AIR POLLUTION CONTROL
(Control of gaseous emissions)
(A general overview)

THE PROBLEM AND THE ENGINEERING TASK:

Air streams are generated in different industrial processes which contain (more or less) harmful chemical components (elements or compounds) for the biosphere (or for some part of it as atmosphere, hydrosphere or lithosphere – soil). These components are mentioned as air pollutants. Some of them are dangerous directly (e.g. some toxic or carcinogenic material) or indirectly through chemical reactions happening after the emission in the biosphere and creating toxic compounds.

To protect the biosphere (including living world as well as mankind) we have to decrease the concentrations of these components below a limit specified by some regulations before the air stream is emitted into the atmosphere (since air streams are generally emitted directly into the atmosphere and not e.g. into the hydrosphere). Volatile organic compounds (VOCs; hydrocarbon derivatives except methane), sulphur-dioxide (SO_2), nitrogen-oxides (generally NO_x or nitrogen-monoxide NO and nitrogen-dioxide NO_2), carbon-monoxide (CO), ammonia (NH_3), methane (CH_4 or marsh gas) and many other gaseous components as well as particulate materials (dust, droplets) may be mentioned.

Air pollutants may be classified according to the origin and to the state of the matter:
Classification according to the origin:
- Primary: emitted to the atmosphere from the process directly;
- Secondary: formed in the atmosphere as a result of a chemical reaction.

Classification according to the state:
- Particulate: finely divided (dispersed) solids or liquids (solids such as dust, fumes and smokes; liquids such as droplets, mists, fogs, and aerosols, etc.)
- Gaseous: true gases such as sulphur-dioxide, nitrogen-oxides, carbon-monoxide, vapours as gasoline, paint solvent, dry cleaning agents, etc.

The gaseous pollutants may be classified as inorganic and organic. **Inorganic pollutants** consist of: sulphur gases (sulphur-dioxide and sulphur-trioxide, hydrogen sulphide), oxides of carbon (carbon-monoxide and carbon-dioxide), nitrogen gases (nitrous oxides, nitric oxide, nitrogen monoxide and nitrogen dioxide), halogens, halides (hydrogen fluoride, hydrogen chloride, chlorine, fluorine, silicon tetrafluoride), photochemical products (ozone, oxidants), cyanides (hydrogen cyanide), ammonium compounds (ammonia) and chlorofluorocarbons (freon). **Organic pollutants** consist of hydrocarbons (paraffins, acetylene, olefins, aromatics), aliphatic oxygenated compounds (aldehydes, ketones, organic acids, alcohols, organic halides, organic sulfides, organic hydroperoxides).

Different technical methods (or processes) and equipment are in use for the gaseous materials and for the particulate materials but my task is to give you information on the methods able to treat the gaseous components.

We have two ways to decrease the concentration of some harmful gaseous component in a gas stream treated:
- removing some part of the harmful component from the gas stream (used e.g. to decrease the concentration of sulphur-dioxide) or
- converting some part of the harmful component into a less harmful or harmless component using some chemical reaction (used e.g. to decrease the concentration of nitrogen-oxides).

To decide which method is used for some specified substance we have to take into account technical and economic standpoints. Having removed the substance from the gas stream (without converting it) it gives a possibility to recover the substance for using it again. If we consider valuable volatile

organic compounds or vapours the recovery may be feasible from economic standpoints, too. The methods used for these substances are shown on the hand-out distributed. In the first row those methods are listed which make possible the recovery of the substances and methods listed in the second row convert the components into less harmful or harmless substance and after the treatment the gas stream may be emitted into the atmosphere (environment). These methods destroy the original component creating a new one which is less harmful or harmless. First of all, I intend to give you a general but short overview of the methods listed in any of the rows and later we are going to discuss in detail the absorption and possibly combustion.

To solve and to evaluate any air pollution problem knowledge of the types and rates of emission is fundamental. A material balance on the process can often help but published emission data can also be used to determine which pollutants are discharged from the various processes. Emission is affected by the techniques employed in the processing, handling or burning operations, by the quality of the material used and by the efficiency of the air pollution control. Many combinations of these factors are possible consequently emissions from one source may not be satisfactory for another one. Care and good judgment have to be exercised to identify the appropriate emission. If it does not help to design an air-pollution control equipment specific experimental source sampling should be conducted.

