

SOLVENT RECYCLING, REMOVAL, AND DEGRADATION

22.1 ABSORPTIVE SOLVENT RECOVERY

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22.1.1 INTRODUCTION

A variety of waste gas cleaning processes¹⁻⁴ are commercially available. They are used to remove organic vapors (solvents) from air emissions from various industries and product lines. The main applications of solvents in various industries are given in Table 22.1.1.

Table 22.1.1. Application of organic solvents. [After references 2-4]

Application	Solvents
Coating plants: Adhesive tapes, Magnetic tapes, Adhesive films, Photographic papers, Adhesive labels	Naphtha, toluene, alcohols, esters, ketones (cyclohexanone, methyl ethyl ketone), dimethylformamide, tetrahydrofuran, chlorinated hydrocarbons, xylene, dioxane
Chemical, pharmaceutical, food industries	Alcohols, aliphatic, aromatic and halogenated hydrocarbons, esters, ketones, ethers, glycol ether, dichloromethane
Fibre production Acetate fibers Viscose fibers Polyacrylonitrile	Acetone, ethanol, esters carbon disulfide dimethylformamide
Synthetic leather production	Acetone, alcohols, ethyl ether
Film manufacture	Alcohols, acetone, ether, dichloromethane
Painting shops: Cellophane, Plastic films, Metal foils, Vehicles, Hard papers, Cardboard, Pencils	Amyl acetate, ethyl acetate, butyl acetate, dichloromethane, ketones (acetone, methyl ethyl ketone), butanol, ethanol, tetrahydrofuran, toluene, benzene, methyl acetate
Cosmetics industry	Alcohols, esters
Rotogravure printing shops	Toluene, xylene, heptane, hexane
Textile printing	Hydrocarbons
Drycleaning shops	Hydrocarbons, tetrachloroethane

Application	Solvents
Sealing board manufacture	Hydrocarbons, toluene, trichloroethane
Powder and explosives production	Ether, alcohol, benzene
Degreasing and scouring applications Metal components Leather Wool	Hydrocarbons, trichloroethylene, tetrachloroethylene, dichloromethane Tetrachloroethylene Tetrachloroethane
Loading and reloading facilities (tank venting gases)	Gasoline, benzene, toluene, xylene

The basic principles of some generally accepted gas cleaning processes for solvent removal are given in Table 22.1.2. For more than 70 years adsorption processes using activated carbon, in addition to absorption and condensation processes, have been used in adsorptive removal and recovery of solvents. The first solvent recovery plant for acetone was commissioned for economic reason in 1917 by Bayer. In the decades that followed solvent recovery plants were built and operated only if the value of the recovered solvents exceeded the operation costs and depreciation of the plant. Today such plants are used for adsorptive purification of exhaust air streams, even if the return is insufficient, to meet environmental and legal requirements.

Table 22.1.2. Cleaning processes for the removal and recovering of solvents

Process	Basic principle	Remarks
Incineration	The solvents are completely destroyed by: thermal oxidation ($>10 \text{ g/m}^3$), catalytic oxidation ($3\text{-}10 \text{ g/m}^3$)	Only waste heat recovery possible
Condensation	High concentration of solvents ($>50 \text{ g/m}^3$) are lowered by direct or indirect condensation with refrigerated condensers	- Effective in reducing heavy emissions, - good quality of the recovered solvents, - difficult to achieve low discharge levels
Absorption	Scrubbers using non-volatile organics as scrubbing medium for the solvent removal. Desorption of the spent scrubbing fluid	Advantageous if: - scrubbing fluid can be reused directly without desorption of the absorbed solvent - scrubbing with the subcooled solvent itself possible
Membrane permeation	Membrane permeation processes are principle suited for small volumes with high concentrations e.g. to reduce hydrocarbon concentration from several hundred g/m^3 down to $5\text{-}10 \text{ g/m}^3$	To meet the environmental protection requirements a combination with other cleaning processes (e.g. activated carbon adsorber) is necessary
Biological treatment	Biological decomposition by means of bacteria and using of bio-scrubber or bio-filter	Sensitive against temperature and solvent concentration
Adsorption	Adsorption of the solvents by passing the waste air through an adsorber filled with activated carbon. Solvent recovery by steam or hot gas desorption	By steam desorption the resulting desorbate has to be separated in a water and an organic phase using a gravity separator (or a rectification step)

This contribution deals with adsorptive solvent removal^{2,12,13} and recovery and some other hybrid processes using activated carbon in combination with other purification steps.

