissions from polycyclic aromatic hydrocarbons, including benzo(a)pyrene. 1 - nitrogen and carbomide injection device, 2 - ultraviolet irradiation device, 3 - ultraviolet irradiation device, 4 - pre-exposure chamber, 5-6 - sample selection, 7 - solid waste disposal device.

Among the technologies for suppressing emissions of benzo(a)pyrene at energy enterprises, it is possible to characterize the following:

Technology for purification of exhaust gases from PAHs by irradiating with a stream of accelerated electrons in the presence of mineral acid vapors, taken in a mass ratio to polycyclic aromatic hydro-

carbons, equal to (1-1.2): 1. [5] This technology is very energy-intensive, since molecular transformations occur due to the collision of all components of the gas emissions with the electron beam introduced into the exhaust gases. At the same time, there is a slight decrease in the content of benzo(a)pyrene in the exhaust gases subjected to irradiation.

Method of reducing the content of PAHs (including benzo(a)pyrene) in the exhaust gases by photo-oxidation of PAHs when irradiated with electric discharge radiation in the wavelength range of 340-410 nm with an average light energy density of 10-3-310-1 J / cm2 at operating temperatures from -20 ° C to + 80 ° C. [1]

Method quite effective due to low energy consumption. Upon irradiation, PAH molecules "pass into an excited singlet state with their subsequent transition due to collisions into a triplet state and the generation of singlet oxygen, which reacts with PAHs, with which some components of gas emissions also react." [1] Moreover, the rate of destruction of benzo(a)pyrene and the degree of purification of industrial emissions is not high, and reaches no more than 30-35%, and the specific energy consumption for each gram of destroyed benzo(a)pyrene reaches 0.5 kW · h and more. A relatively low reaction rate of PAH destruction is also noted.
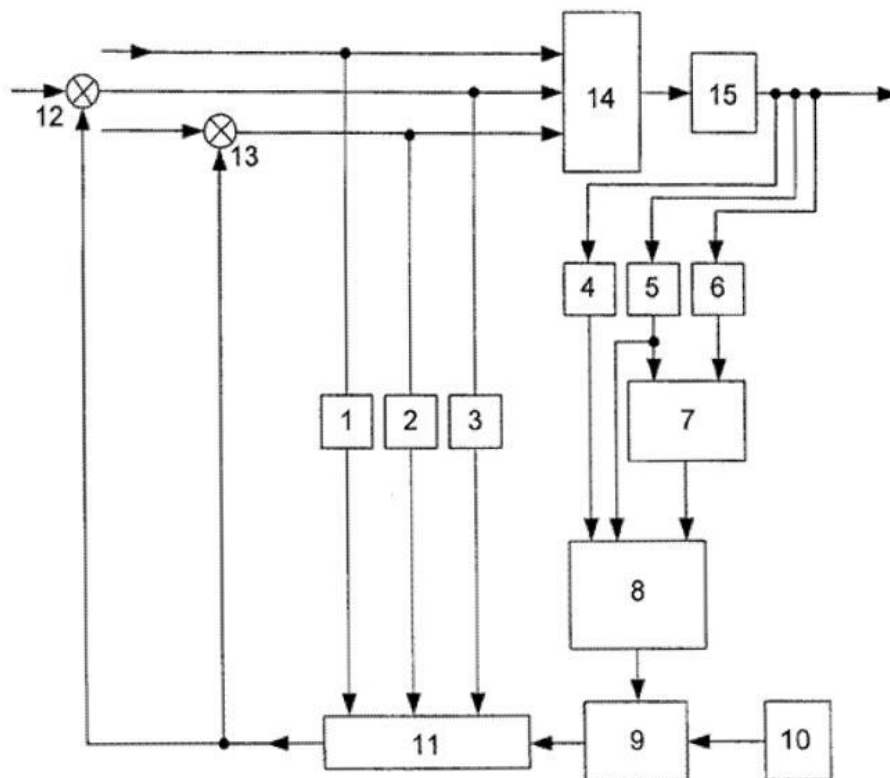

Figure 3. The system of automatic control of the combustion process in a thermal unit. The system contains a fuel consumption sensor 1, an air consumption sensor 2, a water or liquid consumption sensor 3, a nitrogen analyzer 4, a carbon monoxide analyzer 5, an oxygen analyzer 6, a device 7 for calculating the concentration of benzo(a)pyrene, an adder 8 conditional emission toxicity, block 9 for calculating the difference between excesses of the conditional emission toxicity over its permissible standard value, a regulator 10 of the normative component of the emission toxicity, a regulator 11 receiving signals from the sensors 1, 2 and 3 of the fuel, air and water consumption s, secondary regulators 12 and 13, the thermal unit 14 and the exhaust 15.

