Part 1

AIR PROTECTION FROM POWER INDUSTRY EMISSIONS

1.4. Reduction of vanadium- and benzapyrene-containing emissions

1.4.2. Formation and methods of benzapyrene reduction

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Ecological characteristics and standardization of benzapyrene emissions

Benzapyrene (BP) represents a solid crystallized substance in a form of daffodil needles. By a level of affect on a human body BP is referred to the first class of hazard (extremely hazardous substances). Sometimes BP is called as blastomogenic substance, that is, the substance able to cause all possible tumors and neoplasms in the living organism. These formations can be both cancerous (cancer and sarcoma) and others (adenoma, papilloma, etc.). As a result of conducting animal tests and studying the professional cases of cancer development it has been established that all PAHCs (polyaromatic hydrocarbons) have blastomogenic properties, and most of them are carcinogenic as BP. It is also wellknown that by a presence of BP in each specific environment, a presence in it of the majority of other PAHCs is meant. Taking into consideration that BP is the strongest carcinogen, it is accepted as a specific indicator and a parameter of carcinogenic hazard of the studied environment.

Carcinogenic effect of PAHCs is shown as a result of its penetration inside the organism, accumulation to the certain quantity at the definite contact time. Carcinogen accumulation in the organism obviously depends on the applied doze, deformation velocity inside the organism and its secretion. It is ascertained that the human body accumulates and keeps BP better in the childhood and at the age above 50.

Beside the immediate effect, BP as other PAHCs, emitting into atmosphere and interacting with nitrogen oxides, under solar radiation, creates photochemical oxidants, which are the compounds of photochemical smog that is also an additional factor, contributing to ecological situation deterioration.

According to the results of oncologists' and hygienists' studies in our country the following BP maximum concentration limits have been established: $1\cdot10^{-6}$ mg/m³ (average daily) for air in the populated areas; $1.5\cdot10^{-4}$ mg/m³ for air-dry soil and $5\cdot10^{-6}$ mg/l for surface water.

In accordance with "Guidelines for standardization of pollutant emissions into atmosphere for thermal power plants and boiler-houses" RD 153-34.0-02.303-98 for boilers of capacity above 30 t/h, BP is out of the pollution list, emissions of which are subject to obligatory standardization. Along with it on a basis of the document in regions with adverse ecological conditions, local nature protection bodies of Russia have a right to demand from TPPs and boiler-houses the data on BP content in boiler flue gases regardless of their capacity, as well as to set emission standards, if at dispersion calculations TPP creates in the atmospheric air more than 0,05 MPC one-time. As for low-capacity boilers, BP is in the list of substances, subject to the obligatory registration and standardization.

It should be mentioned that for BP only an average daily value is set (MPCa.d.). In this case on the basis of "Procedure of concentration estimation of pollutants in the atmospheric air, containing in emissions of enterprises" OND-86 when estimating a dispersion of the gross BP emissions, its

concentration in the surface air C_{BP} is compared to MPC by the formula:

$C_{\text{BP}} < 10 \text{ MPC}_{\text{a.d.}}$

An influence of constructive features and mode parameters of boilers on benzapyrene generation at combustion of different fuel.

Benzapyrene is one of pyrolysis products of any hydrocarbon fuel. Hence, BP and other PAHCs are generated in this or that degree during all the processes, connected with thermal fuel processing. In connection with it cokechemistry, metallurgy, automobile and aviation transport as well as heat power generation are basic sources of PAHCs in the atmosphere.

The contribution of power objects to the general environmental BP pollution should be examined in two aspects: BP emissions from mean- and large-capacity boilers (above 25 MW) and emissions from steam and hot-water small-capacity boilers. In the first case there is rather a great amount of test data, gained for BP content in combustion products of gas-oil boilers at different modes of fuel burning and in a rather small degree of coal-fired boilers. In the second case available data are extremely few and discrepant in this field.

Gas-oil boilers. The analysis of available test data and an idea about BP generation mechanism during the fuel pyrolysis allow to conclude that with regard to gas-oil boilers a level of BP emissions, discharged together with flue gases, is defined by fuel burning modes; the boiler construction plays the minor role at that. According to data of the majority of authors an influence of mode parameters on BP content is the same as for other products of incomplete combustion (soot, CO, H₂) [1, 2].