CONDENSATION

It is frequently necessary to treat an effluent gas stream consisting of a condensable pollutant (steam or vapour) and a non-condensible gas (generally air). One of the control methods to remove such pollutants from the gas stream is condensation. This is generally accomplished by **decreasing the temperature** of the gas stream, although a similar result may be reached by **increasing the pressure**.
When the air stream contains steam or some vapour cooling may be used to decrease the temperature of the gas stream below the dew-point temperature and consequently some part of the steam or vapour will condense on the cold surface. Having reached the **dew-point temperature** the gas stream becomes saturated and further cooling below the dew-point temperature is required to get condensate (i.e. to decrease the concentration of the substance). The quantity of the condensed part (and the decrease of the concentration of the substance) depends on the difference between the final temperature of the gas stream and the dew-point temperature. To illustrate the cooling process the **psychrometric chart** or the **Mollier-chart** may be used which show the relations between the state variables of a humid gas (as temperature, humidity and enthalpy).

Depending on the requirements and/or economic standpoints air and water of ambient temperature may be used or for more strict regulations liquified nitrogen may be used called as cryogenic cooling (e.g. for VOCs which may be carcinogenic i.e. cause cancer). Using liquefied nitrogen, the temperature of the cooling medium is as low as -180 °C or lower and the dew-point temperature of the gas treated may be as low as – 50 – 60 °C or lower. It follows that using cryogenic cooling only a minor quantity of the components remains back in the gas stream and, consequently the final concentrations of VOCs are very close to zero. Sometimes **inert gas drying** is mentioned in the appropriate literature for this condensation process since the carrier gas does not condense i.e. it is the inert part of the gas stream.

Remark: the boiling point temperature at 1 atmosphere of the liquified nitrogen is 77 K (-196 °C). Using liquified helium is also possible, its boiling point temperature at 1 atmosphere is 4.2 K (-269 °C) but it is more expensive. Helium is the coldest known liquid at -269 °C.

In the equipment used the two streams (i.e. the gas stream to be cooled and the coolant) may be in **direct contact or indirect contact** (connection).

Direct contact means that the phases are in the same space and the condensible component condenses and mixes with the cooling medium (coolant). The equipment for direct contact is called (direct) **contact condenser**. The outlet temperature difference (the temperature approach) between the cooling medium and the gas stream may be very small, so the removal efficiency may be high but large

quantities of the cooling medium are necessary. In direct contact equipment the coolant is generally water or air. Using water as coolant the liquid stream leaving the equipment contains the original cooling water and the condensate. If the condensate is not soluble in the water the system is a real condenser. In this case generally settling by gravity is used to get the condensate in pure state. Of course, settling needs some difference between the densities in the liquid phase. If the condensate is soluble in the cooling water (which is the general case) solvent extraction or distillation may be used to remove the condensate from the mixture to get the condensate in pure state. Settling is the cheapest and the simplest process for the separation and distillation is the most expensive one. If the coolant is air condensate drops are received and then a droplet separator is required to get the condensate. In this case the liquid contains some water since the cooling air becomes saturated and some steam will condense. If the recovery is planned water cooling is rarely used except that case when the condensate is not soluble in water. Without recovery the effluent streams are the water-organic mixture and the non-condensible gas. The liquid mixture needs to be managed because of the organic component which may be harmful (some waste water treatment required). The gas stream at the outlet is generally saturated in the steam and determines the efficiency of the process. The water requirement is generally high since at least 10 to 20 kg of water is required to get 1 kg of steam but for organic compounds it is a little lower (the latent heat is lower). But it has only one advantage since the liquid mixture is very dilute in the organic components. The air quantity is higher because of the lower heat capacity of the air. Mainly spray condensers or barometric condensers are used for direct contact cooling.

Indirect contact means that the phases are separated by a solid wall. The equipment is divided into two spaces, one of them is for the coolant and the other one is for the gas stream to be treated. This type of equipment is called as **surface condenser**. Surface condensers are used frequently in the chemical process industries to remove and/or to recover the pollutants (contaminants) or simply to control their concentrations in the gas streams before the emission. In this equipment the coolant does not contact the condensate. There are different types of surface condensers but the most frequently used are the shell-and-tube heat exchangers and the tubular heat exchangers. Air may also be used as cooling medium instead of water when water is not available. Finned surface may be used too (on the air-side, of course) which increases the installation costs. When water is used as coolant it can be reused after cooling. The temperature increase for the coolant is higher (counter-current flow) consequently less coolant is required than in a contact condenser. Using liquified nitrogen more robust equipment is required because of the low temperature and the heat insulation. This type of the equipment is more expensive than the contact condenser but it is a huge advantage that the condensate is received in pure state (and sale-able or usable more easily). They require more maintenance than the contact condenser. The removal efficiency of the surface cooling is generally very low (except cryogenic cooling; the prefix "cryo" is Greek and means cold or frost). It follows that this method is generally used for pre-treatment prior to some other more efficient method (e.g. as absorber, adsorber, membrane technology, etc).