Method of irradiating gas emissions with ultraviolet radiation of an electric discharge in the working range of wavelengths with an average light energy density of 10-3-3 · 10-1 J / cm2, while irradiation is seen in the presence of saturated liquid vapor. [2] The working temperature of gas emissions is from 0 ° C to 250 ° C, ozone is added to the water.

This method is also distinguished by low efficiency, since the degree of purification of flue gases from benzo(a)pyrene is small. Also, this method leads to acid corrosion of the internal surfaces of the installation, which leads to additional operational costs for equipment repair.

Widely studied way to reduce emissions of benzo(a)pyrene is to introduce water or water vapor into the active combustion zone, as well as to burn water-fuel emulsions. This method is good for its low cost, however, the combustion of water-fuel emulsions is applicable only when using liquid fuels (fuel oil). [4]

Various studies conducted on pulverized coal boilers confirm an increase in the amount of benzo(a) pyrene after measures to reduce emissions of nitrogen oxides (according to some reports, up to 4-5 times). The use of effective ash traps can to some extent correct the situation, but effective ash collection (especially finely divided fractions of fly ash on which benzo(a)pyrene is actively sorbed) can capture only up to 20% of the total emissions of benzo(a)pyrene. [18]
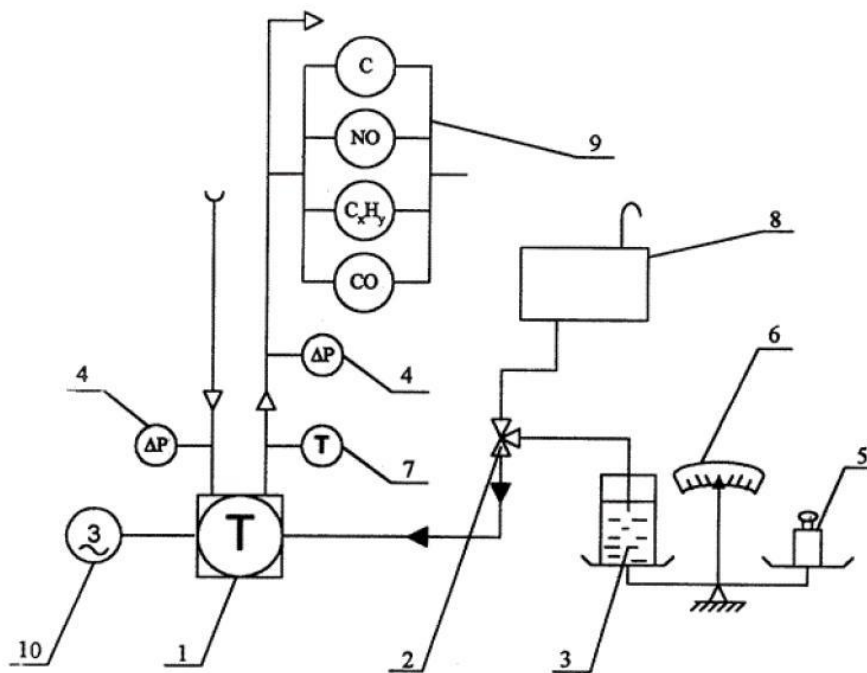

Figure 4. Fuel additive usage scheme: consisting of a diesel engine with standard systems 1, a measuring tank 3 and a fuel supply tank 8 connected to each other and the fuel system of the engine with a three-way valve 2, pressure gauges 4 mounted on the intake and exhaust manifolds of the diesel engine, weights 6 and weighs 5 mounted on the balance, and a thermometer 7 to determine the temperature of the exhaust gases.

There is still a way to automatically control the combustion process in a thermal unit, including measuring the consumption of fuel and air, measuring the concentration of nitrogen and carbon oxides in the flue gases leaving the atmosphere, determining the total allowable conditional emission toxicity, determining the difference in excess of the conditional emission toxicity over its allowable standard value and using this difference as a correction signal. In this method, using an additional sensor, the flow rate of water is measured in the form of liquid or steam, using an additional gas analyzer, the oxygen concentration in the flue gases leaving the atmosphere is measured, the concentration of ben-

zo(a)pyrene is calculated with the help of an additional device, and the total allowable conditional emission toxicity is determined taking into account the influence of the above parameters. The invention allows to reduce the total toxicity of emissions into the atmosphere of pollutants in the flue gas. [6]

