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Procedures for making gaseous industrial waste safe

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ABSTRACT. The application of various methods (adsorption, absorption, thermal afterburning, catalytic purification, and others) for the removal of sulphur and nitrogen oxides, toxic organic compounds, hydrogen sulphide, and carbon monoxide from industrial waste gases is described. Much attention is devoted to the catalytic procedure for making the gases safe using an energy collecting non-stationary method (reversible process).

The advantages and limitations of various gas purification methods are considered.

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I. Introduction

The formation of gaseous compounds contaminating the atmosphere is caused mainly by the combustion of mineral fuels, industrial technological processes, and natural phenomena. The development of industry has led to a constant increase in the amount of waste. Thus in the USA the dominant contribution to the sulphur dioxide waste (76%) is made by fuel combustion processes in stationary plants. Carbon monoxide enters the atmosphere to a large extent as a result of the operation of the engines of automobiles and other means of transportation (76%). Industrial organic solvents and petroleum gas processing are sources responsible for 29% of the emitted hydrocarbons, while 38% is contributed by transport. In the Federal Republic of Germany, the fraction of transport waste in 1982 was 55%, while that of waste generated by thermal electric power stations (TES) was 28% relative to the total amount of nitrogen oxides of industrial origin. In terms of the SO_2 (~150 million tonnes annually) and hydrocarbons (~70 million tonnes annually) ejected into the atmosphere, industry has already become comparable to natural sources.[1,2] The main contribution to the contamination of the atmosphere by carbon monoxide (300 million tonnes annually) also comes from man's industrial activity.[1] Only the amount of nitrogen oxides originating from natural sources is approximately ten times greater than that arising from anthropogenic sources (700 million tonnes annually against 50 million tonnes annually).[1,2] However, as a result of the localisation of this type of waste at sites with the highest population density their negative effect is considerable.

The main procedure for reducing the amount of toxic waste ejected into the atmosphere in technological processes involves the improvement of the latter. For example, in order to reduce the sulphur dioxide waste in the combustion of fuel, use is made of the preliminary elimination of sulphur and its binding during the combustion process.[1,3–6] A decrease in the formation of nitrogen oxides is achieved using a stepwise combustion of fuel,[7,8] with the aid of special types of burners,[8–10] and by a number of other measures. However, in most cases the improvement of technological methods, especially the existing methods, does not permit the attainment of the permissible norms and special additional purification of waste gases to remove toxic impurities is necessary.

The industrial methods for making safe gaseous waste can be divided into the following main groups:[1,11] (1) condensation; (2) absorption; (3) adsorption; (4) thermal combustion; (5) chemical conversion of impurities into non-toxic or readily utilisable compounds; (6) catalytic methods; (7) membrane separation; (8) biochemical purification.

II. Absorption methods

Absorption involves the dissolution of the gaseous component in a liquid solvent. In practice absorption is usually accompanied by a rapid chemical reaction in the liquid phase.

Absorption systems can be divided into aqueous and non-aqueous. In the latter case, involatile organic liquids are usually employed. A liquid is used for absorption only once or it is regenerated with the isolation of the contaminant in a pure form.[1,11] Schemes with a single employment of the absorbers are used in those cases where absorption leads directly to the formation of the finished product or intermediate. As examples, one may point to the synthesis of inorganic acids (absorption of SO_3 in the manufacture of sulphuric acid,[12] the absorption of nitrogen oxides with formation of nitric acid[13]), salts (absorption of nitrogen oxides by alkaline solutions with formation of nitrite-nitrate liquors, absorption by aqueous lime or limestone solutions with formation of calcium sulphate[14]), and other substances (absorption of NH_3 by water to obtain aqueous ammonia[15]).

Schemes with the repeated use of absorbers (cyclic processes) are more common. They are used to trap hydrocarbons,[11] to eliminate SO_2 from TES smoke gases,[16] to eliminate hydrogen sulphide from venting gases by the iron-soda method with formation of elemental sulphur,[17] and for the monoethanolamine removal of CO_2 from gases in the nitrogen industry.[15]

Depending on the method used to generate the phase contact surface, one can distinguish surface, bubbling, and spraying (atomising) types of absorption apparatus. In the first group of

devices, the contact surface between the phases consists of a liquid mirror or of the surface of a flowing film of liquid. Packed absorbers, in which the liquid flows down the surface of the packing immersed in it and made up from bodies of different shapes are also included in this group. In the second group of absorbers the contact surface is increased by dispersing the gas streams in the liquid into bubbles and jets. Bubbling is achieved by passing the gas through a liquid-filled apparatus or in apparatus of column type with plates of different kinds. In the third group, the contact surface is created by spraying the liquid into the bulk of the gas. The contact surface and the efficiency of the process are determined overall by the degree of dispersion of the sprayed liquid.

Packed (surface) and bubbling plate absorbers have come to be most widely used.[1,16] The trapped component must be readily dissolved in the absorption medium and frequently interacts chemically with water, as happens, for example, in the elimination of HCl, HF, NH_3, and NO_2 from gases. In order to absorb gases with a lower solubility (SO_2, Cl_2, H_2S), use is made of alkaline solutions based on NaOH or $Ca(OH)_2$. The addition of chemical reagents increases in many instances the efficiency of the absorption by virtue of the occurrence of chemical reactions in a film.[1,18] An increase in the degree of purification can also be achieved by carrying out the absorption process in two stages.[19] There exist various modifying additives to aqueous solutions. Thus coal tar is introduced to trap naphthalene or formaldehyde,[20,21] phenol is trapped by sodium hydroxide solutions,[22] and the use of alkali metals and tertiary C_3-C_{20} amines is effective for the elimination of phosgene from gases.[23] Gases containing HCl, NH_3, and hydrocarbons are purified by being absorbed in aqueous solutions of formaldehyde and subsequent oxidation.[24] The application of solutions of urea or its derivatives is recommended for the trapping of formaldehyde.[25] Systems in which finely dispersed activated charcoal is added to the absorption liquid to increase the trapping efficiency should be mentioned specially.[26–28] In order to improve the removal of organic substances from gases, an oxidant is also introduced simultaneously into the system.

Absorption or more precisely absorption-chemical procedures for making safe the smoke gases from TES, metallurgical industries, and other objects by removing SO_2 has come to be widely used recently. The first large industrial apparatus in the world for the removal of sulphur, operating on the basis of the wet limestone method and having a productivity corresponding to 3 million $m^3\ h^{-1}$ of combined gases, began to operate at the Magnitogorsk Metallurgical Unit in 1961. At the present time, this plant traps about 100 000 tonnes of sulphur dioxide annually.[14] The volume of TES gases freed from SO_2 now reaches $10^9\ m^3\ h^{-1}$ in Japan, the USA, and the Federal Republic of Germany and the total number of plants is approximately 250.[14,29]

Absorption methods in which a calcium sorbent is employed are most widely used in the purification of TES smoke gases.[30–32] When the wet lime (limestone) process is used,[1,23] a sludge consisting of calcium sulphites and sulphates, which can be stabilised (for example, by heating) in the form of gypsum, is produced. Smoke gases freed from ash pass to a plate absorber irrigated with water containing finely ground limestone and neutralisation products. The purified gases pass through a spray trapping unit and after heating (to prevent condensation) are ejected into the smoke tube. After the absorption of SO_2, the acidified liquid passes through a compartment to which a fresh limestone suspension is added. After the accumulation of 10–15 wt.% of calcium salts in the irrigating liquid, part of the suspension is removed to special compartments and subsequently the resulting sludge is eliminated from the system. In order to produce gypsum, the scheme is supplemented by a line involving the oxidation of calcium sulphite to calcium sulphate and the removal of the salts. Under industrial operating conditions, a stable removal of SO_2 from gases with 90% efficiency is achieved.

A semi-dry method (spray absorption) for the removal of SO_2 from smoke gases[1,14,31] is used in the combustion of types of coal containing between 0.5 and 1.5 wt.% of sulphur. The principal stage is the absorption of SO_2 by droplets of a lime solution evaporating in the waste gases. For this purpose, smoke gases are passed through a spray absorber, whose geometry and hydrodynamic conditions ensure the complete evaporation of the droplets. The reaction product is a dry mixture of calcium sulphite and sulphate. The principal technical difficulty consists in the organisation of the effective mass exchange between the liquid and the smoke gases. For example, the spray driers of the Lurgi company make it possible to obtain droplets 80–100 μm in size with an overall surface of 60 m^2 per litre of liquid.[34] The absence of waste water and the formation of the product in a dry form make it easier to use this method in industry.[16]

Organic absorbents such as dimethylaniline, amines,[1] the dimethyl ether of tetraethylene glycol, and the dimethyl ether of poly(ethylene glycol)[2] are used in non-aqueous systems. Hydrocarbon oils are employed to remove mercaptans.[35–37] Absorption by organic solvents has proved to be most effective for the elimination of organic gaseous impurities. An obligatory condition is naturally a low pressure of the vapour of the wash liquid itself (not more than 1 Pa).