ADSORPTION

Adsorption utilizes the ability of certain solids: they are able to concentrate preferentially (selectively) specific substances from gas phase or liquid phase on their external and internal surfaces. In this manner the components of either gaseous or liquid solutions may be separated from each other. There is a great variety of practical applications in the field of gaseous separation: to dehumidify (remove humidity from) air and other gases; to remove offensive odour and impurities from industrial gases (e.g. carbon dioxide); to recover valuable solvent vapours from dilute mixtures with air and other gases (e.g. in the chemical or pharmaceutical industry, or process industries), and to fractionate mixtures of hydrocarbon gases containing methane, ethane, propane, ethylene, propylene, and propane.

It follows that solid material is used to collect (to bind) components from the gas streams. Theoretically every solid is able to bind components on its surface but special materials are used which are called as **adsorbent**s (or adsorbent solids). Adsorbents are able to collect (to bind) much

more quantity of material bound on its surface. Adsorbents are e.g. **activated carbon, silica gel, zeolite or molecular sieves**. The solid is insoluble phase.

Contacting phases are the gas and the solid phase, the process is called as adsorption and its reverse process is called as desorption. The other notations: the equipment is the **adsorber**, the adsorbing solid is the adsorbent, the gas which may be adsorbed is the **adsorptive** and adsorbed gas molecules on the solid is the **adsorbate**.

During adsorption mass transfer is taking place between the gas phase and the solid phase by which components are transported from the bulk of the gas phase through the interface surface between the two phases into the solid phase where the molecules are bound very differently (or selectively). This mass transfer will be discussed in more details in connection with absorption where a gas phase and a liquid phase are contacted to transfer chemical components from the gas phase into the liquid phase. The rate of adsorption depends on the concentration of the adsorptive in the gas stream, the specific surface of the adsorbent, the pore volume of the adsorbent, and other properties of the adsorbent and the adsorptive.

Components from the gas stream are collected on the surface of the adsorbents differently / selectively depending on their characteristics. There will be a composition difference between the bulk gas phase and the gas phase bound by the solid (adsorbate) depending on the shape of the molecules and the size of the molecules. Components are bound by physical (molecular) forces called van der Waals forces (Johannis Dideris van der Waals was a Dutch physicist – 1837-1923; known mainly after the state law of real gases). Adsorption is the result of the intermolecular forces of attraction between molecules of the solid and the substances adsorbed (adsorbate). There is a physical binding between the molecules of the solid and the gas molecules collected on the surface of the solid. This is the **physical adsorption** (or van der Waals adsorption).

Adsorbent solids: Adsorbents are particulate materials usually used in granular form, varying in size from roughly 10 mm (generally less than 5 to 7 mm) in diameter to as small as 50 μm ($50·10^{-6}$ m). Adsorbents contain pores and capillaries thus they are porous. The pores are usually very small, sometimes in the order of a few molecular diameters in width but their large number provides a huge surface for adsorption. The average pore size is less than 15 nm in general but for activated carbon is between 5 to 7 nm. Thus, the internal surface area is much larger than the external one (geometrical surface area). This surface is called as **specific surface** (adsorption surface) which is the most important property of an adsorbent and is measured in m^2/g adsorbent. The specific surface may be as high as for granulated activated carbon 1000-1500 m^2/g or for silica gel 300-500 m^2/g. Generally, the higher the specific surface the greater the adsorption capacity of the adsorbent. It follows that the adsorbate is mainly bound on the internal surface of the particles. Other important properties of adsorbents are porosity, density, adsorption capacity, selectivity and catalytic properties. The porosity is the ratio of the volume of the pores and capillaries within the particle to the total volume of the particle and is measured in m^3/m^3 or in %. The internal porosity of the particles is between 30 to 80 % but for granulated activated carbon ranges between 60 to 80 %. Activated carbon is the most frequently used adsorbent with an exceptionally large specific surface area. This is why active carbon is applied as adsorbent especially in gas purification operations. Only molecular sieves have a specific surface area that is close to that of activated carbon.