Due to more stringent environmental protection requirements, further increases in the number of adsorption plants for exhaust air purification may be expected.

22.1.2 BASIC PRINCIPLES

22.1.2.1 Fundamentals of adsorption

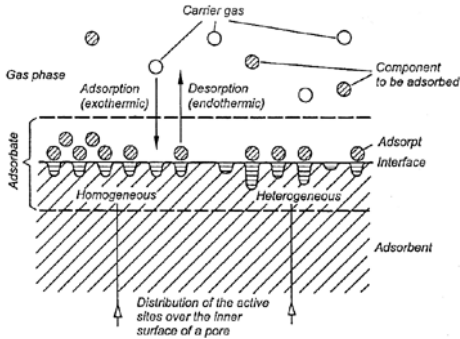


Figure 22.1.1. Adsorption terms (after reference 2).

To understand the adsorptive solvent recovery we have to consider some of the fundamentals of adsorption and desorption¹⁻⁹ (Figure 22.1.1). Adsorption is the term for the enrichment of gaseous or dissolved substances on the boundary surface of a solid (the adsorbent). The surfaces of adsorbents have what we call active sites where the binding forces between the individual atoms of the solid structure are not completely saturated by neighboring atoms. These active sites can bind foreign molecules which, when bound, are referred to as adsorpt. The overall interphase boundary is referred to as

adsorbate. The term, desorption, designates the liberation of the adsorbed molecules, which is a reversal of the adsorption process. The desorption process generates desorbate which consists of the desorpt and the desorption medium.²

A distinction is made between two types of adsorption mechanisms: chemisorption and physisorption. One, physisorption, is reversible and involves exclusively physical interaction forces (van der Waals forces) between the component to be adsorbed and the adsorbent. The other, chemisorption, is characterized by greater interaction energies which result in a chemical modification of the component adsorbed along with its reversible or irreversible adsorption.²

Apart from diffusion through the gas-side boundary film, adsorption kinetics are predominantly determined by the diffusion rate through the pore structure. The diffusion coefficient is governed by both the ratio of pore diameter to the radius of the molecule being adsorbed and other characteristics of the component being adsorbed. The rate of adsorption is governed primarily by diffusional resistance. Pollutants must first diffuse from the bulk gas stream across the gas film to the exterior surface of the adsorbent (gas film resistance).

Due to the highly porous nature of the adsorbent, its interior contains by far the majority of the free surface area. For this reason, the molecule to be adsorbed must diffuse into the pore (pore diffusion). After their diffusion into the pores, the molecules must then physically adhere to the surface, thus losing the bulk of their kinetic energy.

Adsorption is an exothermic process. The adsorption enthalpy, decreases as the load of adsorbed molecules increases. In activated carbon adsorption systems for solvent recovery, the liberated adsorption enthalpy normally amounts to 1.5 times the evaporation enthalpy at the standard working capacities which can result in a 20 K or more temperature increase. In the process, exothermic adsorption mechanisms may coincide with endothermic desorption mechanisms.²

22.1.2.2 Adsorption capacity

The adsorption capacity (adsorptive power, loading) of an adsorbent resulting from the size and the structure of its inner surface area for a defined component is normally represented as a function of the component concentration c in the carrier gas for the equilibrium conditions at constant temperature. This is known as the adsorption isotherm $x = f(c)_T$. There are variety of approaches proceeding from different model assumptions for the quantitative description of adsorption isotherms (Table 22.1.3) which are discussed in detail in the literature.^{2,9,11}

Table 22.1.3. Overview of major isotherm equations (After reference 2)