In the vast majority of cases, the non-aqueous absorber and the absorbed substance do not interact chemically. A typical example of the use of the absorption method may be the removal of benzene vapour from gases by means of a heavy oil (for example, hexadecane).[37] After absorption, the absorbing solution is heated and transferred to the desorber. Since water does not mix with benzene and the oil, the desorption is carried out using hot steam. The vapour emerging from the desorber is directed to a condensing unit to trap the absorber and partly water vapour. After their separation in the separator, the condensed absorber is returned to the cycle. The mixture of water vapour and benzene is recondensed. The non-condensing gases are separated from the liquid in the separator and liquid benzene is separated from water using the difference between their densities.

In conclusion we may note that absorption is most widely used in industry to trap acid components from effluent gases and for the removal of SO_2 from smoke gases.

III. Adsorption methods

Adsorption methods constitute one of the most widely used procedures for the protection of air from contamination. In the USA alone, tens of thousands of adsorption systems have been introduced and used successfully.[38] The principal industrial adsorbents are activated charcoals, complex oxides, and impregnated sorbents. Activated charcoal (AC) is neutral in relation to polar and non-polar molecules of the adsorbed compounds. It is less selective than other adsorbents and is one of the few adsorbents suitable for use in moist gas streams. Activated charcoal is used in particular for the removal of substances with an unpleasant smell from gases, for the recovery of solvents, etc.[1,39]

Oxide adsorbents (OA) exhibit a higher selectivity in relation to polar molecules by virtue of the intrinsic non-uniform distribution of the electrical potential. Their disadvantage is the decrease in efficiency in the presence of moisture. Silica gels, synthetic zeolites, and aluminium oxides belong to the class of oxide adsorbents.

Impregnated adsorbents (IA) are divided into three groups:

(1) Adsorbents impregnated by a chemical reagent. As a result of the occurrence of a chemical reaction on such impregnated adsorbents, the adsorption of substances which are difficult to adsorb is facilitated. For example, the introduction of iodine improves the adsorption of mercury or ethylene vapour on activated charcoal.

(2) Impregnated adsorbents in which the impregnating substance plays the role of the catalyst of the extensive oxidation of the trapped impurities. Catalysis is ensured, for example, by introducing into the activated charcoal oxygen-containing compounds promoting the oxidation of impurities in oxygen-free gases.

(3) Periodically activated impregnated adsorbents. The activation is carried out, for example, by the cyclic increase in temperature after the completion of the adsorption of impurities.

It is possible to differentiate the following principal ways of carrying out adsorption purification processes.[39–41]

1. After adsorption, desorption is carried out and the trapped components are extracted for reuse. Various solvents,[11] carbon disulphide in the manufacture of artificial fibres,[41] and a number of other impurities[42] are trapped in this way.

2. After adsorption, the mixtures are not neutralised but are subjected to thermal or catalytic afterburning.[39,41,43,44] This method is used to purify the gases from chemopharmaceutical and paint and varnish undertakings, the food industry, and a number of other industries. This variety of adsorption purification is economically justified by low concentrations of the contaminating substances and (or) when the contaminants consist of numerous components.[39,41]

3. After purification, the adsorbent is not regenerated but is, for example, stored or combusted together with the strongly chemisorbed contaminant.[1] This procedure is suitable when cheap natural adsorbents are employed.[42]

To desorb the impurities, the adsorbent is heated, evacuated, or flushed by an inert gas while the impurities are displaced by a more readily adsorbed substance, for example water vapour.[1,40,41] Attention has been concentrated recently on the desorption of impurities by evacuation.[45–51] Under these conditions, it is frequently possible to utilise them readily.

A wide variety of different types of apparatus have been developed for adsorption processes.[1,39,41,52,53] The most common are adsorbers with a fluidised bed of a granulated or honeycomb adsorbent. The continuity of the adsorption and adsorbent regeneration processes is ensured by using apparatus with a fluidised bed. The theory of adsorption in fluidised beds has been examined in greatest detail by Krishnaiah and co-workers.[54,55] There also exist adsorbers with a "flowing" adsorbent. By arranging appropriately the sites where the particles are introduced and removed, it is possible to organise the "flow" of the adsorbent along different lines. Adsorbents with a rotating bed are more rarely used in practice.[40,56,57] A variety of the process in which the adsorbent is sprayed into the stream of the gas being purified to produce a finely dispersed aerosol with subsequent trapping and regeneration of the latter has been proposed.[58] Fibrous sorption-active materials have been used increasingly in recent years.[57,59–66] Differing little from granulated adsorbents in their capacity, they are greatly superior to the latter in terms of a number of other parameters. For example, they are distinguished by high thermal and chemical stabilities, the uniformity of their polar structure, the large volume of micropores, and a higher mass transfer coefficient (greater by a factor of 10–100 than for granular sorption materials).[52] Devices employing fibrous materials occupy a much smaller area.[59,60] The mass of the adsorbent in procedures employing fibrous materials is smaller by a factor of 15–100 than in the case where an activated charcoal is used while the mass of the apparatus is smaller by a factor of 10. The resistance of the bed does not then exceed 100 Pa. The technical-economical parameters, of the existing processes can be increased also by the optimum organisation of the desorption stage,[67,68] For example, by means of a programmed temperature rise.[68]

The high efficiency of purification on activated charcoals with a honeycomb (cellular) structure, which exhibits improved hydraulic characteristics, is noteworthy. Such sorbents can be obtained by depositing specific compositions with a charcoal powder on a synthetic resin foam[45,69–71] or by foaming a mixture of specified composition containing the activated charcoal.[69] They can also be produced by burning away a filler from a mixture incorporating an activated charcoal together with a binder.[71]

Yet another way of improving adsorption purification methods involved the development of new modifications of adsorbents—silica gels and zeolites with improved thermal and mechanical stabilities. However, the hydrophilic nature of these adsorbents makes their application difficult. In order to make silica gel hydrophobic, it is modified, for example, by high-molecular-weight organic compounds.[72,73] High-silica and ultrahigh-silica zeolites (UHS-zeolites) in which the $SiO_2:Al_2O_3$ ratio can reach 100 and above making them more hydrophobic, were synthesised in recent years.[52]

The largest-scale adsorption purification apparatus is apparently used in the manufacture of artificial fibres.[38] A chemical fibre plant with average productivity ejects approximately 1.5 million $m^3 h^{-1}$ of venting gases containing H_2S and CS_2. Depending on the H_2S concentration two modifications of the adsorption method for the purification of these gases are distinguished. Since in the presence of oxygen hydrogen sulphide may be oxidised on activated charcoal to sulphur and sulphuric acid, at high H_2S concentrations the gases are subjected to preliminary absorption purification to a residual content of 20–50 mg m^{-3}. After this CS_2 is eliminated by the adsorption method. At low initial H_2S concentrations (not more than 3 g m^{-3}), there is a possibility of the joint removal of hydrogen and carbon sulphides by the adsorption purification of gases. The sulphuric acid formed on the surface of the adsorbent-catalyst is periodically neutralised, for example, with ammonia, after which the salts are washed away with water and the sulphur is removed by washing with solvent (usually with carbon disulphide).

The adsorption purification methods have found an application also in the detoxification of industrial gases by removing mercury vapour.[74] In this case, impregnated charcoals are used for the purification. Activated charcoal is usually impregnated with hydrogen halides (HCl and HI).

Adsorption methods for the extraction of solvents, including organochlorine solvents, from effluent gases have come to be most widely used.[38,40,41,52,53,75] This is associated with the high efficiency of the gas purification process (95–99%), the absence of chemical reactions leading to the formation of secondary contaminants and the short period in which the recovery apparatus pays for itself (usually 2–3 years) as a result of the reuse of the solvents and the long (up to 10 years) useful life of the activated charcoal.[40] Active

studies are being prosecuted on the adsorption extraction of sulphur and nitrogen oxides from gases,[76–78] but these have not been applied on an industrial scale so far.

IV. Condensation methods

Condensation is used to remove impurities from gases by cooling them to a temperature below the dew points of the substances to be removed. This method is most effective and is most often used for the removal (utilisation) of hydrocarbons and other organic compounds which have fairly high boiling points under the usual conditions and are present in the gas phase in considerable amounts.[2,79] The elimination of such contaminants is achieved in condensers with water and air cooling. For more volatile contaminants, two-stage condensation is used: water cooling in the first stage and cooling to low temperatures in the second.[11] Cooling to low temperatures solely with the aim of removing contaminants is not effective, since the purification process cannot be achieved with a sufficient degree of completion. For example, even at 213 K and atmospheric pressure the residual concentrations of different solvents are as follows (mg m^{-3}): 1775 for acetone, 275 for methanol, 8 for toluene, and 0.75 for isopropyl alcohol.[11] In most cases condensation can be usefully treated as a preliminary stage serving for the isolation of valuable solvents and for the reduction of the amount of contaminants before the subsequent treatment of gases.