Industrial adsorbents are usually able to adsorb both organic and inorganic gases and vapours. But activated carbon has superior properties for the adsorption of organic vapours, having hydrocarbon-selective properties and high adsorptive capacity for such materials. Inorganic adsorbents, such as activated alumina or silica gel, can also be used to adsorb organic materials, but difficulties can arise during regeneration. Activated alumina, silica gel, and molecular sieves will also preferentially adsorb any water vapour with organic contaminant.

Adsorption plant: A stationary (fixed) or a moving bed (layer) is formed from the particles (the adsorbent) on a solid surface (above a perforated plate) and through the bed the gas stream flows upwards or downwards. Using moving or fluidised bed some solid loss will be present because of the

powdering (friction between the particles). The solids must have certain engineering properties depending on the application (mechanical strength, hardness, allowable treatment temperature, etc.). In industrial equipment adsorption generally takes place in a stationary/fixed **packed beds** of granular adsorbents (since the movement of the adsorbent is not impossible but is not easy). In most such adsorption plants it is necessary to operate with a small pressure drop through the bed to keep power (operational) cost low. Therefore granular, rather than powered adsorbents are used, and bed depth is relatively shallow (30 to 100 cm) and the equipment has large cross section. The superficial velocity of the gas may be in the range 20-50 cm/s (below the minimum fluidization velocity).

The **capacity** of the adsorbents to collect adsorbate **is final,** when the adsorbent becomes **saturated**. In this case the molecules of the adsorbate will cover the whole surface of the adsorbent particle in one or multi-molecular layer(s) (at most 5-6 layers) and the adsorbate fills the inner voidage of the particles. 1 kg of adsorbent is generally able to bind 0.1-0.5 kg of adsorbate depending on the characteristics of the adsorbent and the adsorptive and strongly depending on the operational temperature. When the capacity is used the adsorbent became saturated and is not able to bind any more molecules and needs regeneration for being able to use it again. **Regeneration** (desorption) is generally done by hot air, inert gas (i.e. nitrogen) or overheated steam. During the desorption process the desorption gas passes through the bed and picks up most of the adsorbate. It takes time which is the regeneration (desorption) time. During regeneration of the saturated adsorber another adsorber is required to fulfil adsorption and depending on the relation between the adsorption time and the desorption time an adsorption plant generally consists of two or more vessels: one of them is in the adsorption cycle while the other is (or the others are) in desorption cycle (regeneration cycle). Generally cooling and drying may be required after the regeneration. The regeneration medium needs further treating (condensation, absorption, combustion etc).

Chemical adsorption: In some cases, none of the adsorbents has sufficient adsorptive capacity for the contaminant to be treated. For these applications, the adsorbent can be impregnated with an inorganic compound or, in rare case, with an organic compound that can react chemically with the particular contaminant. In this case chemical adsorption takes place. For example: iodine-impregnated or sodium-bisulphate-impregnated activated carbons are used for removal of mercury vapour and bromine-impregnated carbons for ethylene or propylene removal. Mercury vapour is a very dangerous pollutant of which the largest industrial sources are chlorine production, various metal works, producers of mercury thermometers and manometers.

SECOND GROUP

As mentioned earlier the components are destroyed by a chemical reaction and less harmful or harmless components are created and after the treatment the gas stream may be emitted into the atmosphere directly assuming that the concentration of the harmful components remained back is less than the limit concentration specified by regulations.

CHEMICAL (WASTE GAS) TREATMENT / COMBUSTION

Chemical waste gas treatment is one of the most effective processes for conversion of organic pollutants but waste gas may also contain solid particles and liquid drops. It was mentioned that it is not a removal but a **chemical conversion** during which harmless or less harmful components are produced by **oxidation**. This is advantageous since:
- complete conversion of all organic pollutants is possible independent of their chemical properties;
- in most cases, there will be no waste water or solid waste treatment problems.

It is important to emphasize: **high price has to be paid for these advantages** because of costs for energy, catalyst and equipment which may be quite high.

The conversion of organic pollutants, for example hydrocarbons, is governed by the following overall chemical reaction:

$$C_m H_n O_p + (m + \frac{n}{4} - \frac{p}{2})O_2 = \frac{n}{2}H_2O + mCO_2 \, .$$
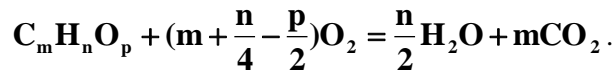
In this simple case the reaction products are water and carbon dioxide. But in the most cases, however, because of intermediate stages of the reaction and partial processes, intermediates may also be produced. One of the most important intermediates is the carbon monoxide which may be converted into carbon dioxide:

$$C + \frac{1}{2}O_2 \Rightarrow CO \, ,$$

$$CO + \frac{1}{2}O_2 \Rightarrow CO_2 \, .$$
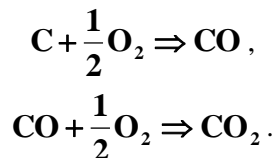
Depending on the composition of the waste gas and the injected fuel (if required), there will also be other products like nitrogen oxides, hydrogen chlorides, sulphur dioxide and others.

