Catalytic Oxidation of Volatile Organic Compounds in Industrial Off-Gases

Yu.V. Ostrovsky¹, G.M. Zabortsev¹, A.A. Shpak¹, Z.R. Ismagilov²*, V.A. Sazonov², V.D. Meshcheryakov², M.A. Kerzhentsev²

¹Novosibirsk State Design-Exploratory Institute “VNIPET”, Bogdana Khmelnitskogo, 2, Novosibirsk, 630075, Russia
²Boreskov Institute of Catalysis, 5 Akad. Lavrentieva av., Novosibirsk, 630090, Russia

Abstract

Processes and apparatuses for catalytic oxidation of VOCs in industrial off-gases are described, including steady state and unsteady state processes, a combined adsorption-catalytic process and an advanced method of ozone induced oxidation for low concentrated exhausts. On the basis of research and development works a series of catalytic incinerators, operating in steady state and unsteady state mode, of various capacity were designed, constructed and tested in the purification of ventilation air and off-gases from VOCs. The principles of operation of different types of catalytic incinerators and possible areas of application are discussed. For VOC concentrations 150-1000 mg/m³ unsteady state catalytic incinerators of KART type should be used, for concentrations 1000-3000 mg/m³ steady state KROT apparatuses are recommended, and for concentrations over 3000 mg/m³ up to 7000 mg/m³ installations TKM-250. It is shown that for the purification of low concentrated gases with the content of organic vapors below 150 mg/m³ adsorption-catalytic method or catalytic oxidation with ozone in the installation OKA-3000 are most effective. Main kinetic dependencies of the ozone induced oxidation of toluene and acetone over copper oxide catalyst are given and discussed. It is shown that the efficiency of this method of VOCs removal is based on low operation temperature 313-343 K, by contrast to conventional catalytic incineration by air requiring preliminary heating of the gases to 523-573 K. A special consideration is given to adsorptive damping as an efficient method for leveling the VOCs concentrations in the real industrial exhausts directed to the catalytic treatment. The use of adsorptive dampers filled with carbon allows elimination of large deviations of pollutant concentrations in the gas entering the catalyst bed, thus increasing the VOCs removal efficiency from average values. For calculations of adsorptive dampers, an equation describing the profiles of VOC concentrations in gas phase along the length of the adsorbate bed in the damper was derived.

Introduction

For the purification of off-gases from volatile organic compounds (VOCs) thermal, catalytic, adsorptive, combined and other methods can be used. The choice of a particular method depends on the volume of gaseous emissions, their qualitative and quantitative composition, availability of free space to install equipment, power supply, etc.

The methods of catalytic incineration can be considered as most suitable for the purification of off-gases from VOCs (especially multi-component VOC containing gas streams) because of its versatility, simplicity, equipment compactness, high cleaning efficiency, continuous operation and the absence of waste waters.

Conventional design steady state installations UKD-250

As in the former USSR a serial production of standard equipment for VOC oxidation was not organized, some enterprises chose the way to develop individual methods and equipment suitable to their needs. In 1980-1981 the Laboratory of Environmental Catalysis of the Boreskov Institute of Catalysis headed by Prof. V.V. Popovsky and the Research Laboratory of the
Novosibirsk State Design-Exploratory Institute “VNIPET” developed a process [1] and equipment for the installation for VOC catalytic incineration - UKD-250 (Fig. 1).

The installation “UKD-250” was implemented at the Production Association “Sever” in 1981 for the purification of the technological off-gases and exhausts from vacuum pumps at the Compound Production Shop. The installation proved to be efficient, simple in operation, reliable. It provided complete removal of VOCs from the gas streams. The self-cost of the purification of 1000 nm³ was 4.9 rubles in prices of 1984.

During the operation of the installation “UKD-250” it became clear that it has excessive metal weight and a too high power of the electric heaters. Due to these and other reasons the installations of this type were not produced commercially.

After 1.5 years of UKD-250 continuous operation it was established that the copper oxide catalyst IC-12-1 decreased in activity by 50-60% due to the interaction of the active component with the Al₂O₃ support at high temperatures and the formation of copper compounds (CuCl₂, CuSO₄) via reactions with the oxidized oil additives [3].

For some of the reactions that can take place during the poisoning of the copper oxide catalyst IC-12-1 the changes in specific (per bond) standard Gibbs energies were calculated and the quantities of newly formed chemical bonds (p) were determined [3,4]. The results of the calculations are given in Table 1.