Condensation is carried out both with direct contact and via indirect cooling. In the former case, the gas to be purified is brought into direct contact with the cooled liquid, while in the latter a tubular surface condenser is used. In direct cooling, the subsequent separation of the heat exchanger and of the trapped impurities is important. For this purpose, one selects components such that under certain conditions they form as a result of phase transitions constituents which can be readily separated.[80,81] Condensation is also carried out by the adiabatic expansion of gases supplied under pressure for purification.[82] In order to separate different impurities present in the cooled gases, ionisation and fractionation in an electric field are employed.[83]

The application of the condensation method is complicated by the formation of a mist on extensive cooling of the gas to be purified. This occurs when the rate of heat transfer greatly exceeds the rate of mass transfer and the main bulk of the gas is cooled to a temperature appreciably below the dew points of the condensed impurities. To prevent mist formation, indirect condensation is used, since in this case the main bulk of the gas is in contact with cooled surfaces (liquid drops or film) and condensate particles are not formed in the bulk phase.[11]

V. Membrane methods

Membrane separation processes include stages involving the transfer of the initial mixture to a membrane, the permeation of the mixture components into the membrane, their transfer through the membrane, and the subsequent removal of the separated products.[84] In practice one uses metallic membranes based on palladium, its alloys, silver, and ruthenium as well as synthetic membranes[85] and ceramic-based membranes.[86] Synthetic membranes are made from polymers based on styrene, acrylonitrile, isoprene, silicone, and other elementary components.[85]

Membrane methods have already proved very useful in the manufacture of pure hydrogen,[86] in the extraction of helium from natural gas,[87] and in the purification of gas waste from atomic power stations.[88]

The solubilities of the following substances and their permeation into polymers have been investigated recently: toluene in polystyrene,[89] alcohols, dichloromethane, and benzene in polyvinylpyridine,[90] ethyl acetate, acetone, methyl chloride, and ethanol in cellulose nitrate,[91] and toluene, xylene, and cyclohexane in 1,2-polybutadiene.[92] It has been shown[93] that the rates of permeation of the vapours of various organic substances through polypropylene and Teflon films are tens and hundreds of times greater than the rate of permeation of water (toluene/water = 200 at 60 °C; n-heptane/water = 360). This makes it possible to create gas purification membrane systems. For example, in order to extract organic solvents from air discarded from painting chambers,[11,94] the air stream is passed through a membrane module whose material consists of polydimethylsiloxane on a polysulphone support. The vapours of organic solvents diffuse across the membrane, while the air "depleted" in the solvent circulates through the painting chamber. A vacuum pump creating a rarefraction to the extent of 10^{-3} Pa ensures effective transport through the membrane. The solvent vapour is then condensed in the heat exchanger. The air flow rate is ~ 500 m^3 h^{-1} and the content of the solvent in the air stream is ~ 20 g m^{-3} at the inlet, the amount of extracted solvent is ~ 10 kg h^{-1}, the surface area of the membrane is ~ 80 m^2, and its useful lifetime is 2 g. The necessary power of the pump required to generate the required vacuum is 10 kW.

Composite membranes, whose permeability to solvents is 60–160 times greater than their permeability to nitrogen, have been developed.[95] This makes it possible to ensure a high efficiency of membrane and various combined procedures for the purification of gases. For example, membrane separation and absorption trapping have been used in succession.[96]

VI. Thermal afterburning

Afterburning constitutes a method for making gases safe by the thermal oxidation of various harmful substances, mainly organic, to virtually harmless or less harmful materials—mainly CO_2 and H_2O. The usual afterburning temperatures for the majority of compounds are in the range 750–1200 °C. The application of the thermal afterburning method makes it possible to attain 99% purification of gases.[11,97] The small size of the devices, the simplicity of their operation, and the low operating costs even at high concentrations of the impurities have led to the extensive application of this method. For example, more than 2000 thermal afterburning devices operated in the USA in the 1970's.[2]

When the possibility and usefulness of thermal detoxification methods are considered, it is essential to take into account the nature of the combustion products formed. The products of the combustion of gases containing sulphur, halogen, and phosphorus compounds can be more toxic than the initial gaseous waste. In this case, additional purification is essential. Thermal afterburning is extremely effective in making safe gases containing toxic substances in the form of solid inclusions of organic origin (soot, carbon particles, sawdust, etc.).[2,98]

The most important factors determining the usefulness of thermal detoxification are the expenditure of energy (fuel) to ensure high temperatures in the reaction zone, the calorie content of the mixture

subjected to detoxification, and the possibility of preliminary heating of the gases being purified. An increase in the concentration of the mixtures subjected to afterburning leads to an appreciable diminution of the consumption of fuel. In some cases the process can take place under autothermal conditions, i.e. the working conditions are maintained solely by the heat of the extensive oxidation reactions of the harmful impurities and by the preliminary heating of the initial mixture by the detoxified effluent gases.

There exist several different systems for thermal detoxification differing from one another by the process temperature, the hydrodynamic conditions in the reaction zone, and the residence time of the gases in the reaction zone.[2,11,99–101] Chamber furnaces, furnaces with cyclone movement of gases, regenerative devices for thermal detoxification, apparatus with flow mixing, and detoxification systems in technological apparatus (for example in boilers) can be distinguished.

Box furnaces[2,98] are some of the first industrial thermal purification devices. The working space within the furnace is usually divided into two chambers: the chamber for the combustion of the fuel introduced into the system and the mixing chamber where the air to be purified is introduced. The hydrodynamic conditions in the above zones within the furnaces differ significantly and special mixing of the streams is therefore required. The residence time of the gases in the mixing chamber is 3–5 s and the specific consumption of heat on the detoxification process is 270–280 kcal per m^3 of the gas to be purified. Thermal detoxification furnaces using the cyclone gas flow principle are nowadays more common. The cyclone principle ensures vigorous mixing of the streams and hence effective afterburning for shorter residence times of the gases in the reaction chamber (0.1–0.5 s) than in box furnaces. Such furnaces are used for the afterburning of gases in the manufacture of bitumen, synthetic aliphatic acids, in petroleum processing factories, and in current lead enamelling workshops of electrotechnical undertakings. The cyclone gas flow permits an appreciable reduction of the consumption of heat (to 200 kcal per m^3 of the purified gas) compared with the afterburning in a box furnace.[2,98,102,103]

Devices with flow mixing of the components to be detoxified are differentiated as a separate group of apparatus. The principal element of the design of such apparatus is a burner with a stabiliser made in the form of a poorly streamlined body which gives rise to a high turbulence.[2] The use of such burners, placed within the stream of the gas to be purified, makes it possible to reduce the temperature of the extensive purification of gases ranging from CO to CH_4 compared with box furnaces by 150–200 °C.

In many instances, oxygen-containing waste is combusted in combustion chambers of boiler and other technological aggregates[98,104,105] where the contaminated air is used to generate the blast. The degree of elimination of organic acids and aldehydes from gases by this procedure reaches 99–100%.[98] Thermal detoxification processes are used in the manufacture of technical carbon for the afterburning of waste gases whose composition is usually (vol.%) 7–8 H_2, 6–7 CO, 0.5–0.7 CH_4, 2–3 O_2, 2 CO_2, 40 N_2, and 40 H_2O. Furthermore, these gases contain up to 2 g m^{-3} of residual soot (carbon). The high heat generating capacity of the gases (360–500 kcal m^{-3}) permits their use as fuel in special boiler aggregates.[106]

One of the most economical and promising methods is believed to be thermal detoxification using heat exchangers capable of being regenerated.[2,107–121] These devices consist of a combustion chamber and two (or more) layers of the regenerative packing. The periodic alteration of the direction of motion of the detoxified gases through the layers of packing or the rotation of the latter for a constant direction of motion of the gases ensure the regeneration of the heat of the hot purified gases and the heating of the initial gas to be purified.[2,110,111,122] The Retherm afterburning devices[108] with a productivity up to 100 000 m^3 h^{-1}, which make it possible to utilise up to 95% of the heat of the gases being purified,[122] have come to be most widely used. Their design rules out the possibility of the release of gas during the switching of the gas streams, which is achieved by employing five regenerative heat exchangers. A similar design has been proposed also in the USSR.[115] When much heat is evolved, it is also possible to utilise the heat given up as a result of the combustion of impurities.[121]

Overall, recent years have been characterised by a vigorous development of thermal detoxification methods based on the regenerative principle of heat exchange.[109–120] In some cases, attempts have been made to combine catalytic and thermal methods by incorporating in the apparatus both burners and layers of extensive oxidation catalyst.[112,118–123] Thermal afterburning has found applications in the most varied branches of industry. Simple versions of afterburning (for example, flame afterburning) are used in metallurgical[98] and chemical (petrochemical) undertakings.[124] Thus thermal afterburning is widely employed for the detoxification of waste gases from cast iron cupolas. The principal combustible component of cupola gases is carbon monoxide, whose content reaches 8–15 vol.%. For CO contents from 11 to 15 vol.% the gas at a temperature of 300–350 °C can be burnt virtually without the consumption of fuel. When the CO content is reduced, an additional supply of natural gas is needed.[98] The converters available at present operate predominantly with the afterburning of the blast gases in the so called cooling units for smoke gases or directly in the flame. The concentration of carbon monoxide in gases changes during the blasting of the converter from 40 to 98%. The temperature of the waste gases is 1100–1400 °C and the residual maximum CO content after afterburning does not exceed 0.2–0.5 vol.%.