To achieve complete combustion sufficient space, (residence) **time**, and **turbulence** (mixing) and a **temperature high enough** to ignite the components **must be provided**. For complete combustion the oxygen must come into intimate contact with the combustible molecules at sufficient temperature and for a sufficient length of time for the reaction to be completed. Incomplete reactions may result in the generation of aldehydes, organic acids, carbon and carbon monoxide.

It is important to emphasize that the chemical conversion of the organic pollutants is an **oxidation process** which within a limited range of concentration of the organic pollutant is **self-propagated** process for **exothermic reaction**s. The lower limit of this concentration is called the **lower explosion limit**, while the upper limit is called the **upper explosion limit**. The explosion range depends on the type of pollutant, composition of the gas mixture, temperature, pressure, ignition temperature and – to a certain extent – on the vessel geometry. The range of self-propagating oxidation, that is the **explosion range**, has to be avoided for the safety of the process. It follows that because of the safety reasons the pollutant concentration must be outside of this dangerous range (the explosion range) and the oxidation process outside of the explosion range is used for technical applications.

The required temperature is generally above 700 °C to avoid the generation of carbon-monoxide and the temperature may be as high as 1200 °C depending on the circumstances (e.g. composition of the gas stream). Using catalysts a lower temperature is required generally from 400 °C to 500 °C. These processes are mentioned as **thermal oxidation or catalytic oxidation,** and the equipment called as **incinerators /after-burners** (frequently simply **combustor**) i.e. thermal incinerator or catalytic incinerator and thermal after-burner or catalytic after-burner.

Thermal chemical conversion is achieved in the temperature range between 700 to 1000 ºC or even higher. In general, continuous combustion of the gas mixture can be achieved only by the introduction of supplementary energy since the (lower) calorific value of the waste gas is not high enough. In some cases, this is necessary only during the start-up operation of the plant, in other cases continuous introduction of supplementary energy is required. The fuel may be natural gas or oil. The heat content of the effluent gas is generally utilized in a heat recovery system for preheating inlet waste gas, fuel, or air which helps to reduce the supplementary energy demand but this will increase installation costs. Because of the high temperature the economy of thermal chemical conversion plants greatly depends on the efficiency of the heat recovery systems. The advantages of thermal combustion are, besides complete removal of the organic components with practically no waste water or solid waste problems, exceptionally good adaptability to changes in waste gas flow rate and composition and relatively simple design.

Because of the high operating temperatures, the reactor must be constructed of metals capable of withstanding this condition. **Heat-resistant alloy** can withstand to high temperatures. Combustion devices are usually constructed with an outer steel shell that is lined with refractory material. Refractory-wall thickness is usually in the 0.05 to 0.25 m range, depending upon temperature considerations (refractory lining).

Catalytic chemical conversion is achieved at the surface of the catalyst in the temperature range from 400 to 500 ºC. This temperature at which the catalyzed reaction takes place is about from 300 to 400 ºC. Because of the lower temperature, the fuel demand is relatively low which makes catalyzed pollutant conversion so attractive. Dust removal from the waste gas may be desirable in order to prevent dust settling on the catalyst surface which would result in a reduced catalytic activity.

The **catalyst** generally consists of a **carrier** substance which is coated with the catalytic **active material**. The carrier substance is either a metal, aluminium oxide or silicate, asbestos, and activated carbon. The catalytic active material is, in most cases, a metal or metal oxide. The catalytic carriers are in general very porous substances to provide a large internal surface area for the active material. The external surface of porous particulate catalysts is negligibly small, compared with the internal surface (like to adsorbents). There are of course so-called solid catalysts consisting of only the active material. Typical forms of catalysts are small spherical particles, rings and rods. Catalyst is an expensive material mainly some precious metal-oxide as V_2O_5 on a carrier which is generally TiO_2. It follows that the catalyst is the most important part of a catalytic after-burner. The mass fraction of the active material is generally less than 5-10 % of the total mass of the catalyst (it follows that the mass fraction of the carrier is generally between 90-95%). Equipment is also expensive because of the high temperatures since generally heat-resistant metals – highly alloyed metals - are required.