A chemical-physical analysis of catalyst samples was carried out, including X-ray phase analysis (in Diffractometer DRON-1.5), and the measurement of the catalytic activity and BET surface area. The presence of additional peaks in diffractograms in the spent catalyst compared to the ones of the fresh catalyst

Table 1

| No | Reaction | $\Delta G^0_{298}$/kJ/mol | $\Delta G^0_{723}$/kJ/mol | p, bonds | $\Delta G^0_{723}/p$, kJ/mol×bond |
|----|----------|--------------------------|--------------------------|---------|---------------------------------|
| 1  | CuO + SO₃ = CuSO₄ | -159.03                   | -94.98                   | 2       | -47.49                          |
| 2  | CuO + 2HCl = CuCl₂ + H₂O | -43.83                   | -49.94                   | 4       | -12.48                          |
| 3  | Al₂O₃ + 3SO₃ = Al₂(SO₄)₃ | -510.69                  | -157.98                  | 6       | -26.33                          |
| 4  | Al₂O₃ + 6HCl = 2AlCl₃ + 3H₂O | 571.81                   | 375.57                   | 12      | 31.30                           |
confirms the formation of new crystal structures during catalyst operation.

The study of the catalyst samples revealed the increase of the sulfur content from 0.0316 to 0.0560, the decrease of the chlorine content from 0.0070 to 0.0043 g/g along the catalyst bed, which can be explained by different thermal stabilities of the compounds formed. During the catalyst operation the BET area decreased by 18-20%, also the reduced activity of the spent catalyst in the CO oxidation was revealed in comparison with the fresh catalyst.

For the elimination of the effects leading to the catalyst poisoning it was recommended to install oil traps at the outlet of the vacuum pumps. In addition, it was recommended to replace the catalyst IC-12-1 by the copper-chromium catalyst ICT-12-8 that was more resistant to catalyst poisons.

Studies of efficiency of VOC oxidation over Cu-Cr catalyst ICT-12-8

The catalyst ICT-12-8 was developed in the Boreskov Institute of Catalysis in cooperation with the Catalyst Design Bureau “Katalizator” (Novosibirsk). This catalyst is intended for the deep oxidation of organic compounds, and it consists of the active component copper chromite deposited on the \( \gamma \)-alumina support.

The studies of the oxidation of a number of widespread VOCs, e.g. toluene, xylene, ethyldiolactose, cyclohexanone and white spirit over the ICT-12-8 catalyst showed that the oxidation reaction had first order with respect to an organic substance and zero order with respect to oxygen. For the above listed compounds the pre-exponential factors and activation energies in the deep oxidation reactions were calculated (Table 2).

At a temperature 700 K, space velocity 10000 h\(^{-1}\) and the concentration range 120-820 mg/m\(^3\) the oxidation efficiency of the compounds over the industrial size ICT-12-8 catalyst is 99.5-99.9%.

Steady-state thermocatalytic installations of advanced design

For the purification of technological off-gases from solvent vapors, in place of the apparatus UKD-250, a series of apparatuses were developed, including a thermocatalytic unit with a screw heat exchanger TKM-250, a catalytic reactor with a slit heat exchanger and a catalytic reactor with a spiral heat exchanger “KROT” [5-7].

The thermocatalytic unit TKM-250 has a monoblock design (Fig. 2) in the form of a column containing inside a single casing a catalytic reactor, a heat recuperator and an electric heater [5].

The catalytic unit consists of a recuperative heat exchanger, a chamber of secondary heating immersed in the heat exchanger, a catalytic chamber and bas-

![Fig. 2. The design of the catalytic unit TKM-250.](image)

### Table 2

| No | Compound       | Temperature range, K | Activation energy (E), kJ/mol | Pre-exponential factor \( (k_0) \), s\(^{-1}\) |
|----|----------------|----------------------|-------------------------------|-----------------------------------------------|
| 1  | Toluene        | 836 - 876            | 79.4 ± 3.5                   | 1.787x10\(^8\)                               |
| 2  | o-Xylene       | 785 - 851            | 100.6 ± 12.0                 | 2.420x10\(^10\)                              |
| 3  | Acetone        | 753 - 853            | 62.8 ± 4.6                   | 8.920x10\(^6\)                               |
| 4  | Ethyldiolactose| 646 - 746            | 58.8 ± 2.5                   | 1.086x10\(^8\)                               |
| 5  | Cyclohexanone  | 726 - 801            | 45.1 ± 3.2                   | 5.390x10\(^5\)                               |
| 6  | White spirit   | 763 - 836            | 48.2 ± 6.5                   | 2.838x10\(^5\)                               |

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kets with the catalyst.

Due to more complete heat utilization in the TKM-250 (the degree of recuperation is 70%) the self-cost of the gas purification is reduced. The thermocatalytic unit TKM-250 is most suitable for the treatment of off-gases with VOC concentration of 3-7 g/m³.

The thermocatalytic reactor with a slit countercurrent heat exchanger has a specific area of 400-600 m²/m³. The contact zone is combined directly with the heat exchanger and is located in the hot zone, thus providing low outer surface of the apparatus simultaneously with high degree of heat recuperation and low pressure drop [6]. Apparatuses of this type with capacity 1000 and 3000 m³/h were designed.