Thermal detoxification is used also for the afterburning of the effluent gases from aluminium and electrode industries. The waste generated in this case in the combustion of petroleum coke contains between 12 and 23 vol.% of gaseous combustible components (CO + H_2 + CH_4) and about 20 g m^{-3} of coke dust.[98]

The principal difficulty in using thermal afterburning arises from the formation of secondary contaminants such as nitrogen oxides, chlorine, SO_2, etc. In order to reduce the NO_x concentration, two-stage combustion is employed; in the first stage, where the process is carried out in the presence of a deficiency of oxygen, a large residual CO content is retained, while in the second stage all the combustible impurities are subjected to extensive oxidation.[125–127] A decrease in the emission of nitrogen oxides is also promoted by recirculation of gases and by the decrease in their preliminary heating.[97,99]

Thermal afterburning of gases containing organochlorine compounds is especially important for chemical industries.[128–137] In the presence of a deficiency of oxygen,[132,134,135,137] organochlorine compounds are oxidised not to elemental chlorine but to HCl, which can be readily bound by alkali. Thermal decomposition in plasmatrons[132] or in inducton arc furnaces[137] is also used for the afterburning of chlorinated hydrocarbons. In order to reduce the process temperature and the amount of chlorine formed, ultraviolet irradiation is employed[133] as well as turbulent afterburning.[136]

Sometimes the gases are passed over the surface of fused iron[138] or aluminium[139] to achieve the afterburning of toxic impurities. One cannot rule out the possibility that the oxide film formed on the metal surface plays the role of the catalyst in such cases.

Much attention has been devoted to the intensification of the existing thermal afterburning processes, for example via the thermal oxidation of impurities in a fluidised bed of heat resistant particles[140,141] or by employing electric arc furnaces.[142] The thermal gas afterburning process, under the conditions of a variable rate of their supply and a variable concentration of the impurities, can be stabilised by employing in the high-temperature zone of the furnace a packing comprising an inert (for example, ceramic) material.[143] Such packing ensures simultaneously a better mixing of the streams and increases the degree of afterburning.

The possibility of using thermal afterburning for making safe non-standard methane–air mixtures ejected from coal mines has been discussed recently. During the ventilation of the amines approximately seven hundred million m^3 of mixtures containing less than 30 vol.% of methane (conditioned mixtures) and about four thousand million m^3 of air containing between 0.5 and 0.75 vol. of methane (non-conditioned mixtures[98]) are ejected into the air annually. The combustion of the non-conditioned ejected mixtures together with solid fuel, their enrichment in natural gas, the combustion of weak mixtures using preliminary additional heating, and the connection of sources of coal mine methane to the overall (collecting) network are apparently the most promising procedures.[144]

Thermal methods have found the main application in the elimination of organic impurities from highly concentrated gases, including gases containing mechanical impurities.

VII. Catalytic methods

Catalytic gas purification methods are distinguished by their universality. With their aid, it is possible to free gases from sulphur and nitrogen oxides, hydrogen sulphide, various organic compounds, carbon monoxide, and other toxic impurities. Catalytic methods make it possible to convert harmful impurities into safe ones, less harmful ones, and even useful impurities. They make it possible to process multicomponent gases with low initial concentrations of harmful impurities, achieving high degrees of purification, to carry out the process continuously, and to avoid in most cases the formation of secondary contaminants. The application of catalytic methods is usually restricted by the difficulty of finding and preparing sufficiently cheap catalysts suitable for prolonged use. The heterogeneous-catalytic conversion of gaseous impurities is achieved in a reactor charged with a solid catalyst in the form of porous grains, rings, pellets, or blocks with a nearly honeycomb structure. Chemical conversion takes place on the extensive inner surfaces of the catalysts, reaching 10^3 $m^2 g^{-1}$.

A wide variety of substances can serve as effective catalysts used in practice. They range from minerals, which are used virtually without any preliminary treatment, and simple massive metals to complex compounds with a specified composition and structure. Catalytic activity is usually shown by solids with ionic or metallic bonds and having strong interatomic fields. One of the principal requirements which must be met by the catalyst is the stability of its structure under the reaction conditions. For example, metals should not be converted during the reaction into inactive compounds.[145,146]

Modern detoxification catalysts are characterised by a high activity and selectivity, mechanical strength, and resistance to the action of poisons and temperature. Industrial catalysts, made in the form of rings and blocks with a honeycomb structure, offer a low hydrodynamic resistance and have a high external specific surface.[146]

Catalytic methods for the detoxification of effluent gases in a stationary catalyst bed have come to be most widely used. It is possible to differentiate two fundamentally different procedures for carrying out the gas purification process—under stationary and artificially created non-stationary conditions.

1. The stationary method

Rates of chemical reactions suitable for practical use are attained in the presence of the majority of cheap industrial catalysts at 200–600 °C. After the preliminary removal of dust (up to 20 mg m^{-3}) and various catalytic poisons (As, Cl_2, etc.), the temperature of the gases is usually appreciably lower.

The gases can be heated to the required temperatures by introducing combustible smoke gases or with the aid of an electric heater. After passage through the catalyst bed, the purified gases are released into the atmosphere, which requires an appreciable energy consumption. A reduction of energy consumption can be achieved if the heat of the effluent gases is used to heat the gases entering the purification process. Regenerative tubular heat exchangers are usually employed for heating.

Under certain conditions, where the concentration of combustible impurities in the effluent gases exceeds 4–5 g m^{-3}, the process in accordance with a scheme employing a heat exchanger makes it possible to avoid additional consumption of heat. When reversible exothermic reactions take place, the attainment of a high degree of purification requires the intermediate removal of heat, which appreciably complicates the technological scheme. The processing of gases by the above method is difficult if the gas is supplied at a variable rate and when the concentration of impurities in it is not constant. The presence of an external heat exchange increases the parametric sensitivity of the system and enhances the risk of overheating and sintering of the catalyst even after a slight increase in the concentration of impurities and (or) decrease in the gas flow rate. Such devices can operate effectively only at constant concentrations (flow rates) or when ideal systems for the automatic regulation of the process are employed. These difficulties can be overcome by carrying out the gas purification under non-stationary conditions.

2. The non-stationary method (flow reversal process)

If the stationary catalyst bed is initially heated to a temperature ensuring the occurrence of the chemical reaction at an appreciable rate and the reaction mixture, whose temperature is insufficient for the occurrence of the reaction is directed to it, then after a certain time interval a thermal front is established in the bed.[148,149] It moves at a rate smaller by a factor of 100–1000 than the rate of filtration of the gas through the catalyst. A second feature of the thermal front, consisting in the fact that the difference between the maximum and inlet temperatures can greatly exceed the temperature drop due to the adiabatic heating with complete conversion of the initial mixture (ΔT_{ad}), gives rise to the possibility of a technological application of this phenomenon.

The non-stationary method is illustrated schematically in Fig. 1. It provides for the periodic alteration of the directions of filtration of the gas mixture in the catalyst bed with the aid of valves *1* and *2*.[150] The process proceeds as follows. The catalyst bed is heated initially to a temperature at which the catalytic process proceeds at a high rate. After this, the gas to be purified is supplied to the apparatus at a low temperature (T_{inp}) at which the rate of the chemical reaction is negligible. As a result of direct contact with the solid material, the gas is heated and catalytic reactions begin to

occur at an appreciable rate in the catalyst bed. Giving up its heat to the gas, the layer of the solid material (catalyst) is gradually cooled to the temperature equal to that of the gas at the inlet. Since heat is evolved during the reaction, the temperature in the bed can exceed the temperature resulting from the initial heating. A thermal wave is formed in the reactor and moves in the direction of the filtration of the reaction mixture, i.e. in the direction of the outlet from the bed. Periodic reversal of the direction of the supply of the gas makes it possible to retain the thermal wave indefinitely within the limits of the bed.

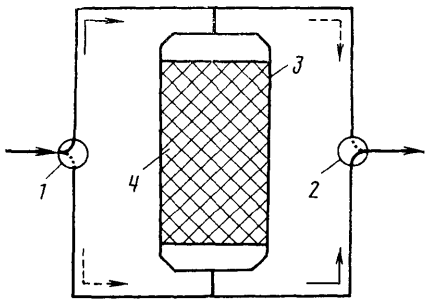


Figure 1. Technological scheme of the gas detoxification process in a non-stationary regime: *1*, and *2*, switching devices; *3*, catalytic apparatus; *4*, catalyst bed.

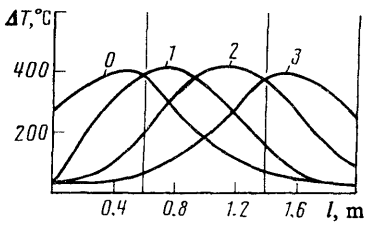


Figure 2. Variation of temperature along the length of the catalyst bed (l) during a half-cycle (O) before change of direction of filtration; *1*, *2*, and *3*, 6, 15, and 25 min respectively after the change of direction.