The determinative mode factors for BP generation are the air excess factor in the furnace, a temperature mode and conditions of mixture formation. Besides, it has been revealed that application at the gas-oil boilers of technological DeNOx methods, connected with deceleration of the mixing process, decrease in the torch temperature as well as increase in combustion duration, as a rule, results in significant growth of BP formation [1, 2]. With this regard it has been established that the following factors influence on a level of BP concentration in flue gases:

- heat-tension of furnace volume;
- air excess factor in the furnace;
- boiler load;
- a method of arrangement and a degree of recirculation gases supplied into the boiler furnace;
- a method of arrangement and a degree of secondary blasting supply at the staged fuel combustion;
- moisture injection into the furnace for DeNOx purposes;
- purification of convectional surfaces at the boiler operation.

Fig. 1.50 demonstrates a diagram, showing a degree and a direction of influence of fuel combustion main modes on BP generation.

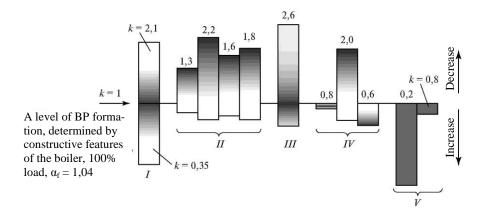


Fig.1,50. A diagram of influence of mode factors on BP generation in the furnaces of gas-oil boilers (k values are resulted relatively to the initial level):

I— excess air factor α_n'' , k=2,1 at α_n'' decrease from 1,04 to 1,01, k=-0,35 at α_n'' increase from 1,04 to 1,1 (minus by figures is BP generation reduction); II— recirculation of flue gases into the furnace: k=1,3 at the gas input into the furnace bottom, k=2,2 at the input into air or a separate burner canal, k=1,6 at the input into nozzles opposite the burners, k=1,8 at the input into nozzles under the burners; III— boiler load, k=2,6 (at the load decrease from 100 to 50 %); IV— staged burning, k=-0,8 at turning off a half of upper level burners (by fuel), k=2,0 at the staged vertical combustion, k=-0,6 at the staged horizontal combustion; V— injection of the moisture into combustion zone, k=-0,2 at the moisture injection into a wall zone as well as at the zonal injection, k=-0,8 at the input into the blast air

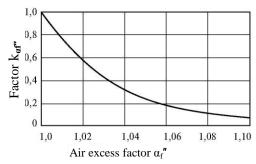


Fig. 1.51. BP concentration in combustion products of gas-oil boilers vs excess air factor in the furnace

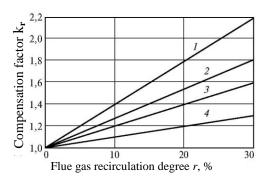


Fig.1.53. Influence of different gas recirculation methods, supplied into the furnace of gas-oil boilers, on BP concentration in combustion products:

I — gas injection into the blast air; 2 — into nozzles under burners; 3 — into nozzles opposite burners; 4 — into the furnace bottom

On the basis of experimental data a number of empirical dependences have been received. These dependences allow making a quantitative estimation of influence of the mentioned factors on BP emission level for gas-oil boilers. In Figs.1.51 – 1.55 quantitative dependences, characterizing a relative change in BP concentration in the combustion products of boilers, vs the change in fuel combustion conditions, are shown.

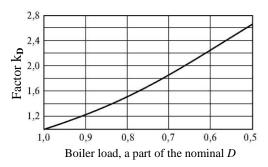
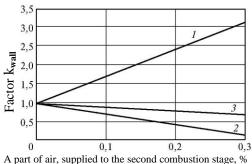


Fig. 1.52. Influence of the boiler load on BP concentration in combustion products of gas-oil boilers



A part of air, supplied to the second combustion stage, %

Fig.1.54. Influence of the staged fuel combustion on BP concentration in combustion products of gas-oil boilers:

I — for the scheme in which vertically staged combustion is arranged; 2 — the same for the horizontal one; 3 — in case of switching off a half of burners of the upper level (by fuel)

A basis of technological methods for NOx emission reduction, presently applied at boilers, are processes, connected with delaying of the burning process, which, as a rule, lead to increase in generation of BP and other products of incomplete burning. In Fig 1.56 a relationship between NO_x concentration as well as total furnace losses at gas and oil combustion and the excess air factor for some boilers is presented. It can be seen that in the zone of extremely low

excess air factor there is a sharp increase in the content of incomplete combustion products in flue gases and, hence, BP content consequently. At the same time in the range of excess air factor changing from 1,00 to 1,06 the dependences for nitrogen oxides are quite opposite.