The results of calculations of the parameters of different apparatuses with slit heat exchanger and capacity of 1000 and 3000 m³/h are presented in Table 3. The self-cost of purification of 1000 m³ of gases is 1.2 rubles in prices of 1984.

| Capacity m³/h | 1000 | 3000 | 1000 | 1000 | 1000 | 3000 |
|---------------|------|------|------|------|------|------|
| Dimensions, m | 0.7x1.0x2.1 | 1.4x1.0x2.7 | 0.8x0.8x3.0 | 0.8x0.8x3.4 | 0.8x0.8x2.6 | 1.3x1.0x3.4 |
| Area of heat exchange surface, m² | 504 | 1344 | 302 | 519 | 386 | 1055 |
| Catalyst volume, m³ | 0.05 | 0.15 | 0.05 | 0.5 | 0.05 | 0.5 |
| Pressure drop, Pa | 150 | 310 | 85 | 75 | 60 | 160 |
| Inlet gas temperature, K | 293 | 293 | 293 | 293 | 293 | 293 |
| Outlet gas temperature, K | 342 | 342 | 362 | 362 | 352 | 352 |
| Catalyst temperature | 623-673 | 623-673 | 623-673 | 623-673 | 623-673 | 623-673 |
| Adiabatic heating temperature, K | 323 | 323 | 343 | 323 | 333 | 333 |
| Pitch between the heat exchanger plates, mm | 2.5 | 2.5 | 4.5 | 3.5 | 3.5 | 3.0 |
| Gas space velocity, thousands h⁻¹ | 10-20 | 10-20 | 10-20 | 10-20 | 10-20 | 10-20 |
| Purification efficiency, % | 98-99 | 98-99 | 98-99 | 98-99 | 98-99 | 98-99 |
| Weight of the apparatus, kg | 2600 | 6000 | 2200 | 3000 | 2200 | 5500 |
| Catalyst type | Porous metal plates with 1 mm thickness with deposited active component |

The catalytic reactor of the “KROT” type is designed as a mono-block vertical construction with a circular or oval cross section containing a compact two-way heat exchanger with a horizontal axis of the spiral, with a catalytic section and an electric heater [7].

The two-way heat exchanger has a higher heat transfer coefficient than the flat-parallel one due to the centrifugal force of the gas stream, in addition, its efficiency is increased with the increasing velocity of the gas inside the heat exchanger spiral. The design documentation for reactors with capacity of 150, 200, 800, 1800, 2500 nm³/h.

A reactor of the KROT type with a capacity of 2500 nm³/h was designed and constructed for the treatment of the ventilation exhausts of the lithographic section at the Novosibirsk Plant of Domestic Chemicals (now “SIBIAR”) (Fig. 3). At the area of the heat exchanging surface 180 m² the calculated efficiency of heat recuperation is equal to 80-85%.

Catalytic reactors of the KROT type are all-welded that is advantageous for operation with hazardous and radioactive gas streams. The reactor of this type can be used for the oxidation of hydrogen evolved due to water radiolysis in tanks with aqueous highly active wastes formed at nuclear material processing plants.
A scheme of the ventilation of the tanks was proposed with catalytic oxidation of hydrogen and reversion of the part of purified air to the tank. This scheme allows the reduction of the oxygen concentration in the air above the liquid in the tank, ensuring the safety of radioactive solutions storage, and the reduction of the volume of the gas directed for final purification and emission to atmosphere.

Unsteady-state catalytic apparatuses

The Institute VNIPiET with participation of the Laboratory of Mathematical Modeling of the Boreskov Institute of Catalysis elaborated, designed and tested a catalytic reactor KART-720 with regenerative heat exchangers having a capacity of 720 m³ of gas treated per hour. This apparatus works in an unsteady state mode (reverse process) (Fig. 4). The apparatus is intended for the oxidation of VOCs in ventilation gases. The KART-720 consists of a head part and two sections – each containing a heat exchanger fabricated from alternating flat and sinusoidally corrugated stainless steel plates and a catalyst bed. The head part connected to the both sections contains electric heaters. The plates of the heat exchangers are assembled in batches with air gap between them.

The total surface area of the heat exchangers is 1500 m². The consumed power of electric heaters is 15 kW.

For the calculation of the VOC oxidation efficiency in the apparatus “KART-720” we proposed a formula that takes into account the catalyst activity, the gas overflows inside the apparatus, the free volumes of the heat exchangers and around the catalyst and the time of the half-cycle.

\[
\alpha_{\text{app}} = \alpha_{\text{cat}} \times (1 - \Pi/W) \times (1 - \tau_{\text{valve}}/\tau_{1/2\text{cycle}} - L \times S \times \varepsilon / W \times \tau_{1/2\text{cycle}})
\]

where \(\alpha_{\text{cat}}\) is the catalyst efficiency, %; \(\tau_{\text{valve}}\) and \(\tau_{1/2\text{cycle}}\) are the time for the switching of the valves, s; \(L\) is the length of one half of the heat exchanger, m; \(S\) is the area of the heat exchanger cross-section, m²; \(\varepsilon\) is the fraction of the free volume of the heat exchanger (\(\varepsilon = 0.75\)); \(\Pi\) is the gas overflow inside the heat exchanger, m³/s; \(W\) is the gas flow rate, m³/s.