Adsorption isotherm by	Isotherm equation	Notes
Freundlich	$x = K \times p_i^n$	low partial pressures of the component to be adsorbed
Langmuir	$x = \frac{x_{\max} b p_i}{1 + b p_i}$	homogeneous adsorbent surface, monolayer adsorption
Brunauer, Emmet, Teller (BET)	$\frac{p_i}{V(p_s - p_i)} = \frac{1}{V_{MB}C} + \frac{C - 1}{V_{MB}C} \frac{p_i}{p_s}$	homogeneous surface, multilayer adsorption, capillary condensation
Dubinin, Raduskevich	$\log V = \log V_s - 2.3 \left(\frac{RT}{\epsilon_s \beta} \right) \left(\log \frac{p_s}{p_i} \right)^n$	potential theory; $n = 1, 2, 3$; e.g., $n = 2$ for the adsorption of organic solvent vapors on micro-porous activated carbon grades

where: K , n - specific constant of the component to be adsorbed; x - adsorbed mass, g/100 g; x_{\max} - saturation value of the isotherm with monomolecular coverage, g/100 g; b - coefficient for component to be adsorbed, Pa; C - constant; T - temperature, K; p_i - partial pressure of component to be adsorbed, Pa; p_s - saturation vapor pressure of component to be adsorbed, Pa; V - adsorpt volume, ml; V_{MB} - adsorpt volume with monomolecular coverage, ml; V_s - adsorpt volume on saturation, ml; V_M - molar volume of component to be adsorbed, l/mol; R - gas constant, J/(kg K); ϵ_s - characteristic adsorption energy, J/kg; β - affinity coefficient

The isotherm equation developed by Freundlich on the basis of empirical data can often be helpful. According to the Freundlich isotherm, the logarithm of the adsorbent loading increases linearly with the concentration of the component to be adsorbed in the carrier gas. This is also the result of the Langmuir isotherm which assumes that the bonding energy rises exponentially as loading decreases.

However, commercial adsorbents do not have a smooth surface but rather are highly porous solids with a very irregular and rugged inner surface. This fact is taken into account by the potential theory which forms the basis of the isotherm equation introduced by Dubinin.

At adsorption temperatures below the critical temperature of the component to be adsorbed, the adsorbent pores may fill up with liquid adsorpt. This phenomenon is known as capillary condensation and enhances the adsorption capacity of the adsorbent. Assuming cylindrical pores, capillary condensation can be quantitatively described with the aid of the Kelvin equation, the degree of pore filling being inversely proportional to the pore radius.

If several compounds are contained in a gas stream the substances compete for the adsorption area available. In that case compounds with large interacting forces may displace less readily adsorbed compounds from the internal surface of the activated carbon.

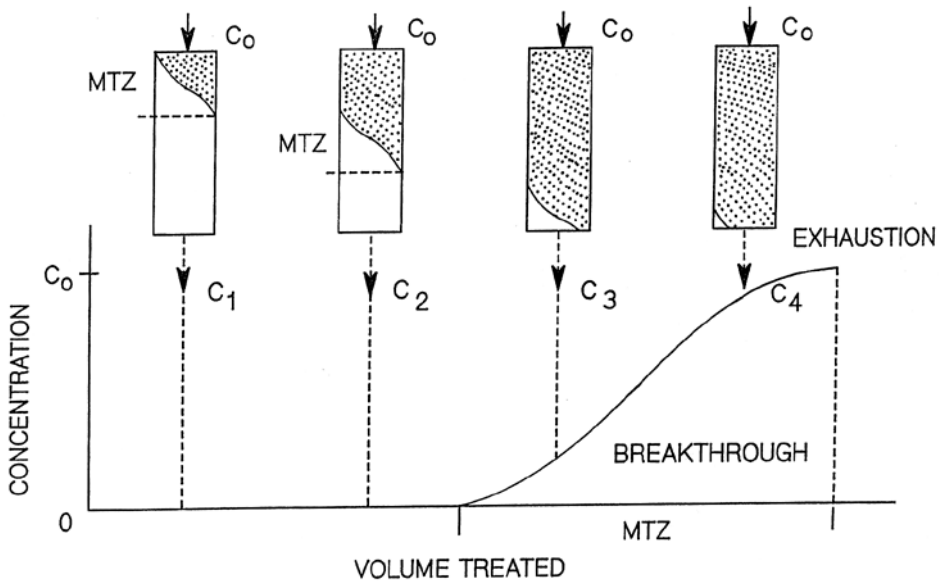


Figure 22.1.2. Idealized breakthrough curve of a fixed bed adsorber.

As previously stated, the theories of adsorption are complex, with many empirically determined constants. For this reason, pilot data should always be obtained on the specific pollutant adsorbent combination prior to full-scale engineering design.

