ENVIRONMENTAL ASPECTS OF NEUTRALIZATION OF GAS EMISSIONS FROM CHEMICAL-RECOVERY PRODUCTION

***Belokon Karina**, Assoc. Prof.,*
Zaporizhzhia National University, Zaporizhzhia, Ukraine
kv.belokon@gmail.com

The cast iron and steel production occupies the important place in economy of Ukraine. The metallurgical branch of industry not only satisfies completely need of the home market, but also is one of the largest exporter to its product. Considering significant volumes of cast iron and steel production, it is impossible to ignore the influence of metallurgical production on environment. Chemical-recovery production occupies not the last place on ecological pressure. Thereby, reduction of materials, emitted in atmosphere formed during coke production, is an actual problem.

At present coke is irreplaceable part of charge of blast-furnace production. The raw materials for production of coke are special sorts of coal. The whole process consists of three stages: preparation to coking, coking proper, catching and conversion of the flying products.

Preparation comprises enrichment and crushing of coal for their averaging on composition and coarseness. Sometimes mixing of different types of coal is needed.

Prepared charge is loaded in camera through special holes. The stove is heated through lateral surfaces (which walls are lined with firebricks) for account of gas burning. At the average, the process occupies 14-16 hours and occurs at the temperature 900-1200°C. Then agglomerated layers of coke are extracted from stove by coke pushers and cooled (put out) by water or inert gas.

The gas, extracting while coking, falls into gas collector, and leads then through gas pipeline up to air and water refrigerators . At the point cooling and condensation occurs, formed mixtures of water and resin are led in concrete or iron reservoirs. In reservoir resin-water mixture is subjected to settling with the result of receiving of tar water and resin directly. Soaking pipe, equipped by pump, is led to the lower part of reservoir for settling. By means of the pipe resin is pumped out into special tanks – storages, whence it comes for the further conversion.

Since resin must be in viscous condition, reservoirs are warmed constantly, mainly by steam. The temperature of the maintenance of the resin in condition suitable for conversion is found within from 70 up to 80 C. At such temperature the separation of flying forming of resin occurs, presenting toxic material itself and requiring neutralization before emission in atmosphere. The averaged composition of emissions from storehouse of resin is presented in tabl. 1.

At analysis of the given data, considering toxicity of emission, it's needed to draw attention on neutralization of phenol, benzene and benzpyrene.

Proceeding from above stated composition of emission, volume of deleted gas the most acceptable methods for their neutralization are: adsorptive method; absorptive method; method of thermal after-burning; catalytic method.

Table 1 – Composition of the main emissions of the place of resin storage of chemical-recovery production

Name of material	Emission concentration мg/м^3	MPC, мg/м^3
Ammonia	100	0,2
Hydrogen sulfide	130	0,008
Cyanic hydrogen	20	0,01
Phenol	1200	0,003
Benzene	100	0,8
Mothballs	350	0,003
Benzpyrene	0,00182	0,1 мкг/100 м^3

Adsorptive method is one of the wide-spread means of air protection. It's founded on absorption of the admixtures by solid bodies with developed surface – adsorbents. The main industrial adsorbents are activated carbons, complex oxides and impregnated sorbents. Activated carbon is neutral to polar and non-polar molecules of adsorbed combinations. Its selectiveness is less than many other sorbents, and it's one of the few suitable to functioning in humid gas flow. Oxide adsorbents possess the more high selectiveness to polar molecules because of their own dissimilar sharing of the electric potential. Their defect is a reduction to efficiency in presence of moisture. Adsorptive methods using allows us to bring back into production the number of valuable compounds. Their main defects come to big duty of desorption stage and the following division that vastly complicates its using for multi-component mixtures, small velocity of purification, impossibility to clean the dust-laden gases.