In the equation (1) the second factor implies the reduction in the purification efficiency due to the gas overflow inside the apparatus, the third factor is responsible for the effect of the gas slip during the switching of the valves (second term in parenthesis) and the blowing of the free volume around the catalyst (third term in parenthesis).
During the tests of the apparatus “KART-720” under industrial conditions good agreement between the experimental results and the efficiency calculated by mathematical modeling was observed.

The apparatus “KART-720” was applied in industry for the purification of the ventilation air from painting chambers and the technological off-gas of the thermochemical destruction compound at the Production Association “SEVER”. Using the catalyst ICT12-8 at a temperature 723-773 K, gas space velocity 10000 h⁻¹, and the time of the half-cycle over 100 s values of the gas purification efficiencies were obtained of 92-94% for toluene vapor oxidation, which is close to the theoretically predicted values.

The apparatus “KART-720” operates under autothermal regimes at VOC concentration of 2 g/m³. At lower concentrations additional fuel is added at the apparatus inlet. In this case the toluene removal efficiency is decreased to 85-87% due to the emission of the non-purified gas from the free volume around the catalyst during the reverse of the gas flow.

The supply of the fuel (or gas-vapor mixture containing the fuel at the 1-5% of the total gas supply) between the catalyst beds is more efficient [8]. In this case the purification efficiency of the ventilation gas containing 2.5-2.8 g/m³ of toluene at the catalyst temperature 803 K is 99.1-99.7% (see Table 4).

| No | Place where toluene vapor is fed | Temperature of the catalyst, K | Inlet toluene concentration, mg/m³ | Outlet toluene concentration, mg/m³ | Purification efficiency, % |
|----|-------------------------------|-------------------------------|-----------------------------------|-----------------------------------|--------------------------|
| 1  | At the apparatus inlet         | 723                           | 1897                              | 345                               | 81.8                     |
|    |                               | 728                           | 2448                              | 462                               | 81.1                     |
|    |                               | 728                           | 2448                              | 345                               | 85.9                     |
|    |                               | 733                           | 2475                              | 356                               | 85.6                     |
|    |                               | 763                           | 2101                              | 178                               | 91.5                     |
|    |                               | 808                           | 3019                              | 464                               | 84.6                     |
|    |                               | 823                           | 2937                              | 273                               | 90.7                     |
|    |                               | 863                           | 1429                              | 224                               | 84.3                     |
| 2  | Between the catalyst layers    | 808                           | 2819                              | 9.05                              | 99.7                     |
|    |                               | 835                           | 2559                              | 15.4                              | 99.4                     |
|    |                               | 893                           | 2832                              | 24.9                              | 99.1                     |
|    |                               | 893                           | 3281                              | 30.8                              | 99.1                     |
|    |                               | 893                           | 2697                              | 13.3                              | 99.5                     |
electric energy required for the gas transportation through the adsorbent bed. The scheme of the realization of this process is shown in Fig. 5.

Fig. 5. The block diagram of the adsorption-catalytic method of off-gas treatment.

### Adsorption-catalytic method of VOC removal from gas streams

The analysis of various methods for the purification of low concentrated VOC containing gases (VOC concentration below 150 mg/m³) shows that the decrease of the energy consumption at the high purification efficiency can be realized by the adsorption-catalytic method based on the purification of the gas by adsorption followed by catalytic oxidation of the products obtained in the process of thermal desorption [10].

Out of numerous adsorbents studied, such as activated carbons, silica gels, zeolites, coked alumina, activated carbons are the most suitable ones for the adsorption-catalytic method because they have high adsorption capacity for organic compounds (5-10%) even in humid gases.

Based on the results of laboratory studies, a pilot adsorption-catalytic installation for the purification of the ventilation gas from painting chambers with a capacity of 75 m³/h was created at the Production Association “SEVER”. The installation consists of an adsorber of 0.16 m height filled with activated carbon AP-3, a heater, UKD-250 installation for VOC oxidation, and a fan. The VOC catalytic oxidation was carried out over the catalyst IC-12-1 at 450-500°C.

The purification of the ventilation gas from painting chambers was complicated by the presence of paint aerosol particles at a concentration of tens of mg/m³. To exclude the deactivation of the adsorbent a gravel filter was installed before the adsorbent bed.

After 80 h operation of the installation the solvent vapor slip was observed at the outlet of the adsorber and the regeneration of the adsorbent was started. The regeneration was carried out using hot air at the temperature of 130°C or preferably by the mixture of air with steam (steam conc. 60%) because of the carbon flammability. The time for the adsorbent regeneration was 3-4 h.

The supply of the regenerating agent was conducted in the direction opposite to that of the flow of the ventilation gases during their purification.

The capacity of the activated carbon AP-3 for the adsorption from humid gases with VOC concentration 350 mg/m³ was 7-8 wt.% and the maximum outlet toluene concentration was in the range of 10-18 mg/m³. To prevent the catalyst overheating the desorbed gas was diluted by air.