22.1.2.3 Dynamic adsorption in adsorber beds

For commercial adsorption processes such as solvent recovery not only the equilibrium load, but also the rate at which it is achieved (adsorption kinetics) is of decisive importance.⁹⁻¹⁵ The adsorption kinetics is determined by the rates of the following series of individual steps:

- transfer of molecules to the external surface of the adsorbent (border layer film diffusion)
- diffusion into the particle
- adsorption

The adsorbent is generally in a fixed adsorber bed and the contaminated air is passed through the adsorber bed (Figure 22.1.2). When the contaminated air first enters through the adsorber bed most of the adsorbate is initially adsorbed at the inlet of the bed and the air passes on with little further adsorption taking place. Later, when the inlet of the adsorber becomes saturated, adsorption takes place deeper in the bed. After a short working time the activated carbon bed becomes divided into three zones:

- the inlet zone where the equilibrium load corresponds to the inlet concentration, c_0
- the adsorption or mass transfer zone, MTZ, where the adsorbate concentration in the air stream is reduced
- the outlet zone where the adsorbent remains incompletely loaded

In time the adsorption zone moves through the activated carbon bed.¹⁸⁻²¹ When the MTZ reaches the adsorber outlet zone, breakthrough occurs. The adsorption process must be stopped if a pre-determined solvent concentration in the exhaust gas is exceeded. At this

point the activated carbon bed has to be regenerated. If, instead the flow of contaminated air is continued on, the exit concentration continues to rise until it becomes the same as the inlet concentration. It is extremely important that the adsorber bed should be at least as long as the mass transfer zone of the component to be adsorbed. The following are key factors in dynamic adsorption and help determine the length and shape of the MTZ:

- the type of adsorbent
- the particle size of the adsorbent (may depend on maximum allowable pressure drop)
- the depth of the adsorbent bed
- the gas velocity
- the temperature of the gas stream and the adsorbent
- the concentration of the contaminants to be removed
- the concentration of the contaminants not to be removed, including moisture
- the pressure of the system
- the removal efficiency required
- possible decomposition or polymerization of contaminants on the adsorbent

22.1.2.4 Regeneration of the loaded adsorbents

In the great majority of adsorptive waste gas cleaning processes, the adsorpt is desorbed after the breakthrough loading has been attained and the adsorbent reused for pollutant removal. Several aspects must be considered when establishing the conditions of regeneration for an adsorber system.^{2-4,6,13-16} Very often, the main factor is an economic one, to establish that an in-place regeneration is or is not preferred to the replacement of the entire adsorbent charge. Aside from this factor, it is important to determine if the recovery of the contaminant is worthwhile, or if only regeneration of the adsorbent is required. The process steps required for this purpose normally dictate the overall concept of the adsorption unit.

Regeneration, or desorption, is usually achieved by changing the conditions in the adsorber to bring about a lower equilibrium-loading capacity. This is done by either increasing the temperature or decreasing the partial pressure. For regeneration of spent activated carbon from waste air cleaning processes the following regeneration methods are available (Table 22.1.4).

Table 22.1.4. Activated carbon regeneration processes (After references 2,16)

Regeneration method	Principle	Application examples	Special features
Pressure-swing process	Alternating between elevated pressure during adsorption and pressure reduction during desorption	Gas separation, e.g., N ₂ from air, CH ₄ from biogas, CH ₄ from hydrogen	Raw gas compression; lean gas stream in addition to the product gas stream
Temperature-swing process: Desorption	Steam desorption or inert gas desorption at temperatures of < 500°C	Solvent recovery, process waste gas cleanup	Reprocessing of desorbate
Reactivation	Partial gasification at 800 to 900°C with steam or other suitable oxidants	All organic compounds adsorbed in gas cleaning applications	Post-combustion, if required scrubbing of flue gas generated

Regeneration method	Principle	Application examples	Special features
Extraction with: Organic solvents	Extraction with carbon disulfide or other solvents	Sulphur extraction Sulfosorbon process	Desorbate treatment by distillation, steam desorption of solvent
Caustic soda solution	Percolation with caustic soda	Phenol-loads activated carbon	Phenol separation with subsequent purging
Supercritical gases	e.g. extraction with supercritical CO ₂	Organic compounds	Separation of CO ₂ /organic compounds

- Pressure-swing process
- Temperature-swing process
- Extraction process

In solvent recovery plants, temperature-swing processes are most frequently used. The loaded adsorbent is direct heated by steam or hot inert gas, which at the same time serves as a transport medium to discharge the desorbed vapor and reduce the partial pressure of the gas-phase desorpt. As complete desorption of the adsorpt cannot be accomplished in a reasonable time in commercial-scale systems, there is always heel remaining which reduces the adsorbent working capacity.