Service life of **catalysts** may be reduced by **poisoning**, that is the deposition of substances on the surface or the reaction of substances.

BIOLOGICAL TREATMENT

Microorganisms (generally bacteria) are used to treat odorous outlet gases in an environmentally safe and economic manner. The biofiltration equipment (process) consists of a porous filter media through which a waste gas flows. Microorganisms are attached to the porous filter media (substrate) and consume the pollutants. The substrate provides the support and the nutrients for the microbes. The biofiltration process is similar to the conventional activated sludge treatment since in both processes the microorganisms are used to oxidize the organic compounds into carbon-dioxide and water according to the next general bio-chemical reaction:

organic compounds + oxygen + bacteria= water + carbon-dioxide + biomass.

Depending on the layout the equipment may be
bio-filter, bio-scrubber, bio-trickling,
but the simplest equipment is the bio-filter similar to the fixed-bed adsorbers which is possibly the most frequently used.

The most common **filter materials** (substrates) in use today are soils or compost produced from leaves, bark, wood chips, activated sludge, paper, or other organic materials. Their porous structure should provide an appropriate surface area at a reasonable low pressure drop. As the gas flows through the bed the pollutants are transported from the bulk of the gas phase to the biofilm on the surface of the particle where the pollutants are absorbed in the water and are decomposed by the microorganisms present in the biofilm (the microbes live within the biofilm). The same natural biodegradation process takes place than in biological wastewater treatment. The temperature of the process is close to the ambient one. Consequently, it may be said that it is **environmental-friend process**. Biofilter is economic when the concentration of the pollutants is very low (generally less then 1000 ppm, but data are published where the concentration was as high as 5000 ppm) and the waste gas is oxygen rich.

Inorganic pollutants soluble in water (e.g. ammonia and hydrogen sulphide) can also be readily decomposed by the aerobic process.

The **microorganisms** used are practically the same bacteria and fungi which are used in the activated-sludge wastewater treatment. Genetic engineering produces microbes which can digest man-made chemical substances. The composition of the raw (inlet) gas is very important in order to get high removal efficiency of the pollutants and the life expectancy of the microbes let be also good enough. The inlet gas must contain the following: an ambient oxygen content, pollutant concentrations below the lethal levels and lethal gas components must be absent.

In a biofilter the particulate filter material rests on a holder and the depth of the bed is around 1 m through which the gas stream flows and its velocity is less than 10 cm/s in order to have residense time long enough to finish the bio-chemical reaction. To distribute the inlet gas over the cross section of the equipment as even as possible is also important. Particulate material can be deposited and damage the pore structure of the filter bed and increases the pressure drop including operational costs. Thus, dust removal in front of the biofilter is suggested. Temperature, humidity and pH are the important parameters for the operation.

The recommended **operating temperature range** for high destruction efficiency is between 20 to 40 ºC, with an optimum temperature of 37 ºC. At lower temperatures, the bacteria growth will be limited, and at extremely low temperatures the bacteria could possibly be destroyed. At temperatures above the recommended range, the activity of the bacteria is also damaged. Extremely high temperatures will destroy the bacteria within the filter bed. It follows that the waste gas temperature is one of the most important factors to use a biofilter or another method. Temperature adjustment in front of the biofilter is also important.

The microorganisms that digest the targeted pollutants live in a thin water layer, in the biofilm that surrounds the filter substrate. Without the biofilm, the microorganisms would die. Therefore, maintaining a wetted surface within the filter bed is crucial. Insufficient moisture can also lead to shrinking and cracking of the filter media, resulting in reduced active surface area and gas by-passing. **Humidification** of the gas stream is the preferred method to keep the filter bed moist. Moisture is usually added to the incoming gas stream by either water spray or steam.

It is a great advantage that an organic filter media contains the micro-organisms. **Inorganic material** as e.g. activated carbon also may be used which has a much higher specific surface area but **inoculation** with micro-organism is required.

During the process the **filter material** is decomposed by the micro-organism. It follows that after a certain time depending on the operation **must be renewed**. According to the experience the **life time** of a properly selected and operated filter material can be **a few years**. It is important that during the operation the porosity of the filter bed decreases so the biofilter material should be **loosened** in certain time (e.g. ones half a year) to keep the pressure loss as low as possible to avoid the increase of the operational costs.