The concentration of solvent vapors at the outlet of the adsorption-catalytic installation did not exceed 6 mg/m³ – the value consistent with the emission standards.

The results obtained were used for the preparation of Technical Specifications for the Design of an industrial installation with a capacity of 30000 m³/h [11,12]. The self-cost of the purification of 1000 m³ of gas did not exceed 0.35 rubles in prices of 1984.

### Ozone induced catalytic oxidation of organic compounds in off-gases

Some approaches for the solution of the problem of purification of ventilation gases from VOCs (with VOC concentrations below 150 mg/m³) are presented above.

However, it is not always economically expedient to heat the gas to high temperature or to use flammable adsorbents. Therefore the search for economic gas purification methods – simple in operation and fabrication is an urgent task.

One of methods meeting these requirements is ozone induced VOC catalytic oxidation [13-15].

All known deep oxidation catalysts exhibit sufficiently high activity at temperatures 523-573 K, there-
fore the catalytic incineration process consume much energy to heat the gas before the treatment. In this connection, the development of methods of deep catalytic oxidation permitting the decrease in operation temperature is of great scientific and practical importance.

Thermodynamic analysis of the reactions of total oxidation of different hydrocarbons by ozone using specific (per bond) change in standard Gibbs energies \( -\Delta G^\circ_{298}/p \) was performed. The comparative analysis shows that the oxidized compounds can be arranged in the following sequence according to the increasing thermodynamic preference for the process occurrence: dimethylphthalate, styrene (acetone), \( o \)-xylene, toluene, butylacetate, cyclohexanone.

The equilibrium concentrations of hydrocarbons subjected to oxidation are much lower than their maximum allowable concentrations in air because of very large values of the equilibrium constants of the reactions of VOCs oxidation by ozone (\( \lg K_p > 100 \)).

The study of ozone induced catalytic oxidation of organic compounds (toluene, \( o \)-xylene and acetone) over the catalyst ICT-12-9 with 0.40-0.63 mm granule size was conducted at \( T = 313-388 \) K, gas space velocity \( W = 3000-50000 \) h\(^{-1} \) and gas humidity \( P_{H_2O} = 1600 \) Pa. Catalyst steady state in the flow reactor was attained in 1.5-2 h for toluene and in 3.5-4 h for \( o \)-xylene and acetone.

In the range of 313-343 K the temperature has no substantial effect on the degree of toluene oxidation by ozone over ICT-12-9 catalyst, therefore the experimental points for different temperatures lie on the same curve (Fig. 6).

In a wider temperature range 303-388 K, the temperature dependence exhibit a more complex behavior (Fig. 7). At temperatures below 333 K the raising of the temperature results in the increase of the conversion, but at higher temperatures the decrease of the toluene conversion is observed, probably, due to the prevailing of the process of ozone decomposition.

An adverse effect of humidity on the efficiency of the ICT-12-9 catalyst in the ozone induced VOC oxidation was established. The observed decrease in the oxidation efficiency is explained by the adsorption of water vapor on the catalyst surface.

The rate of toluene oxidation is proportional to the ozone concentration; i.e. the order of the reaction over copper oxide ICT-12-9 catalyst with respect to ozone is equal to 1 [16].

The obtained experimental data on the effects of temperature and residence time on the toluene degree of conversion upon oxidation with ozone showed that the order of the reaction with respect to toluene is zero, which is explained by strong toluene adsorption on the catalyst surface at low temperatures.

Ozone induced oxidation of the mixture of acetone and toluene vapors was carried out at \( T = 333 \) K, space velocity \( W = 10000 \) h\(^{-1} \); \( C_{oil}=0.11 \) g/m\(^3\); \( C_{acet}=0.35 \) g/m\(^3\); \( P_{H_2O} = 1390 \) Pa. of conversion upon oxidation with ozone over ICT-12-9 catalyst versus ozone at temperatures: - 313K, \( \Delta - 323 \) K, \( \times -333 \) K, \( W =10000 \) h\(^{-1} \), \( P = 990 \) Pa.

![Fig. 6. Toluene degree of conversion during oxidation by ozone over ICT-12-9 catalyst versus ozone at temperatures: - 313K, \( \Delta - 323 \) K, \( \times -333 \) K, \( W =10000 \) h\(^{-1} \), \( P = 990 \) Pa.](image)

![Fig. 7. Temperature dependence of the degree of toluene oxidation by ozone over the catalyst ICT-12-9 at \( W = 10000 \) h\(^{-1} \); \( C_{oil}=0.11 \) g/m\(^3\); \( C_{acet}=0.35 \) g/m\(^3\); \( P_{H_2O} = 1390 \) Pa.](image)

Ozone induced oxidation of the mixture of acetone and toluene vapors was carried out at \( T = 333 \) K, space velocity \( W = 10000 \) h\(^{-1} \) and gas humidity 1170 Pa. A distinct difference between the reactivity of these organic compounds in the reaction with ozone was found both in experiments with mixtures and with the individual compounds. The reaction of toluene oxidation proceeded at much higher rate than that acetone oxidation. The competition of toluene and acetone for catalyst active sites was established.