Oxidic adsorbents offer the advantage that their adsorptive power can be restored by controlled oxidation with air or oxygen at high temperatures.

22.1.3 COMMERCIALY AVAILABLE ADSORBENTS

Adsorbents used for air pollution control and solvent recovery predominantly employ activated carbon. Molecular sieve zeolites are also used. Polymeric adsorbents can be used but are seldom seen.

22.1.3.1 Activated carbon

Activated carbon¹⁻⁸ is the trade name for a carbonaceous adsorbent which is defined as follows: Activated carbons⁵ are non-hazardous, processed, carbonaceous products, having a porous structure and a large internal surface area. These materials can adsorb a wide variety of substances, i.e., they are able to attract molecules to their internal surface, and are therefore called adsorbents. The volume of pores of the activated carbons is generally greater than 0.2 mlg⁻¹. The internal surface area is generally greater than 400 m²g⁻¹. The width of the pores ranges from 0.3 to several thousand nm.

All activated carbons are characterized by their ramified pore system within which various mesopores ($r = 1-25$ nm), micropores ($r = 0.4-1.0$ nm) and submicropores ($r < 0.4$ nm) each of which branch off from macropores ($r > 25$ nm).

Figure 22.1.3. shows schematically the pore system important for adsorption and desorption.¹⁷ The large specific surfaces are created predominantly by the micropores. Activated carbon is commercially available in shaped (cylindrical pellets), granular, or powdered form.

Due to its predominantly hydrophobic surface properties, activated carbon preferentially adsorbs organic substances and other non-polar compounds from gas and liquid phases. Activated alumina, silica gel and molecular sieves will adsorb water preferentially from a gas-phase mixture of water vapor and an organic contaminant. In Europe cylindrically-shaped activated carbon pellets with a diameter of 3 or 4 mm are used for solvent recovery, because they assure a low pressure drop across the adsorber system. Physical and

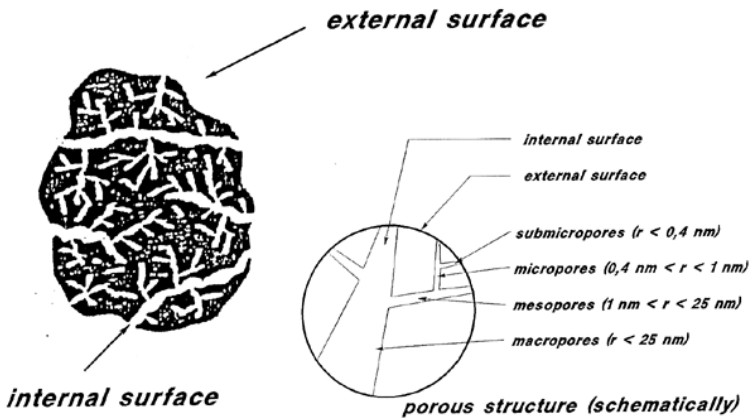


Figure 22.1.3. Schematic activated carbon model (After reference 17).

chemical properties of three typical activated carbon types used for solvent recovery are given in Table 22.1.5.

Table 22.1.5 Activated carbon types for waste air cleaning (After reference 2)

Adsorbent	Applications (typical examples)	Compacted density, kg/m ³	Pore volume for pore size d < 20 nm, ml/g	Pore volume for pore size d > 20 nm, ml/g	Specific surface area, m ² /g	Specific heat capacity, J/kgK
Activated carbon, fine-pore	Intake air and exhaust air cleanup, odor control, Adsorption of low-boiling hydrocarbons	400 - 500	0.5 - 0.7	0.3 - 0.5	1000-1200	850
Activated carbon, medium-pore	Solvent recovery, Adsorption of medium-high boiling hydrocarbons	350 - 450	0.4 - 0.6	0.5 - 0.7	1200-1400	850
Activated carbon, wide-pore	Adsorption and recovery of high-boiling hydrocarbons	300 - 400	0.3 - 0.5	0.5 - 1.1	1000-1500	850