The removal efficiency depends on the compounds to be removed and for material easily biodegradable greater than 90 % removal efficiencies can be obtained (water-soluble organics such as alcohols, aldehydes, and amines). Water-soluble inorganics, such as sulphuretted hydrogen (H_2S) and ammonia (NH_3) can also be readily undergo aerobic decomposition.
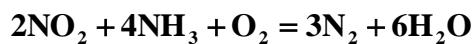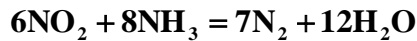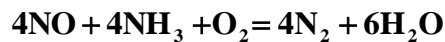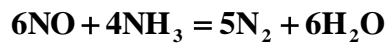
Important to emphasize it again that biofiltration is really an environment-friend process.

Biofilter is used to control the inlet gas emission from composting and rendering plants, from plants of chemical and food industries, etc.

NOx TREATMENT (DECREASING NOx CONCENTRATION)

Nitrogen (N_2) does not burn since it is an incombustible inert gas component but at higher temperatures (above 1000 °C) the nitrogen burns and some nitrogen-oxygen compound will be created, mainly nitrogen-monoxide and nitrogen-dioxide (NO and NO_2 or simply as NO_x). These components are in-direct green house-gases (indirectly cause global warming). NO_x emitted to the atmosphere causes acid rain and Los-Angeles smog (or photo-chemical smog) and destroys ozone-layer (mentioned as ozone-layer depletion).
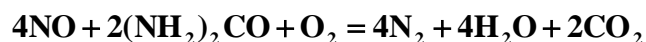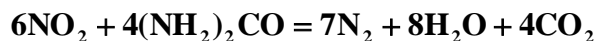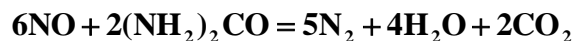
The regulations are strict to lessen their concentrations in the air stream before emitted into the atmosphere. There are more possibilities to fulfil that. It is a possibility **to oxidize** nitrogen-monoxide to nitrogen-dioxide and to produce nitric acid (chemical absorption). **Adsorption** may be used also. Mainly the **reduction** is used by the help of ammonia (NH_3) as reducing agent. The exothermic reactions with or without oxygen:

$$6NO + 4NH_3 = 5N_2 + 6H_2O$$
$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O$$
$$6NO_2 + 8NH_3 = 7N_2 + 12H_2O$$
$$2NO_2 + 4NH_3 + O_2 = 3N_2 + 6H_2O$$
$$NO + NO_2 + 2NH_3 = 2N_2 + 3H_2O$$

The optimum reactions are shown here but other reactions also may take place depending on the circumstances. The products of the reaction are nitrogen and water which may be emitted into the atmosphere as harmless chemical components.

The controlled quantity of ammonia (depending on the NO_x concentration in the waste gas) is injected into the gas stream before it flows through the catalyst layer. The even distribution of the ammonia over the cross section of the equipment is important because of the efficiency of the chemical reactions (the molecules of the components have to meet to take into reaction). Ammonia that has not reacted is called ammonia slip and is undesirable, since the ammonia can react with other combustion species, such as sulphur-trioxide to form ammonium salts. Ammonia slip occurs when ammonia is over-injected into the gas stream, temperature is too low for ammonia to react, or the catalyst has degraded.

Remark: several **reductants** are currently used in SCR applications including anhydrous ammonia, aqueous ammonia or urea (carbamide). Pure anhydrous ammonia is extremely toxic and difficult to safely store, but needs no further conversion to operate within an SCR. Aqueous ammonia must be hydrolyzed in order to be used, but is substantially safer to store and transport than anhydrous ammonia. Urea is the safest to store, but requires conversion to ammonia through thermal decomposition in order to be used as an effective reductant. The overall optimum reactions by urea are as follow:

$$6NO + 2(NH_2)_2CO = 5N_2 + 4H_2O + 2CO_2$$
$$6NO_2 + 4(NH_2)_2CO = 7N_2 + 8H_2O + 4CO_2$$
$$4NO + 2(NH_2)_2CO + O_2 = 4N_2 + 4H_2O + 2CO_2$$
$$2NO_2 + 2(NH_2)_2CO + O_2 = 3N_2 + 4H_2O + 2CO_2$$

Selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) is used to decrease the concentration of the nitrogen oxides and the reactor is called **DeNox reactor**. Without catalyst the **selective non-catalytic reduction** (**SNCR**) requires higher temperature between from 850 to 1200 °C. With catalyst the **selective catalytic reduction** (**SCR**) requires lower temperature between from 300 to 400 °C. The catalyst is vanadium-pentoxide (V_2O_5); the carrier material is titanium-dioxide (TiO_2).