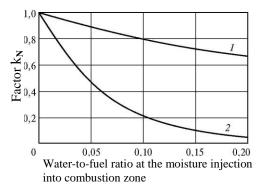


Fig.1.55. Influence of the moisture injection into combustion zone on BP concentration in combustion products of gas-oil boilers:

I — moisture injection into the blast air; 2 — moisture injection into the wall zone of the furnace and zonal injection

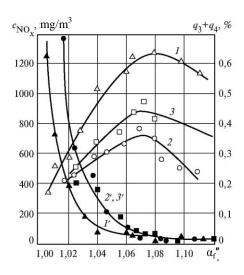


Fig.1.56. Relationships between NO_x concentration (curves I-3) as well as the total furnace losses (curves I-3) and an excess air factor a_f at oil combustion in boilers TGMP-114 $(I,\ I),\ TGM$ -94 $(2,\ 2')$ and at gas combustion in boiler TGM-94 $(3,\ 3')$

Results of the majority of tests, conducted at boilers, equipped with different process facilities for NO_x reduction show that application of flue gas recirculation and arrangement of the multistaged fuel combustion cause a significant growth of BP concentration in combustion products (Figs. 1.53, 1.54). For example, at gas-oil boilers achievement of the maximum reduction efficiency of NOx generation at simultaneous application of the mentioned measures was accompanied by 5...6-time increase in BP concentration in flue gases.

Considering that these DeNO_x methods, applied at gas-oil boilers, obtained a wide application and are presently the only economically available for TPPs, their implementation at boilers should be accompanied by the execution of complex works for optimization of furnace modes to support a permissible level of BP emissions into atmosphere.

Research results of combustion in oil-fired boilers have shown that the achievement of design efficiency of NOx emission reduction with the twofold increase in BP concentration in flue gases without deterioration of technical and economic indicators of the boiler operation could be received due to adjustment of furnace units as well as to burning process optimization (particularly, at TGM-96B boiler) at the simultaneous application of gas recirculation into burners and two-staged oil combustion. Along with it, it has been shown that an insignificant concentration (to $10~\text{mg/m}^3$) or a total absence of CO in combustion products can serve as the indirect criterion for assessing the optimal combustion process for the mentioned purposes. Taking into account a complex conduction of the direct measurements of BP content, CO_2 concentration in combustion products of the boiler, at which technological (process) DeNO_x methods are applied, can be in some degree used for indication of the exceeding of the permissible BP concentrations in flue gases.

Coal-fired boilers. BP concentration in flue gases of boilers at solid fuel combustion is defined by the following parameters:

- heat of coal combustion;
- construction of the furnace bottom (dry-bottom or slag-tap boilers);
 - excess air factor in the furnace;
 - · boiler load;
 - ash collector type and their operational efficiency.

Investigations showed that an influence of the mode factors at solid fuel combustion in coal-fired boilers is less in comparison with gas-oil boilers. A change in the excess air factor in the furnace greatly affects BP generation only in the field of extremely low values of $a_{\rm f}$, and at $a_{\rm f}$ >1,20 BP concentration in combustion products is stabilized in most cases.

An influence of a type of the combusted coal on a level of BP generation has been noticed: at other conditions being equal it is proportional to fuel combustion heat. From the design factors BP generation is influenced by a presence or an absence of a boiler throat. In slag-tap boilers a level of its generation is 1,5 times higher in average.