22.1.3.2 Molecular sieve zeolites

Molecular sieve zeolites^{2,10,11} are hydrated, crystalline aluminosilicates which give off their crystal water without changing their crystal structure so that the original water sites are free for the adsorption of other compounds. Activation of zeolites is a dehydration process accomplished by the application of heat in a high vacuum. Some zeolite crystals show behavior opposite to that of activated carbon in that they selectively adsorb water in the presence of nonpolar solvents. Zeolites can be made to have specific pore sizes that impose limits on the size and orientation of molecules that can be adsorbed. Molecules above a specific size cannot enter the pores and therefore cannot be adsorbed (steric separation effect).

Substitution of the greater part of the Al_2O_3 by SiO_2 yields zeolites suitable for the selective adsorption of organic compounds from high-moisture waste gases.

22.1.3.3 Polymeric adsorbents

The spectrum of commercial adsorbents² for use in air pollution control also includes beaded, hydrophobic adsorber resins consisting of nonpolar, macroporous polymers produced for the specific application by polymerizing styrene in the presence of a crosslinking agent. Crosslinked styrene divinylbenzene resins are available on the market under different trade names. Their structure-inherent fast kinetics offers the advantage of relatively low desorption temperatures. They are insoluble in water, acids, lye and a large number of organic solvents.

22.1.4 ADSORPTIVE SOLVENT RECOVERY SYSTEMS

Stricter regulations regarding air pollution control, water pollution control and waste management have forced companies to remove volatile organics from atmospheric emissions and workplace environments. But apart from compliance with these requirements, economic factors are decisive in solvent recovery. Reuse of solvent in production not only reduces operating cost drastically but may even allow profitable operation of a recovery system.

22.1.4.1 Basic arrangement of adsorptive solvent recovery with steam desorption

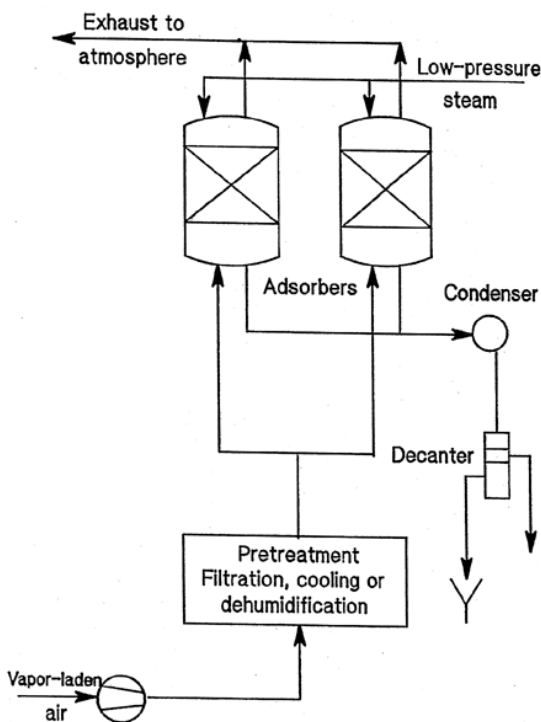


Figure 22.1.4. Flow sheet of a solvent recovery system with steam desorption.

Adsorptive solvent recovery units have at least two, but usually three or four parallel-connected fix-bed adsorbers which pass successively through the four stages of the operation cycle.^{1-4,18-23}

- Adsorption
- Desorption
- Drying
- Cooling

Whilst adsorption takes place in one or more of them, desorption, drying and cooling takes place in the others. The most common adsorbent is activated carbon in the shape of 3 or 4 mm pellets or as granular type with a particle size of 2 to 5 mm (4 x 10 mesh). A schematic flow sheet of a two adsorber system for the removal of water-insoluble solvents is shown in Fig 22.1.4.