Fig. 2 presents typical temperature profiles along the catalyst bed at different times after the change in the direction of the supply of the initial reaction mixture. It is seen that the sections located near the inlet are gradually cooled, while in the middle part of the bed the temperature rises. The increase in temperature is caused by the accumulation of the heat of reaction within the catalyst grains, while the cooling is caused by the removal of heat by the stream of the gas mixture. After 25 min (the half-cycle time), the direction of supply is again altered and subsequently the switching is performed with the same periodicity.

An integral heat balance is maintained in the steady cyclic regime: $T^{av}_{outp} = T_{inp} + \Delta T_{ad} x^{av}_{outp}$ (x^{av}_{outp} is the degree of conversion and T^{av}_{outp} is the average temperature at the outlet). The autothermal nature of the cyclic regime is ensured solely by the heat of the exothermic chemical reaction of the impurities present in the gas undergoing purification.

The principal advantages of the non-stationary method of carrying out heterogeneous catalytic reactions are as follows:[148,150,151]

(1) The autothermal nature of the non-stationary process is achieved with a minimal adiabatic heating of the mixture (of the order of 15 °C).

(2) The complete conversion of the reacting components (or an equilibrium in the case of reversible reactions) is achieved in the catalyst bed.

(3) Variations in the concentrations of the combustible impurities and in the temperature of the input stream and in its volume flow rate do not have a significant effect on the principal parameters of the non-stationary regime in the reactor—the maximum temperature and the degree of conversion—as a consequence of the fairly high heat capacity of the catalytic unit.

(4) Heat exchange takes place within the catalyst bed itself, which not only accelerates the reaction but also ensures the regeneration of heat.

(5) In the processing of gas mixtures, whose adiabatic heating exceeds 100–150 K (which is equivalent to a content of organic substances of 3–5 g m^{-3}), non-stationary devices can become a source of secondary energy resources in the form of steam, hot water, hot gases, etc., obtained as a result of the utilisaton of heat in the zone of maximum temperatures.

(6) In the non-stationary regime, a satisfactory approximation to the theoretical optimum conditions for reversible exothermic reactions is achieved without intermediate heat exchangers. In the case of a fairly close approximation to the theoretical optimum conditions for reversible exothermic processes, the catalytic process can be significantly simplified and a single-stage process can be used instead of a multistage one.

3. The application of catalytic methods in the elimination of toxic compounds from gases

(a) Nitrogen oxides

Among all the possible ways of removing nitrogen oxides from effluent gases, catalytic procedures are most widely used nowadays since they require relatively low capital and operating costs, permit the use of comparatively simple designs, and at the same time are highly effective.[152] Among catalytic methods which have not so far gone beyond laboratory tests, the procedure for the direct decomposition of NO_x into molecular nitrogen and oxygen appears extremely attractive. However, this method is not applicable to oxygen-containing gases. The study of the catalytic activity[40] of metal oxides in the reaction involving the decomposition of NO_x into nitrogen and oxygen showed that in all cases the reaction is retarded by oxygen.[153]

The catalytic methods for the reduction of NO_x adopted in industry can be divided arbitrarily into two main groups: (1) the high-temperature reduction which occurs only in an oxygen-free medium using combustible gases as the reductant; (2) selective catalytic reduction (SCR) whose characteristic feature is the interaction of the reductant employed with nitrogen oxides in the presence of oxygen.

Hydrogen, carbon monoxide, kerosene vapour, and petroleum and natural gases are used for the high-temperature reduction of nitrogen oxides.[154] Nitrogen oxides are reduced to nitrogen, while other reaction products may be water and carbon dioxide. Metals on carriers are employed as catalysts of the high-temperature reduction process. The active components are usually platinum, palladium, and copper–chromium alloys.[155] The process tempera-

ture is normally 300–500 °C.[154] The reduction occurs only in an oxygen-free atmosphere and the first stage is therefore the "burning away" of oxygen. Since the content of nitrogen oxides does not in most cases exceed 0.2 vol.%, the consumption of combustible gases is virtually determined solely by the oxygen content in the smoke gases. In the catalytic "burning away" of 3–8 vol.% of oxygen, the gas temperature increases by 400–1000 K.[154] The disadvantages of the method considered are the high initial reaction temperature, a considerable consumption of the reductant in the removal of oxygen, the cost involved in the utilisation of the heat of the effluent gases, the necessity to maintain a definite temperature process regime, and the possibility of the presence of carbon oxides in the effluent gases as a consequence of the employment of a reducing atmosphere.[152,154,155]

In the selective catalytic reduction of nitrogen oxides, the reductant interacts with NO_x in the presence of oxygen. Under industrial conditions, NH_3 is widely used as the reductant.[156,157] Apart from gaseous ammonia, reagents which evolve it can also be used in SCR processes: various organic nitrogen compounds or the products of the decomposition of the corresponding salts;[158] compounds with amino- or imino-groups;[159] aqueous ammonia solutions.[160]

The activity of the catalyst decreases in the following sequence in reactions involving reduction by ammonia:[154] Pt > MnO_2 > V_2O_5 > CuO > Fe_2O_3 > Cr_2O_3 > CoO_3.

In industry, mainly vanadium-containing catalysts are used for the selective reduction of nitrogen oxides by ammonia.[157] Vanadium pentoxide (V_2O_5), deposited either on Al_2O_3 or TiO_2, possesses a high activity at relatively low temperatures (<400 °C) and is highly resistant to the action of sulphur oxides, which is very important in the detoxification of sulphur-containing gases from thermoelectric power stations.[161] Attempts are being made to create industrial SCR catalysts based on iron and chromium oxides,[162,163] zeolites,[163–165] and platinum and ruthenium.[162]

The SCR method is applied mainly for the removal of NO_x from gases in the manufacture of nitric acid and in the combustion of fuel. The application of the SCR method to the purification of gases from thermal electric power stations has a number of characteristic features associated with the degree of contamination of the gases by dust, their sulphur content, and their high temperature. Dust-containing gases are purified on catalysts with a ceramic honeycomb structure (blocks) at high linear flow rates—up to 60 m s^{-1}.[166] Catalysts with this structure have walls of identical thickness and form throughout the length of the bed channels with a hydraulic diameter from 2 to 30 mm. The porosity of such a block is 50–80%. Instead of ceramic blocks the active component is sometimes deposited on the surfaces of metallic plates[167] or heat exchange tubes.[168]

In the course of the operation of catalytic reactors for the selective reduction of NO_x, the activity of the catalysts falls both as a result of the blocking of the active surface by dust and the erosion wear of the blocks and as a result of the deposition of salts (sulphites, sulphates, and nitrates). For the partial regeneration of the catalyst, the temperature at the inlet to the bed is periodically raised[169,170] or substances (alcohols, ketones, aldehydes, etc.) promoting the decomposition of the salts are introduced into the reactor.[171] For example, ammonium salts are decomposed by removing the catalyst from the reactor and regenerating it in individual devices.[172–175] Sulphates are eliminated by washing the catalyst with various aqueous solutions.[162]

The principal ways of increasing the cost effectiveness of the SCR processes in thermal electric power stations are a decrease in the energy expenditure and an increase in the useful lifetime of the catalyst. In order to increase the cost effectiveness, rotating heat exchangers are employed nowadays. The hot effluent smoke gases at a temperature of 350–400 °C are mixed with ammonia and are subsequently applied to a rotating plate reactor-heat exchanger. After passage through the reactor-heat exchanger, dust and sulphur dioxide are trapped from the NO_x gases. Fresh air for combustion enters during this period the other half of the apparatus, where it is heated and then supplied to the furnace. The rotation of the heat exchanger is regulated in such a way that a virtually constant temperature is maintained throughout its volume.[1]

Favourable catalyst operating conditions are created naturally when the SCR systems are placed beyond the devices for the removal of dust and sulphur from smoke gases. In this case, one can use much less catalyst and its useful lifetime increases to five years compared with 1–3 years when it operates in dust-contaminated gases.[176] However considerable operating and capital costs involved in heating the gases to 300–350 °C after the removal of sulphur have held back hitherto the extensive industrial application of such procedures. The endeavour to reduce energy expenditure has led in recent years to the use of regenerative heat exchangers in the application of the SCR method.[162,164,165,177]

When the flow reversal process is used to remove nitrogen oxides from gases, the catalyst is placed between inert material beds.[178–180] The ammonia for the reduction of nitrogen oxides is introduced in such a way that the formation of ammonium nitrite and nitrate is virtually ruled out. Certain technological characteristics of the industrial process are presented in Table 1. When the initial content of nitrogen oxides was varied widely and in the presence of a 15% excess of ammonia relative to its required stoichiometric amount, the degree of conversion of nitrogen oxides was not less than 98% with a virtually complete conversion of ammonia. The maximum temperatures in the reactor were in the range 350–450 °C.

The heat evolved in the reduction of NO_x by ammonia in a mixture containing 1 g m^{-3} of nitrogen oxides is sufficient to heat the mixture by 7–10 K. This is sufficient to carry out the process on block catalysts in an autothermal regime. The autothermal nature of the process on granular catalysts is ensured at an initial NO_x concentration of 1.5–2 g m^{-3}.