The more reactive toluene occupied the catalyst surface hindering acetone oxidation by ozone. As a
result, the rate of acetone oxidation by ozone decreased in the presence of toluene. The effect of the adsorptive inhibition of the reaction rate explains the contradiction between the thermodynamic analysis of the process and the experimentally obtained results.

It should be noted that selective ozone induced oxidation can be used for the separation of mixtures in case when one or several components should be removed from a mixture.

The chromato-mass-spectroscopy technique showed the absence of products of partial oxidation during oxidation of mixtures of toluene and acetone over ICT-12-9 catalyst.

During long exploitation of the catalyst ICT-12-9 in the process of ozone induced oxidation of VOCs in humid gases the catalyst deactivation was observed. This was displayed by the decrease of the VOC conversion, and the change of the color of the frontal part of the catalyst bed from black to light blue. The cause of the catalyst deactivation is probably the formation of copper carboxylates and hydrocarbonates on the catalyst surface. For the elimination of these compounds and reclamation of the catalyst activity the samples of partly deactivated ICT-12-9 catalyst were calcined in airflow at temperatures 373, 413, 478 and 523 K. The catalyst calcination was found to increase the efficiency of toluene oxidation with ozone by 10-15%. The temperature of regeneration should be above 413 K.

Summarizing the above given data, it can be concluded that in the oxidation of VOCs with ozone over the ICT-12-9 catalyst the competitive processes of adsorption of VOCs, water vapor and ozone take place. The low temperatures of the ozone-induced oxidation provide high coverage of the surface by organic molecules and water. Ozone decomposition occurs on free surface sites. Monatomic oxygen formed in this process oxidizes the adsorbed organic molecules. Simultaneously the process of dioxygen formation takes place, which explains the fact that only part of the decomposed ozone participates in the oxidation reactions.

As the rate of ozone decomposition over the ICT-12-9 catalyst is higher than the rate of VOC oxidation, and to provide the necessary efficiency, additional supply of ozone to the purified gas may be required to compensate for ozone decomposition, which can be done efficiently in a ‘multishelf’ reactor [17].

Figure 8 shows the calculated dependencies of the concentrations of toluene and ozone in a three-shelf reactor.

It should be noted that in the process of toluene oxidation with ozone only frontal parts of the catalyst layers work efficiently. In order to increase the efficiency of the ozone use in the principal reaction the ‘zone’ of ozone decomposition should be extended. This can be done by increasing catalyst granule size.

**Catalytic decomposition of ozone**

The development of the process of ozone induced VOC oxidation is closely connected with the problem of the decomposition of residual ozone before the purified gas emission to the atmosphere. In this connection, studies were carried out to elucidate the dependencies of the degrees of ozone decomposition over the catalysts IC-12-1 and ICT-12-9 on the ozone concentration, gas humidity, catalyst granule size and residence time at different temperatures as well as on the concentration of toluene vapors present in the gas [18,19].

Over the catalyst IC-12-1 the process was studied at a space velocity $W = 10000-30000 \text{ m}^3/\text{h}$ and $T = 293-333 \text{ K}$. As the temperature is raised the degree of ozone decomposition increases. The increase of ozone concentration or space velocity at temperatures below 308 K results in the reduction of the ozone decomposition degree.

The activity of the ICT-12-9 catalyst in ozone decomposition is higher than that of IC-12-1. At a space velocity $W = 50000 \text{ h}^{-1}$ the degree of ozone decomposition over the ICT-12-9 catalyst attains 95%, which is close to the values obtained over the most active silver-manganese catalyst.

It was found that the process of ozone decomposi-
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The studied copper oxide catalysts work with sufficient stability in humid atmosphere. Table 5 shows the dependencies of the ozone decomposition degree on humidity under the following conditions: for IC-12-1 at W = 30000 h⁻¹, T = 313 K; for ICT-12-9 at W = 50000 h⁻¹, T = 293 K.

Table 5
Dependences of degree of ozone decomposition on humidity

| No | IC-12-1 | ICT-12-9 |
|----|---------|----------|
|    | P_H2O Pa | α, %     | P_H2O Pa | α, %     |
| 1  | 1260     | 82.8     | 1230     | 96.6     |
| 2  | 1420     | 77.4     | 1430     | 94.5     |
| 3  | 1580     | 71.6     | 1580     | 88.4     |
| 4  | 1840     | 66.7     | 1800     | 79.2     |
| 5  | 2070     | 61.5     | 2070     | 60.8     |
| 6  | 2320     | 56.1     | -        | -        |
| 7  | 2620     | 54.3     | -        | -        |

These data show that the increase of the gas humidity leads to the decrease of the efficiency of both catalysts in the reaction of ozone decomposition.