The adsorber feed is pre-treated if necessary to remove solids (dust), liquids (droplets or

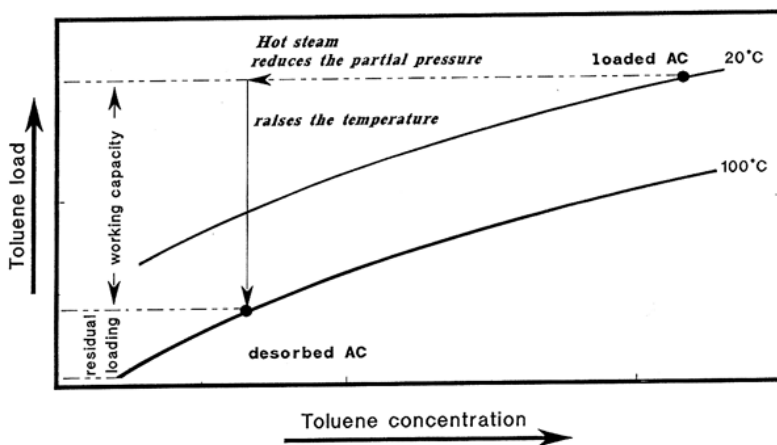


Figure 22.1.5. Principle of steam desorption.

aerosols) or high-boiling components as these can hamper performance. Frequently, the exhaust air requires cooling.

To prevent an excessive temperature increase across the bed due to the heat of adsorption, inlet solvent concentrations are usually limited to about 50 g/m^3 . In most systems the solvent-laden air stream is directed upwards through a fixed carbon bed. As soon as the maximum permissible breakthrough concentration is attained in the discharge clean air stream, the loaded adsorber is switched to regeneration. To reverse the adsorption of the solvent, the equilibrium must be reversed by increasing the temperature and decreasing the solvent concentration by purging.

For solvent desorption direct steaming of the activated carbon bed is the most widely used regeneration technique because it is cheap and simple. Steam ($110\text{--}130^\circ\text{C}$) is very effective in raising the bed temperature quickly and is easily condensed to recover the solvent as a liquid. A certain flow is also required to reduce the partial pressure of the adsorbate and carry the solvent out of the activated carbon bed. A flow diagram for steam desorption for toluene recovery is given in Figure 22.1.5.

First, the temperature of the activated carbon is increased to approx. 100°C . This temperature increase reduces the equilibrium load of the activated carbon. Further reduction of the residual load is obtained by the flushing effect of the steam and the declining toluene partial pressure. The load difference between spent and regenerated activated carbon - the "working capacity" - is then available for the next adsorption cycle.

The counter-current pattern of adsorption and desorption favors high removal efficiencies. Desorption of the adsorbed solvents starts after the delay required to heat the activated carbon bed. The specific steam consumption increases as the residual load of the activated carbon decreases (Figure 22.1.6). For cost reasons, desorption is not run to completion. The desorption time is optimized to obtain the acceptable residual load with a minimum specific steam consumption. The amount of steam required depends on the interaction forces between the solvent and the activated carbon. The mixture of steam and solvent vapor from the adsorber is condensed in a condenser. If the solvent is immiscible with water the condensate is led to a gravity separator (making use of the density differential) where it is separated into a aqueous and solvent fraction.

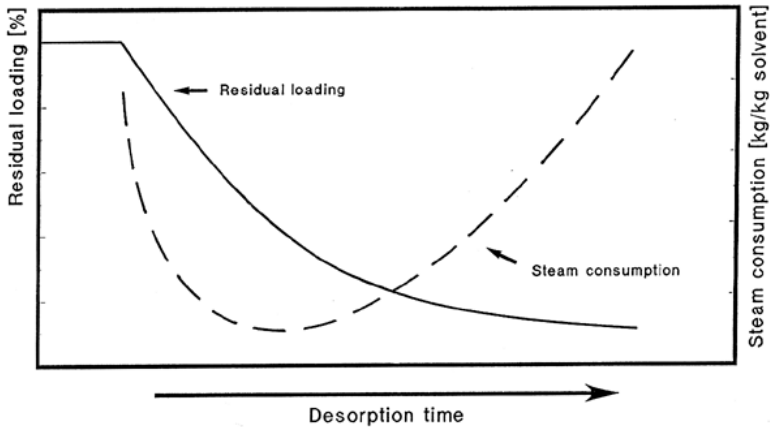


Figure 22.1.6. Desorption efficiency and steam consumption.