Absorptive emission clearing is used either for extraction of the valuable component from gas and for sanitary gas cleaning. Absorptive processing is used for discharge, which pollutants are well dissolved in absorbent. It's reasonable to use the given method if the concentration of the extracted component in gas flow forms over 1%. Absorption is the most wide-spread process of gas mixtures clearing in many branches. It's used for emission clearing from hydrogen sulfide, other sulfury compounds, vapor of sulfuric and hydrochloric acids, cyanic compounds, organic matters (phenol, formaldehyde and others). As absorbent water or organic liquids, boiling under high temperature, are mostly used. The defects of the method are high cost of clearing, additional expenses on regeneration of absorbent, necessity of significant production areas for organization of gas purification process.

The method of thermal after-burning is founded on high-temperature (700-1200°C) burning of bad admixtures, contained in gas emission. It is used firstly under high concentration of admixtures and significant contents of oxygen. The process of the thermal oxidation of leaving gases under low temperature is power-hungry, since it requires use of additional fuel for gases heating to high temperature. As a rule, admixtures are burned in stoves with use of gaseous or fluid fuel. Installations are rather simple as constructions, occupy the small area. Their efficiency does not depend on lifetime. The defects of the thermal neutralization are: formation of nitrogen oxides in process of high-temperature burning, significant fuel consumption.

The catalytic methods of gas purification are versatile. They allow us to convert the bad gas admixtures into harmless, less bad or easy deleted. The method enables to process the multi-compounds gases with low concentration of bad materials, obtain the high cleaning degree, lead the process continuously, avoid secondary pollutants formation. The catalytic methods are founded, as a rule, on heterogeneous catalysis, which processes run on surfaces of solid bodies - catalysts. The feature of the catalytic processes lies in the fact that they run under small concentration of the deleted admixtures. The main merit of the method is that it gives the high cleaning degree, but its defect is formation of new, not always harmless materials, which must be deleted from gas by other methods.

Thereby, founding on above mentioned analysis of existing ways of toxic gaseous emission neutralization, it's reasonable to use the catalytic method for leaving gases neutralization on the area of resin keeping.

Iron-based systems of stechiometric composition $FeAl_3$ synthesized by combustion in thermochemical pressing mode were used as investigated catalysts for oxidation of hydrocarbons. In order to increase the catalytic activity, the $FiAl_3$ intermetallide was modified with different amounts of transition metals. In particular, $FeAl_3$ catalysts with manganese (Mn), cobalt (Co) and copper (Cu) additions in amounts up to 15 mass % were obtained. After synthesis, the material is a two-layer product consisting of an oxide phase and a metallic phase. The target metallic phase is separated from the oxide phase, after which it is crushed and fractionated. A precursor fraction of 0,1-0,3 mm was used to obtain the catalyst. The samples were leached using a 20% NaOH solution. A sample was either poured into the alkali solution or immersed in the solution in small portions and incubated for 30 minutes at room temperature, and then subjected to boiling for one hour. After that, the sample was left in the solution for another 24 hours at room temperature. After 24 hours, the alkaline solution was drained and the samples were treated with a 10% hydrogen peroxide solution to remove residual hydrogen from the catalyst surface and stabilize the sample. The catalyst was then washed on a filter with distilled water until it reacted neutrally. After that the samples were dried in the desiccator at 120°C.

The installation of catalytic gas neutralization includes the reactor and the traction-blow device. The installation works as follows. Emissions, cleaned beforehand on absorptive installations, enter in catalytic reactor, where they get through tubular heat exchanger. At that their temperature increases up to the temperature 200-250°C. After heat exchanger gas moves to the zone of electric heating elements, where it is warmed up to the temperature 350-450°C. This temperature is sufficient for quick passing of chemical reactions of oxidation of aromatic hydrocarbon by means of Fe-Co-Mn-Cu catalyst. In layer of the catalyst the reaction of hydrocarbon oxidation of air-gas mixture occurs till practically harmless dioxide carbon and water. After catalyst refined hot gas enters newly on heat exchanger on external part of pipe space and, cooling, is removed in gas-outlet tract of the installation.

Thereby, use of the catalytic way of gas neutralization leaving from the area of resin storage allows us to reduce the concentration of the phenols on 96 %, benzene on 94%, benzpyrene on 53%, that corresponds to the installed rate of emissions.