At low temperature T = 293-313 K and high humidity P_H2O > 1600 Pa the deactivation of ICT-12-9 catalyst occurs accompanied by the change of the color of the frontal part of the catalyst bed from black to light blue.

The partly deactivated catalyst ICT-12-9 was used for the study of the ozone decomposition kinetics. The reaction rate is described satisfactorily by an equation of the first order in ozone. The close values of the activation energies of the fresh and deactivated catalysts ICT-12-9 (Table 6) can be the evidence that the deactivation has no effect on the mechanism of ozone decomposition.

After thermal treatment at T = 528 K for 2 h in air flow the restoration of the initial black color of the deactivated ICT-12-9 catalyst sample occurred.

The degree of ozone decomposition over the regenerated ICT-12-9 catalyst is lower than that observed over the fresh catalyst. The activation energy of ozone decomposition over the regenerated ICT-12-9 turned out to be close to the activation energy found for the fresh catalyst IC-12-1 (Table 6).

Some decrease in the catalyst activity during its exploitation can be compensated by the increase of the operation temperature by 10-15 K.

High activity of the catalyst ICT-12-9 in the reaction of ozone decomposition is probably due to the presence of copper (I) oxide forming in the catalyst during its mechanical activation upon preparation. Copper (I) oxide is found in the composition of active sites responsible for ozone decomposition on IC-12-1 catalyst. The deactivation of the latter is due to the interaction of copper (II) oxide and small amounts (1.5% of monolayer) of copper (I) oxide present in the catalyst ICT-12-9 with ozonized air components: CO2, H2O, O2 and O3 leading to the formation of CuCO3, Cu(HCO3)2, Cu2CO3(OH)2 (malachite) and other compounds on the catalyst surface.

The comparison of specific (per 1 bond) Gibbs energies show that the reactions with copper (I) oxides are more preferable [20]. The oxidation of copper (I) oxide to copper (II) oxide by ozone proceeds preferentially by ozone rather by oxygen. This explains the absence of the ICT-12-9 catalyst color change upon its treatment by humid air without ozone, though the carbonization and hydration of the mechanically activated CuO surface is well known.

Thermal regeneration of the catalyst ICT-12-9 leads to the destruction of CuCO3, Cu(HCO3)2, Cu2CO3(OH)2 and the formation of copper (II) oxide, which is evidenced by the close values of the activation energies for the regenerated catalyst ICT-12-9 and the fresh catalyst IC-12-1 (Table 6). The transition of copper (I) oxide to copper (II) oxide upon the interaction with CO2, H2O, O2 and O3 and the subsequent thermal treatment of the catalyst ICT-12-9 leads to the disappearance of copper oxide (I) and...
as a consequence to the change in the activation energy of the process of ozone decomposition.

High activity of copper oxide catalysts ICT-12-9 and IC-12-1 favors their application in industry. These catalysts exhibited stable performance, and the decrease in the degree of ozone decomposition during 220 h operation did not exceed 5-6%.

**Adsorptive damping of VOC concentration fluctuations**

The concentrations of most pollutants in ventilation off-gases change with time. These fluctuations are caused by the periodic character of the operation of the equipment emitting pollutants. A typical example of such gas emissions are ventilation exhausts from painting chambers, in which the content of organic solvent vapors varies from 0.05 to 5.0 g/m³. These conditions complicate the purification of ventilation air because in the case of adsorptive purification the amount of adsorbent and apparatus size must be excessive, i.e. taken with the allowance for organics concentration fluctuations; in the case of catalytic incineration an abrupt increase of VOC content can lead to catalyst overheating and damage. To overcome these difficulties, the gases are diluted with air, or emergency gas emission to the atmosphere is conducted in case of abrupt jump in pollutant concentrations. This leads to worsening of the performance of gas treatment equipment and the environment pollution.

The fluctuations of the concentration of pollutants can be considerably reduced by the use of the method of adsorptive damping [21] that can be effectively used for prevention of catalyst overheating and the prolongation of its lifetime.

When a gas mixture flows through an adsorbent bed any changes of an adsorbate inlet concentration lead to considerably less changes in an adsorbate surface concentration, because the latter, as a rule, is greater by more than one order of magnitude than the equilibrium concentration in the gas mixture. As the result of adsorption-desorption processes the adsorbate concentration at the outlet of the bed changes only slightly. Thus the adsorptive damping can be an effective technique for the stabilization of the adsorbate concentration.

A principal feature of a cyclic adsorption process is the incompleteness of individual stages, resulting in their mutual influence.

At the frontal layers of an adsorbent equilibrium characteristics are determining and at the rear layers kinetic characteristics are of greater importance. In the region of equilibrium regimes substantial concentration fluctuations take place while in the kinetic region the amplitude of fluctuations is less compared to the inlet one.