The disadvantage of this method is that this method of regulation should be secondary to the main system for regulating the load of the thermal unit and in the event of a conflict of control commands, the commands of the primary regulation system will be executed first, ignoring the environmental component. [9]

Of particular interest is a separate type of solution for the suppression of harmful substances - the use of special fuel additives. An example of this type of solution is additive adapted for internal combustion engines. [7] According to the author's data, the additive contains tetraethoxysilane and 0.1-1.0% transition metal acetylacetonates in the ratio. Its introduction into the fuel at a concentration of 0.01% leads to a decrease in the content of harmful substances in the fuel combustion products: carbon monoxide by 20-85%; unburned hydrocarbons by 15-80%; nitrogen oxides by 15-55%; 40-90% smoke; benzo(a)pyrene by 15-70%. [3]

The use of such additives at thermal power plants is potentially possible. However, it is necessary to conduct additional research aimed at adapting additives to the characteristics of technological processes for the combustion of various fuels.

3. Results

The main problem in this situation is that the content of benzo(a)pyrene in the gross emissions of pulverized coal and gas-oil boilers in the surface air layer does not exceed 0.05 maximum permissible concentration, which, on the basis of current regulatory documents, is not subject to standardization and accounting. At the same time, emissions of sulfur and nitrogen oxides are not only standardized and taken into account, but also become the objects of implementation of measures to reduce them (for example, changing combustion modes in boiler furnaces), which, in turn, can easily lead to significant emissions of benzo(a)pyrene.

The relationship between the decrease in sulfur content in fuel and the increase in emissions of benzo(a)pyrene is most pronounced. An example of this dependence for the BKZ-220 boiler with different sulfur content in the fuel is presented in figure 5.
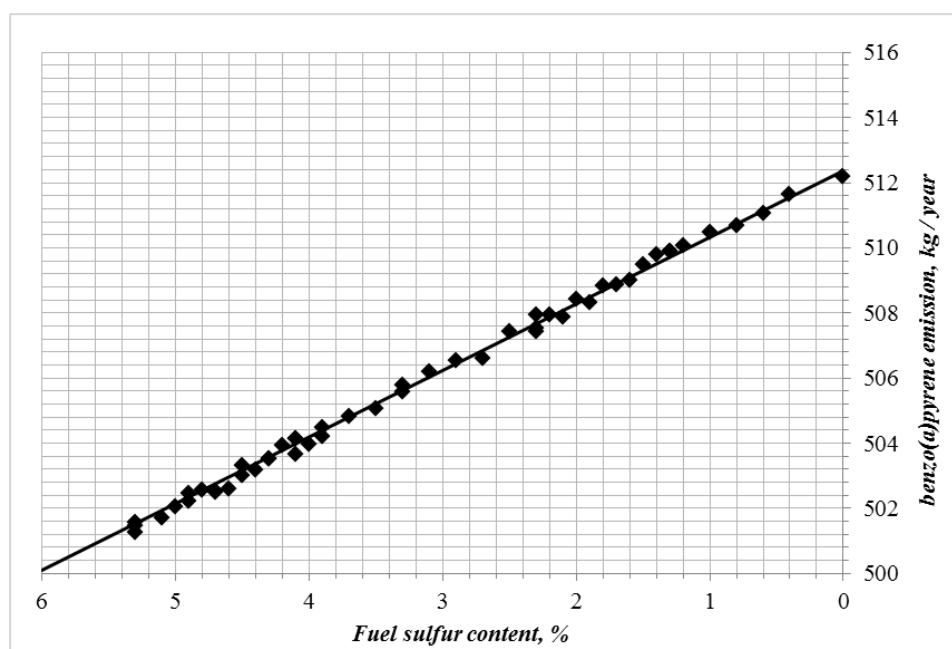

Figure 5. Dependence of benzo(a)pyrene emissions on sulfur content in fuel.

Thus, the relationship between a decrease in the content of sulfur oxides and nitrogen oxides and an increase in the content of benzo(a)pyrene poses a rather serious complex problem of minimizing harmful emissions in flue gases.

4. Conclusion

The insufficient knowledge of the mechanisms of the occurrence and suppression of benzo(a)pyrene, the high risk to human health, the absence of regulatory documents that control its emissions pose a challenge for modern researchers - to find a balance between the suppression of some emissions of thermal power plants, while not increasing others.

The mechanism of occurrence of polycyclic aromatic hydrocarbons during fuel combustion has not been sufficiently studied to date. A number of authors note the existence of a correlation between measures to suppress emissions of sulfur and nitrogen oxides and the concentration of benzo(a)pyrene in the flue gases of thermal power plants, but it is impossible to establish the connection between these processes without extensive experimental studies.

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