Generally, 10 % of the mass of the catalyst is the active material and 90 % is the mass of the carrier. Other catalysts and carriers also may be used. The DeNox reactor has a **rectangular cross-section** since bricks are formed from the catalyst (brick-shaped catalyst). The gas to be treated flows through the catalytic bed. Generally, two layers are placed in the equipment and free space is left in the equipment for a third layer which is placed when the activity of the first layer is used or starts to decrease significantly. It was found that the economy is better using this practice. The heat content of the effluent gas may be used to preheat the incoming gas or the ammonia. The typical operational lifetime is about 16000-40000 hours in coal-fired plants, depending on the flue gas composition, and is up to 80000 hours in cleaner gas-fired power plants

SCR systems are **sensitive to contamination** and plugging resulting from normal operation or abnormal events. Plugging contaminants are: fine particulate, ammonia-sulphur compounds, ammonium bisulphate and silicon compounds. Many of these contaminants can be removed while the unit is on line, for example by soot blowers. There are more concern to the SCR poisons, which will destroy the chemistry of the catalyst and cause the ineffective reduction of NO_x and unwanted oxidation of ammonia (forming more NO_x).

Both reduction processes can achieve the same **removal efficiency** of **about 90 %**, but practical constraints of temperature, time, and mixing often lead to worse results in practice. However, SNCR has an economic advantage over SCR, because of the cost of the catalyst.

Remark: **Diesel engines** can be operated with a lean burn air-to-fuel ratio (over the stoichiometric ratio), to ensure the full combustion of soot and to prevent the exhaust of unburnt fuel. The excess of oxygen necessarily leads to generation of nitrogen oxides (NO_x). Selective catalytic reduction is used to reduce the concentration of NO_x released into the atmosphere. **Diesel exhaust fluid** is injected into the exhaust pipeline the aqueous urea vaporizes and decomposes giving ammonia and carbon dioxide. Within the SCR catalyst, the NO_x are catalytically reduced by the ammonia into water and nitrogen and these are then released through the exhaust. Diesel exhaust fluid (**DEF**), commonly referred to as **AdBlue**, is an aqueous urea solution made with 32.5% high-purity urea and 67.5% deionized water. DEF is used in selective catalytic reduction (SCR) in order to lower NO_x concentration in the diesel exhaust emissions from diesel engines. When the urea solution is injected into the hot exhaust gas stream the water evaporates and the urea thermally decomposes giving ammonia. The urea solution is clear, non-toxic and safe to handle. However, it can corrode some metals and so must be stored and transported carefully. DEF is stored in a tank on board the vehicle, and injected into the exhaust stream by a metering system. The injection rate depends on the specific after-treatment system, but is typically 2-6% of diesel consumption volume. This low dosing rate ensures long fluid refill intervals and minimises the tank's size.

Economic standpoints

How can a separation process be selected to solve a given problem? A few factors influence the choice of the separation process and specific criteria often has to be met but are not generally applicable. However, two general criteria apply to all separation processes:
- the separation must be feasible technically and
- the separation must be feasible economically.

The first criterion is not surprising since the separation process must be able to put into practice the desired separation and achieve a quality product. Sometimes a combination of two or more separation processes is necessary to attain the requirements which are valid for solving air-pollution problems.

To solve an air-pollution problem, the problem must be characterized in detail. A number of factors must be considered prior to select a particular type of equipment. In general, these factors can be grouped into three categories as environmental, engineering and economic. The environmental factors include the equipment location, the available space, ambient conditions, availability of utilities (i.e. power, water, etc.) and ancillary system facilities (i.e. waste

treatment and disposal, etc.), aesthetic considerations (i.e. visible steam or water-vapour plume, etc.) and contribution of the air-pollution control equipment to wastewater, land pollution and plant noise levels.

On the other side of the page you can see information on the economic application ranges of the technical methods discussed for VOC using logarithmic scales on both axes. It is clear from the figure that the economy depends on the volumetric flow rate (m^3/hr) of the gas stream and the inlet concentration of the pollutant (g/m^3). We emphasize that the graph provides a schematic overview and for a specific application studying the literature is suggested. In the case of adsorption techniques, it should be remarked that the adsorbed VOCs have to be recovered and further treated (e.g. oxidized) or reused (e.g. after condensation). Important to say that other parameters have to be considered in the selection of the most appropriate technique, e.g. safety or flammability aspect, volatility and variability of the VOCs, presence of humidity and dust in the gas stream, costs (operating and installation), etc. In any industrial application it is suggested to ask for advice from an experienced specialist.