Experimental data showed high damping ability of the activated carbon AP-3. This adsorbent provides substantial (10-15 times) smoothening of concentration oscillations. After 5-6 cycles the average (calculated) concentration of toluene vapor comes to plateau, and the experimental points obtained in steady state circumscribe sinusoid. Smoothening of concentration oscillations depends on the time of the cycle; the shorter the time the greater the smoothening. Independently of the cycle duration, the average (calculated) concentrations coincide for different experiments.

The study of adsorptive damping of hydrocarbon mixtures in the activated carbon AP-3 showed that the smoothening of the concentration oscillations proceeds according to the same laws as found for individual compounds.

For calculations of adsorptive dampers an equation (2) describing the correlation of concentrations of hydrocarbon vapors in gas phase along the length of the adsorbate bed under steady state conditions was derived:

\[
C = C_{\text{MIN}} + \frac{(C_{\text{MAX}} - C_{\text{MIN}}) \times \Theta}{T} + \sum_{k=1}^{k} \frac{1}{\beta} \times T \times \\
\sin \left( \frac{k \pi \Theta}{T} \right) \times \frac{2 \times (C_{\text{MAX}} - C_{\text{MIN}}) \times l}{\pi \times (1 - \Theta)} \times \\
\exp \left[ -\frac{\beta \times l}{u \times (1 + \alpha_k^2)} \right] \times \cos \left[ \frac{2 \pi k}{T} \right] \times \\
\left\{ \frac{l - \frac{l}{u} \times \left( \frac{\alpha_k^2}{m \times (1 + \alpha_k^2)} \right)}{t} \right\} \tag{2}
\]

where \(C_{\text{MAX}}, C_{\text{MIN}}, C\) are maximal, minimal and current adsorbate concentrations, g/m³; \(m\) - constant - a value reciprocal to Henry’s constant; \(\varepsilon\) - void fraction of adsorbent bed; \(\beta\) - coefficient of mass exchange between gas flow and the surface of adsorbent grains related to 1 m³ of adsorbent bed, s⁻¹; \(t\) - time, s; \(u\) - gas velocity related to a free cross section of an apparatus, m/s; \(l\) - coordinate running along the length of the bed, m; \(T\) - duration of the cycle; \(\Theta\) - duration of concentration uprise pulse; \(\alpha = m \times \omega_k; \omega_k = \frac{2 \pi k}{T};\)
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\[ k = 1, 2, 3, \ldots \]

Figure 9 shows the comparison of toluene vapor concentrations at the outlet of an adsorber: with the activated carbon AP-3 calculated from the above equation and determined experimentally. The calculated values are sufficiently close to the experimental ones.

![Graph showing toluene vapor concentrations](image)

Fig. 9. The appearance of inlet pulse 1, calculated concentration curve 2 and experimental data on adsorptive damping of toluene vapor in AP-3 activated carbon at: \( T=298 \text{ K} \), \( \Theta=600 \text{ s} \) and \( t_c = 900 \text{ s} \).

The adsorptive damper can be used in analytical chemistry [22, 23], in particular for the determination of average pollutants concentrations [24].

These laboratory investigations were the basis for the elaboration of a complete set of design documentation for pilot installation OKA-3000 [25, 26] for ozone induced VOC oxidation. This installation (Fig. 10) consist of: an adsorptive damper 1, air filters 2, 9; a heat utilizer 4, fans 7, 8; ozone generator 3 and specially designed three-shelf catalytic reactor 6 with layer by layer ozone introduction.

The advantages of the “OKA-3000” installation are low energy consumption, minimum non-productive ozone losses, high space velocity of the treated gas, possibility to purify gases with mixtures of VOCs, efficient operation with variable inlet concentrations.

The calculated purification efficiencies are the following: toluene 94%, o-xylene > 95%, acetone > 72%. The calculated cost of the purification of 1000 m³ of gas is 0.6-0.65 rubles in prices of 1984.

**Application of unsteady state gas treatment technique for ozone induced VOC oxidation**

It is proposed to realize the process of ozone induced VOC oxidation under unsteady state conditions. In this method the oxygen-ozone or air-ozone mixture is supplied between two catalyst beds, and the process is carried out at a temperature of 323-353 K [27].

![Flow diagram of ozone induced oxidation of VOCs in the installation “OKA-3000”](image)

Fig. 10. Flow diagram of ozone induced oxidation of VOCs in the installation “OKA-3000”.

Low temperature of the process and an efficient regenerative heat exchanger allow substantial reduction in the gas treatment cost.

**Conclusion**

On the basis of research and development works a series of catalytic incinerators, operating in steady state and unsteady state mode, of various capacity are designed and constructed for the purification of ventilation air and off-gases from organic compounds. For VOC concentrations 150-1000 mg/m³ unsteady state catalytic incinerators of KART type should be used, for concentrations 1000-3000 mg/m³ steady state KROT apparatuses are recommended, and for concentrations over 3000 mg/m³ up to 7000 mg/m³ the TKM-250 installations. It is shown that for the purification of low concentrated gases with the content of organic vapors below 150 mg/m³ the adsorption-catalytic method or the catalytic oxidation with ozone in the installation OKA-3000 is most effective.

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