Table 1. Technical characteristics of industrial equipment for the catalytic detoxification of gases in a non-stationary regime.

Parameter	Oxidation of SO_2 to SO_3 (Ref.183)	Removal of organic compounds	Removal of NO_x by selective reduction
Volume of gases to be purified (10^3 m^3 h^{-1})	35.0	1.0	10–11
Concentration of removable impurities at inlet	2 vol.%	0.5–0.7 g m^{-3} (methanol, phenol, formaldehyde)	4–15 g m^{-3}
Temperature at inlet, °C	30–40	15–20	30–40
Maximum temperature in catalyst bed, °C	480–550	400–550	300–450
Degree of conversion (purification), %	95–97	Methanol—99.9; formaldehyde—99.6; phenol—97.0	98–99
Period between reversals of direction, min	20	30–45	5–25

(b) Sulphur dioxide

Sulphur dioxide, whose concentration is not less than 0.5–0.7 vol.% in effluent smoke gases, is trapped in the vast majority of cases by absorption-chemical methods.[1,14,16] At a SO_2 concentration in excess of 1 vol.%, its utilisation in the form of sulphuric acid or elemental sulphur is economically justified. In order to obtain the acid, sulphur dioxide is oxidised in the presence of a catalyst to SO_3, which is absorbed by a solution of sulphuric acid in a scrubber.[12,181,182] The effluent gases from smelting furnaces for non-ferrous metals, in which the SO_2 concentration is between 4 and 11%, are usually converted into sulphuric acid.[181] Non-ferrous metallurgy supplies about 24% of the entire sulphuric acid produced in the USSR.[12]

The industrial oxidation of sulphur dioxide is achieved in the presence of vanadium catalysts. The active component has a complex composition and one can assume to a first approximation that it consists of potassium sulpho- and pyrosulpho-vanadates dissolved in an excess of potassium pyrosulphovanadate. Under the reaction conditions, the active component is in the fused state on the surface of the solid carrier, usually silica. The liquid state of the active component is a precondition for the occurrence of the reaction in the bulk of the melt after the preliminary dissolution of the gaseous components.[145] The oxidation is as a rule carried out in multichamber reactors with intermediate removal of heat. The sulphur trioxide formed is absorbed to form commercial sulphuric acid. At initial SO_2 concentrations in excess of 5 vol.%, it is useful to employ the double contact method—double absorption, which makes it possible to utilise 99.5–99.9% of the sulphur and to achieve a SO_2 content at the outlet which is the same as after chemical purification, i.e. 0.02–0.05%.[12] The complexity and expense of the manufacture of sulphuric acid are associated with the significant reversibility of the reaction $SO_2 + {}^1/_2O_2 = SO_3$ in the temperature range 400–600 °C, where vanadium catalysts exhibit an acceptable activity.

In order to obtain sulphuric acid from gases in which the SO_2 concentration is less than 3–3.5% in multichamber apparatus, it is necessary either to heat the gases continuously to 400–450 °C or to "fortify" the dilute gas with sulphur dioxide obtained by combusting sulphur in a stream of air[182] or by the effluent gases from autogenic processes containing more than 11 vol.% of SO_2.[183]

The catalytic oxidation of SO_2 in a non-stationary regime in the presence of the traditional vanadium catalyst significantly simplifies the process and lowers its cost.[178,184] This method makes it possible to reduce the amount of metal required for the catalytic unit by a factor of 1.5–5, to decrease the hydraulic resistance by a factor of 1.5–2, to diminish the total capital cost by 30–80%, and to reduce the intrinsic cost of sulphuric acid by 5–20% compared with the existing method. It does not require the consumption of fuel for heating the mixture in the processing of gases containing more than 0.6% of SO_2, while in the presence of more than 4–5% of the dioxide additional heat can be obtained.

A characteristic feature of the non-stationary method for the oxidation of SO_2 to SO_3 is the appearance along the length of the catalyst bed of a region where the temperature decreases (Fig. 2). This gives rise to the possibility of achieving a temperature regime close to one which is theoretically optimal for irreversible exothermic processes, makes it possible to reduce the number of catalyst layers, and virtually obviates the need for intermediate heat exchangers in an industrial reactor. The use of industrial reactors[185–197] operating under periodic mixture reversal conditions showed that they can be readily regulated, permit a stable processing of gases in which the concentration of sulphur dioxide varies by an order of magnitude, and retain their working temperatures when the process is arrested even for several days. It is noteworthy that, at initial sulphur dioxide concentrations less than 2.5–3%, it is possible to achieve a degree of conversion of SO_2 into SO_3 of 97–98% on a single-bed reactor. The technical characteristics of one of the industrial catalytic types of apparatus for the oxidation of SO_2 to SO_3 on the basis of the reversal process are presented in Table 1. In terms of technological parameters (degree of purification, maximum temperatures), the experimental data obtained on industrial apparatus agree satisfactorily with the values calculated on the basis of mathematical models for non-stationary processes.[148]

(c) Hydrogen sulphide

The hydrogen sulphide contained in acid gases resulting from the processing of petroleum and natural gas is one of the main sources of sulphur.[188] The Claus process is usually employed to extract sulphur. In this method, the gas containing predominantly hydrogen sulphide and carbon dioxide is oxidised at high temperatures in a Claus furnace by air or oxygen with formation of elemental sulphur, sulphur dioxide, and also a certain amount of COS and CS_2. Air (or oxygen) is supplied in an amount such that the concentration ratio $H_2S:SO_2 = 2$ is ensured at the outlet from the furnace. The degree of conversion of hydrogen sulphide into sulphur reaches 60–70%. Next, the mixture is cooled, condensed, and the sulphur is separated, while the gases are subjected to catalytic conversion using active alumina, bauxites, titanium dioxide, etc. as catalysts.[189,190] The reversible exothermic reaction $2H_2S + SO_2 = 3S + 2H_2O$ takes place on the catalyst. The equilibrium degree of conversion increases rapidly with decrease in temperature. However, at low temperatures, the sulphur formed condenses, blocking and thereby deactivating the catalyst. The process is therefore performed in several catalytic stages with the intermediate cooling and separation of sulphur.

A degree of extraction of sulphur up to 96% (overall degree of extraction including the degree of extraction of sulphur in the Claus surface) is attained in the two-stage process, while in the three-stage process the degree of extraction is up to 98%. In order to attain higher parameters, different fairly expensive processes for the additional purification of residual gases are used: afterburning, including catalytic afterburning, to give SO_2 with subsequent processing or ejection to the atmosphere; hydrogenation to H_2S with subsequent conversion into sulphur; preparation of sulphur by the Claus method but under specific conditions.[191–195] Schemes involving "dry" additional purification of gases, based on carrying out the Claus reaction at temperatures below the dew point of the sulphur formed, have come to be most widely used.[191] The process is usually carried out as follows. The reaction is performed at 120–135 °C, which ensures a high degree of conversion, but the sulphur formed is condensed in the pores of the catalyst (alumina). After the saturation of the bed, the catalyst is regenerated at 300–350 °C, the regeneration being accompanied by the evolution and subsequent condensation of sulphur. In order to ensure the continuity of the process, it is carried out in several parallel reactors, each of which operates in succession under catalytic conditions—adsorption of sulphur, regeneration, and cooling. By 1986, about 70 industrial plants with "dry" additional purification, ensuring an average extraction of H_2S of 99–99.5%, operated throughout the world.[191]

The actively developing liquid-phase methods for the additional purification of the residual gases from the Claus process are an alternative to the "dry" methods,[191-193] but their wide scale industrial application is prevented by the high capital costs, the formation of acid waste, and the low quality of the sulphur formed.[194]

The non-stationary method for the manufacture of sulphur on the basis of the Claus method in a stationary catalyst bed under periodic mixture reversal conditions[196,197] makes it possible to reduce greatly the capital and energy (operating) expenditure.

The process is carried out as follows. The initial gas mixture at a low temperature (120–116 °C) is supplied to the catalyst bed, which was heated beforehand. The sulphur formed then condenses in the reaction zone suppressing the activity of the catalyst until its complete deactivation. After the introduction of the mixture into a "fresh" bed, the initial sections of the bed are gradually deactivated and the reaction zone slowly shifts into the bulk of the bed in the direction of the filtration of the gas. A moving "sulphur condensation front" is thus produced together with the temperature and concentration fronts associated with it. After a certain time, the direction of motion of the reaction mixture is reversed. An analogous condensation front then begins to move from the opposite side and the previously condensed sulphur vaporises as a result of the heat of reaction. The use of various modifications of the Claus flow reversal process makes it possible to achieve a degree of elimination of H_2S from the gas above 99%.