With regard to large- and mean-capacity boilers, BP concentration in flue gases is determined by a type of the burned coal and, mainly, by ash collector operation efficiency, because while cooling of combustion products along the boiler path as well as forming heterogeneous surfaces of ash and soot particles, there is an active condensation of BP steam at them. By this, it is obvious, that BP absorption happens, mainly, at fine fly ash fractions, having a high specific surface, therefore, a high degree of BP collecting inside the ash-collectors can be reached at present only by the increase in collecting efficiency of small ash fractions. Approximate data of BP collecting efficiency of different ash collectors are resulted below:

Ash collector type	BP collecting efficiency, %
Electrostatic precipitator	60 80
Scrubber	6070
Battery cyclone	4050
Combined ash collector*	70 80

^{*} Battery cyclone and EPS; scrubber and ESP.

Fig. 1.57 demonstrates the diagrams, which show the average levels of BP concentration in the boiler flue gases at combustion of different type of fuel. As it could be seen from Fig. 1.57, BP concentration in flue gases of the coal-fired boilers before passing through ash collectors is at an average 4 times as much as in emissions from oil-fired boilers. However, for BP collecting in ash collectors, BP concentration in flue gases decreases to values, which are comparable to the

similar ones for TPP, where liquid fuel is combusted.

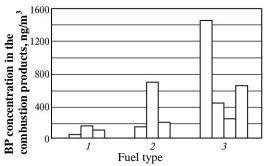


Fig.1.57 A diagram of BP concentration in combustion products of the boiler of capacity of 25 MW: l — gas (without DeNO_x measures, measures for NO_x neutralization, with DeNO_x measures after the furnace process optimization); 2 — oil (the same as for gas); 3 — coal (before ash collectors, after ash collectors —scrubbers, ESPs, battery cyclones accordingly)

This way it could be considered that at effective operation of ash collectors the gross BP emissions from oil- and coal-fired boilers of the same capacity are about the same. But in a number of cases BP dispersion for coal-fired TPPs is lower, therefore, they create a higher local pollution in regions of their location. Besides, it should be taken into consideration that the great part of BP together with the collected fly ash is conveyed to ash disposal areas. By that, the secondary soil and surface water pollution occur. Adequate attention is not paid to this problem, but it requires a special study.

Recommendations on reduction of BP emissions into atmosphere, discharged together with boiler flue gases

Investigations, conducted at gas-oil boilers, showed that application of some technological measures for nitrogen oxide generation reduction (recirculation and staged combustion) results in considerable BP concentration growth (4...5 times) in flue gases, especially, in the zone of extremely low excess air factor at appearance of products of fuel incomplete

combustion in flue gases.

Optimization of furnace modes could be achieved due to the maximum efficiency of technological methods of NO_x reduction at the permissible increase in BP emissions (1,5-2 times). A main condition of furnace processes in this case should be a zero CO_2 concentration in flue gases.

At coal-fired boilers the main method for BP emission reduction into atmosphere is an increase in fly ash collecting efficiency, especially, of their fine fractions, at which BP is the most intensively absorbed while cooling of combustion products along the boiler path.

At the same time it should be mentioned that in the most cases estimations of gross BP emission dispersion both for gas-oil boilers and for coal-fired boilers show that BP concentration in the surface air does not exceed 0,05 MPC, therefore, on a basis of the acting standards, BP emissions are not subject to registration and regulation.

Thermal and Combined Heat Power Plants with the rundown and outdated boiler and furnace facilities are an exclusion. They are, mainly, coal-fired ones as well as large boiler-houses, located in industrial centers with high background BP pollution, where the local nature protection bodies set stricter requirements for pollutant emission sources.

Summarizing the mentioned above, it can be ascertained that although at present large boiler-houses and TPPs are not the basic sources of BP emissions into atmosphere, but a high $C_{20}H_{12}$ hazard requires an attention and caution at introduction of measures, changing the burning modes in boiler furnaces, for example, for NO_x emission reduction. Any measures should be worked out so that BP emissions are kept in the permissible limits.

References to 1.4.2

- Gavrilov A.F., Anichkov S.N. Estimation of BP concentration in flue gases from TPP boilers //Thermal engineering. 1988. № 7. P. 72—73.
- 2. Sigal I.Ya. Air protection at fuel combustion. L.: Nauka, 1988.
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