It is sometimes desirable to utilise the sulphur dioxide from sulphur-rich gases in the form of elemental sulphur.[188-190] For this purpose, SO_2 is subjected to thermal reduction by various reductants (carbon, CO, CH_4, H_2, hydrocarbons), after which the catalytic Claus reaction between SO_2 and H_2S is carried out. The SO_2 is reduced both using solid catalysts[198] and a non-catalytic procedure in a homogeneous phase.[199]

The utilisation of SO_2 from metallurgical gases can be achieved by means of the liquid-phase sulphur elimination method developed at the Institute of Catalysis of the Siberian Division of the USSR Academy of Sciences[200,201] based on the liquid-phase reduction of sulphur dioxide by hydrogen sulphide. The chemical sorbent, recirculating during the process, is an aqueous solution of ammoniacal phosphate salts and a homogeneous catalyst based on soluble silicon or aluminium salts, which significantly accelerate the reduction of SO_2 by hydrogen sulphide compared with other known liquid-phase methods.[201]

(d) Organic compounds

The elimination of organic compounds from gases involves the oxidation of the impurities to carbon dioxide and water. Catalytic methods are widely used to make safe the effluent gases from the manufacture of synthetic fibres,[202-204] the gaseous waste from petroleum processing and petrochemical undertakings,[205,206] the venting gases from painting and drying workshops,[207-209] and in the manufacture of electrotechnical articles.[206,210] The relevant reviews[147,211-214] show that the application of catalytic detoxification methods is expanding continuously.

Both catalysts containing precious metals (Pt, Pd)[215,216] and catalysts based on copper, chromium, cobalt, and iron oxides as well as complex oxide systems (chromites, ferrites, cobaltites, etc.)[213] are used for the catalytic afterburning of toxic impurities. Detailed data about Soviet detoxification catalysts have been published.[217] Depending on the nature of the toxic components in the gases, different catalysts are used.

Not only hydrocarbons and carbon monoxide but also nitrogen-containing[218,219] and halogen-containing organic compounds[220,221] can be trapped from gas mixtures by means of catalytic oxidation. By a successful selection of catalysts and process conditions, nitrogen-containing impurities can be oxidised to elemental nitrogen, CO_2, and water,[218] whilst chlorine-containing impurities can be oxidised to HCl, which is bound by alkali.[221]

The temperature of the gases at the inlet to the catalyst bed, required to ensure high degrees of purification, varies from 160–200 °C in the elimination of formaldehyde from gases on platinum-containing catalysts[206,213] to 400–600 °C in the elimination of isopropylbenzene and bitumen vapour from gases on oxide catalysts.[206]

Catalytic afterburning processes are being improved by creating catalysts capable of propagating the oxidation at low temperatures. For example, catalysts for the oxidation of CO to CO_2 at 30 °C have been proposed.[222] In order to reduce the hydrocarbon oxidation temperature, ozone has been introduced as the oxidant into the gas undergoing purification.[223,224] An adsorption-catalytic method is developing vigorously.[225-228] It consists of the adsorption of toxic compounds (for example, styrene[228]) on various catalysts (zeolite-containing catalysts,[225] copper chromite,[226] and a manganese catalyst[228]) with subsequent oxidation of the impurities on raising the temperature at the inlet.

A two-stage process with the intermediate removal of heat and afterconversion of impurities on a second catalyst bed is used to make safe concentrated gaseous waste.[147,229-232] Different catalysts oxidising different impurities can be used in each stage.

The improvement of catalytic processes also involves an increase in the degree of recovery of heat using heat exchangers with turbulisation of the stream.[233] This makes it possible to increase the degree of recovery of heat to 80–85% and to reduce correspondingly the amount of fuel used.

The elimination of various organic substances and CO from industrial effluent gases under conditions involving the periodic reversal of the flow of mixture through a stationary catalyst bed[234-237] ensures the following features compared with the traditional stationary procedure: (a) a decrease in the capital cost of the building of plants by a factor of 1.5–3; (b) a decrease in the intrinsic cost of the purification of gases by a factor of 1.5–2; (c) the autothermal nature of the process under the conditions of variable and low (on average above 0.5 g m^{-3}) contents of toxic impurities; (d) the generation of potentially highly useful heat in the detoxification of gases containing more than 3 g m^{-3} of toxic impurities, which can also ensure that the detoxification process is economical.

For the purification by the non-stationary method of gases at low concentrations, whereupon the adiabatic heating of the mixture (ΔT_{ad}) on complete conversion of harmful substances into CO_2 and water does not exceed 15 K, it has been suggested[235] that an additional minimum amount of fuel which would ensure, together with the toxic components, the necessary degree of heating be introduced into the gas being purified. Such a process has been developed for the detoxification of the effluent gases from painting and drying workshops.

In contrast to the reversible sulphur dioxide oxidation and Claus reactions, oxidation reactions leading to the removal of organic compounds from gases take place reversibly with formation of water and carbon dioxide. This makes it possible to purify gases under non-stationary conditions at the maximum temperatures without the use of fuel and with the minimum amount of catalysts.

The technical parameters of one of the industrial plants for the elimination of organic compounds from gases are presented in Table 1.

Industrial non-stationary catalytic methods for the elimination of the principal industrial gaseous contaminants (NO_x, SO_2, hydrocarbons) from gases have been developed on the basis of the flow reversal process and applied in industry. The efficiency of the non-stationary method has been confirmed by the vigorous development of studies on these lines both in the USSR and abroad.[238–243]

VIII. Non-catalytic chemical methods

If undesirable impurities are removed from gases as a result of a virtually irreversible chemical reaction, whose role is decisive compared with other processes, then such methods of purification will be referred to as chemical. From this standpoint, the methods for the elimination of SO_2 from effluent gases using lime or limestone, for example, are frequently referred to as absorption methods since the decisive operation involves in this case processes in the absorption scrubber. The chemical purification methods are based primarily on the chemical transformation of toxic compounds into harmless (or less toxic) ones or on the activation of chemical reactions. It is useful to include among them also radiation-chemical methods based on the employment of accelerated electrons.[244–247] In many cases, it is useful to introduce ozone into the gases undergoing purification in order to activate chemical reactions.[162,248,249] Examples of the use of chemical purification methods in industry are presented below.

The elimination of NO_x from gases involves the reduction of the impurities to N_2 and H_2O. The homogeneous reduction of NO_x by ammonia occurs mainly at 900–1000 °C. At higher temperatures, the rate of oxidation of ammonia to nitrogen oxides increases significantly, which lowers the degree of purification. This process has been developed mainly by the American Exon Company.[250] The average degree of elimination of NO_x from gases by this method does not at present exceed 60–70%.[152,251,252] The principal ways of increasing the process efficiency involve the improvement of the systems for the mixing of small amounts of ammonia with hot (900–1000 °C) smoke gases,[253] which makes it possible to raise the degree of purification to 80–90%, and the search for new reductants permitting the expansion of the temperature range in which the process can be carried out.[254] Thus it has been suggested that urea be used for the reduction and that the process be performed at 600–1100 °C.[254]

On exposure to a stream of electrons, chemical reactions in gases are appreciably accelerated. This method is suitable mainly for the elimination of NO_x and SO_2 from the smoke gases generated in thermal electric power stations.[244–247] The stream of smoke gases is initially freed from ash, after which ammonia is supplied and the gas mixture is irradiated. This results in the formation of a mixture of the salts $(NH_4)_2SO_4$ and $(NH_4)_2SO_4.2(NH_4)_2SO_3$ from ammonia, nitrogen oxides, and sulphur. After the separation of the salts (for example, on an electrofilter or on a sleeve filter), the gas is ejected through a smoke tube and the mixture of salts is used as a fertiliser. The output of the largest plant operating in the USA is 32000 $m^3 h^{-1}$. The principal advantages of the method are its simplicity and the absence of secondary contaminants, including waste water. The degree of elimination of NO_x attained is usually 70–90%.[244,245] Various modifications of the methods are being developed: with recycling of the purified gas[255] and with irradiation of the gas in two stages, whereupon most of the radiation dose is absorbed in the first stage.[256] The principal disadvantage of the method is believed to be the considerable energy expenditure. Evidence has recently appeared indicating the possibility of the laser irradiation of the gases undergoing purification.[257] The wavelength is then selected so that the preliminary absorption of radiation by sulphur and nitrogen oxides should entail their dissociation with liberation of elemental sulphur and N_2.

Ozone methods are used to remove the toxic SO_2 and NO_x from smoke gases and to deodorise the gaseous waste in industrial undertakings. The introduction of ozone accelerates the oxidation of NO to NO_2 and of SO_2 to SO_3.[257] After the formation of NO_2 and SO_3, ammonia is introduced into the smoke gases and the mixture of the complex fertilisers formed (ammonium sulphate and nitrates) is isolated. The duration of contact between the gas and ozone necessary for the removal of SO_2 (80–90%) and NO_x (70–80%) is 0.4–0.9 s. The energy expenditure on the purification of gases by the ozone method is estimated as 4–4.5% of the equivalent power output of the energy unit, which is apparently the main cause holding back the industrial application of this method.[249]

The use of ozone to destroy the odour of gaseous waste is based on the oxidative decomposition of substances with an unpleasant smell. In one group of methods, ozone is introduced directly into the gas being purified, whilst in another the gases are washed with water which was ozonised beforehand. The subsequent passage of ozonised gas through a layer of activated charcoal[257–261] or its application to the catalyst[262–264] have also been used. When ozone is introduced and the gas is subsequently passed through the catalyst, the temperature of the conversion of substances such as amines, acetaldehyde, and hydrogen sulphide is reduced to 70–80 °C. Both Pt/Al_2O_3 and copper, cobalt, and iron oxides on a carrier are used as catalysts.[263] The ozone methods for the destruction of odour have been used primarily in the purification of gases evolved in the processing of raw material of animal origin in meat (fat) processing plants.[249] This method has so far been scarcely applied in the USSR.

Either pelleted material (crushed charcoal with added lime) is used for the chemical binding of SO_2 or powdered limestone or dolomite is introduced into carbon dust in the combustion of spray-injected fuel. The use of grains containing added lime with the ratio C : S = 3 : 5 reduces the concentration of sulphur dioxide in smoke gases resulting from the combustion of fuel in grate furnaces by 50–70%.[34] In the combustion of coal dust with added lime, the degree of binding of SO_2 reaches 80%.[30] SO_2 is bound similarly after the introduction of sodium salts and in this case there is a possibility of using lower temperatures (110–150 °C).

Three filters are employed for the subsequent separation of the salts formed. The disadvantages of this method are believed to include the inadequate, in many instances, degree of elimination of SO_2 and the solubility of the salts formed.[1]

The different reactivities (differing by a factor of 5) of different kinds of limestone in relation to SO_2 have not so far been adequately explained.[30]

Chemical methods make it possible to achieve the combined elimination of compounds of different types from gases. An example is provided by the method for the simultaneous removal of sulphur dioxide and hydrocarbons from gases.[265] For this purpose, the gas is passed through a layer of hot limestone at a temperature sufficient for the cracking of the hydrocarbons. Sulphur dioxide is

simultaneously converted into calcium sulphide. The regeneration is carried out with oxygen, which affords elemental sulphur.

IX. Biochemical methods

Biochemical purification methods are based on the ability of microorganisms to decompose and transform various compounds. The substances are decomposed on treatment with enzymes generated by microorganisms in the gases undergoing purification. When the gas composition is frequently altered, the microorganisms are unable to adapt by developing new enzymes and the degree of decomposition of harmful impurities becomes incomplete. Biochemical systems are therefore most suitable for the purification of gases of constant composition.

The biochemical purification of gases is carried out either in biofilters or in bioscrubbers. In biofilters, the gas undergoing purification is passed through a layer of packing irrigated with water, which gives rise to a moisture content sufficient to maintain the vital activity of microorganisms. The surface of the packing is coated with a biologically active biofilm (BF) comprising microorganisms. In the course of their vital activity, the microorganisms of the biofilm absorb and decompose the substances contained in air, which results in the growth of their mass. The efficiency of the purification is determined to a large extent by the mass transfer from the gas phase to the biofilm and by the uniform distribution of the gas in the layer of packing. Filters of this kind are used, for example, to deodorise air.[11,266] In this case, the gas stream undergoing purification is filtered under conditions where its flow is parallel to that of the irrigating liquid containing nutrient substances. Beyond the filter, the liquid enters settling chambers and is then again directed to irrigating units.

At the present time biofilters are already used fairly widely for the removal of ammonia, phenol, cresol, formaldehyde, organic solvents introduced in the painting and drying processes, hydrogen sulphide, methanethiol, and other organosulphur compounds from effluent gases. The degree of purification of effluent gases is 95–99%.[267–269] Under normal operating conditions, complete deodorisation is observed beyond the biofilters as a result of the elimination of compounds with an unpleasant smell, for example, methanethiol and hydrogen sulphide. The hydraulic resistance of biofilters ranges from 250 to 2000 Pa and the average contact time is 10–25 s.[266,267]

Bioscrubbers are absorption devices in which the irrigating liquid (absorbent) is an aqueous suspension of active sludge with microorganisms. The gas being purified is usually supplied to the scrubber from below and passes through a packing in a countercurrent relative to the irrigating absorbent. The decomposition reactions of the trapped impurities occur in the aerator-reactor. In order to maintain the vital activity of the microorganisms, the necessary nutrient substances are continuously introduced into the system. Bioscrubbers have found applications for the purification of effluent gases from metal casting industries containing phenol, formaldehyde, ammonia, hydrocyanic acid, and cracking products[267,270] and also in the elimination of butyl acetate, xylene, and alcohols from painting workshop gases.[266]

The overall content of impurities in the gases to be purified can be 750–800 mg m^{-3}.[266] The productivity of bioscrubbers reaches 300 000 $m^3 h^{-1}$, the contact time does not usually exceed 10 s, and the hydraulic resistance is 1000–1500 Pa. The degree of purification reaches 75–98%.

Further improvement of biochemical gas purification systems involves the intensification of the decomposition reactions of the trapped impurities, which is promoted by the injection of highly dispersed activated charcoal into the irrigating liquid.[271] In this case, the microorganisms are adsorbed on the large internal surface of the charcoal.[272–274] Attempts have been made to intensify the biochemical purification by applying electric fields to the system containing the activated charcoal.[275]

The development of biochemical purification methods has led to the creation of biofilters with an artificially formed structure and a specially grown biofilm. The linear flow rates of the gases being purified in such systems can reach 0.5–1.0 m s^{-1}, which is higher by a factor of 80 than in processes involving the use of natural materials. The largest biofilters of this type are being used in the Federal Republic of Germany (70 000 $m^3 h^{-1}$).[276] This procedure is most applicable to the purification of gases with a low concentration of impurities. Polymeric materials [polyethylene, poly(vinyl chloride)] are widely used in bioscrubbers. Apart from the Federal Republic of Germany, the biochemical gas purification method has found practical applications in Japan.[266,277–279] Biological gas purification methods have been recommended for the deodorisation of the effluent gases from veterinary-sanitary product factories, food processing undertakings, sewage processing plants, etc.[277]

X. Conclusion

A large number of different methods for the removal of the principal contaminants (NO_x, SO_2, H_2S, carbon monoxide, and various organic substances) from gases have now been developed and tested in industry. We shall indicate the principal applications of these methods and their present state. The absorption methods are used mainly to trap acid components from gaseous waste (SO_2, H_2S, HCl, SO_3, NO_x, NH_3, etc.). In many cases, this makes it possible to obtain useful products—acids and salts. This method is used in practice much more rarely for the removal of hydrocarbons from gases, which is caused primarily by the high cost of absorbents. The principal disadvantages of absorption methods are the formation of liquid waste and the cumbersome apparatus used.

The adsorption methods are some of the most widely used industrial procedures for the purification of gases. Their application makes it possible to return to industry many valuable compounds. At impurity concentrations in the gases more than 2–5 g m^{-3}, the purification is actually profitable. The principal disadvantage of the adsorption method is the large energy consumption in the desorption and subsequent separation stages, which greatly complicates its application to the purification of multicomponent mixtures.

Thermal methods are widely used to eliminate toxic combustible compounds from effluent gases. The afterburning plants developed in recent years are distinguished by their compactness and low energy expenditure. The application of thermal methods is effective for the afterburning of multicomponent and dust-saturated effluent gases.

The principal aspects of the development of catalytic methods are the creation of cheap catalysts operating effectively at low temperatures and resistant to various poisons as well as the development of energy saving technological processes with low capital costs for equipment. Catalytic methods have found the largest-scale application in the elimination of nitrogen oxides from gases, in the detoxification and utilisation of a wide variety of

sulphur compounds, and in the detoxification of organic compounds and CO.

Condensation methods are used on an industrial scale normally in the presence of high concentrations of the impurities to be trapped. In order to attain the necessary degree of purification after condensation, it is as a rule essential to employ some other methods, for example, catalytic methods.

The development of chemical methods is associated with the search for effective procedures for the activation of chemical gas-purification reactions. Methods involving the homogeneous reduction of NO_x and ozone methods for the deodorisation of compounds with an unpleasant smell found fairly extensive industrial applications.

The experience gained in the prolonged use of biochemical plants and the simplicity of their technical operation and the apparatus involved make it possible to recommend this procedure for extensive application, primarily for the elimination of organic compounds from gaseous waste with low concentrations of impurities. Among the disadvantages of biochemical methods, one should include, firstly, the low rate of biochemical reactions, which increases the size of the equipment, secondly, the specificity (high selectivity) of the strains of microorganisms, which hinders the processing of multicomponent mixtures, and, thirdly, the difficulty of processing variable-composition mixtures.

The industrial application of membrane methods is being held back so far by the low specific productivity of membranes, the low degree of purification, the necessity to generate a high excess pressure, the large size of the equipment, and the large capital and operating costs.

The improvement of traditional purification methods (adsorption, absorption, thermal afterburning, and condensation) and the development of new ones (catalytic, membrane, chemical, and biochemical) tend to reduce the capital and operating costs (mainly energy expenditure) involved in their application. In most cases, the problems associated with the purification of effluent gases can be solved in different ways. For example, solvents can be removed from gases with the aid of adsorption, by thermal and catalytic oxidation, and by biochemical and absorption methods, each procedure permitting the attainment of virtually any degree of purification. In every specific case, the choice of the detoxification method is an economic problem. There are no poor and good methods. There are only expensive and cheap ones.

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