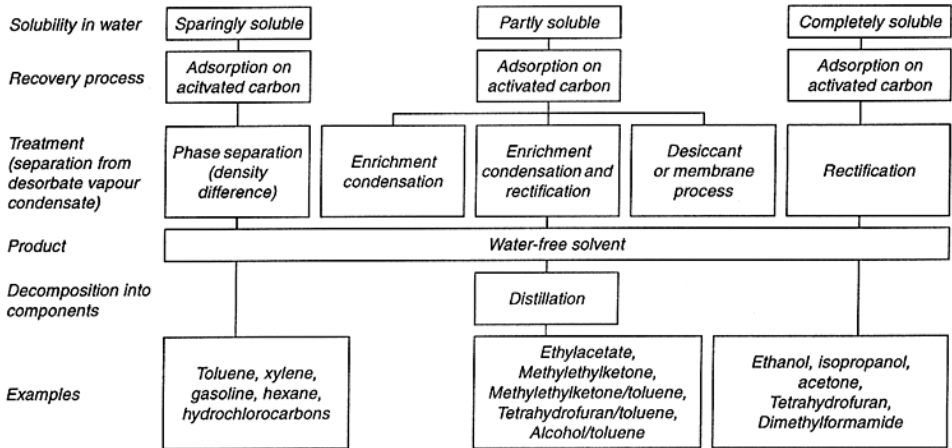


Figure 22.1.7. Options for solvent recovery by steam desorption (After references 2, 3,12).

If the solvents are partly or completely miscible with water, additional special processes are necessary for solvent separation and treatment (Figure 22.1.7). For partly miscible solvents the desorpt steam/solvent mixture is separated by enrichment condensation, rectification or by a membrane processes. The separation of completely water-soluble solvents requires a rectification column.²

After steam regeneration, the hot and wet carbon bed will not remove organics from air effectively, because high temperature and humidity do not favor complete adsorption. The activated carbon is therefore dried by a hot air stream. Before starting the next adsorption cycle the activated carbon bed is cooled to ambient temperature with air. Typical operating data for solvent recovery plants and design ranges are given in Table 22.1.6.

Table 22.1.6. Typical operating data for solvent recovery plants

Operating data		Range of design	
Air velocity (m/s):	0.2-0.4	Solvent concentration (g/m ³):	1-20
Air temperature (°C):	20-40	Solvent adsorbed by activated carbon per cycle (% weight):	10-20
Bed height (m):	0.8-2	Steam/solvent ratio:	2-5:1
Steam velocity (m/s):	0.1-0.2	Energy (kWh/t solvent):	50-600
Time cycle for each adsorber		Cooling water (m ³ /t solvent):	30-100
Adsorption (h):	2-6	Activated carbon (kg/t solvent):	0.5-1
Steaming (h):	0.5-1		
Drying (hot air, h):	0.2-0.5		
Cooling (cold air, h):	0.2-0.5		

22.1.4.2 Designing solvent recovery systems

22.1.4.2.1 Design basis^{1-3,18-23}

Designing an activated carbon system should be based on pilot data for the particular system and information obtained from the activated carbon producer. The basic engineering and the erection of the system should be done by an experienced engineering company. Solvent recovery systems would also necessitate the specification of condenser duties, distillation tower sizes, holding tanks and piping and valves. Designing of a solvent recovery system requires the following information (Table 22.1.7).

Table 22.1.7. Design basis for adsorption systems by the example of solvent recovery (After references 1-3)

Site-specific conditions	Emission sources: Production process(es), continuous/shift operation		
	Suction system: Fully enclosed system, negative pressure control		
	Available drawings: Building plan, machine arrangement, available space, neighborhood		
	Operating permit as per BimSchG (German Federal Immission Control Act)		
Exhaust air data (max., min., normal)	- Volumetric flow rate (m ³ /h)	- Temperature (°C)	
	- Relative humidity (%)	- Pressure (mbar)	
	- Solvent concentration by components (g/m ³)		
	- Concentration of other pollutants and condition (fibers, dust)		
Characterization of solvents	- Molecular weight, density	- Boiling point, boiling range	
	- Critical temperature	- Explosion limits	
	- Water solubility	- Corrosiveness	
	- Stability (chemical, thermal)	- Maximum exposure limits (MEL)	
	- Safety instructions as per German Hazardous Substances Regulations (description of hazards, safety instructions, safety data sheets)		
	- Physiological effects: irritating, allergenic, toxic, cancerogenic		
Utilities (type and availability)	- Electric power	- Steam	- Cooling water
	- Cooling brine	- Compressed air, instrument air	- Inert gas
Waste streams (avoidance, recycling, disposal)	- Solvent	- Steam condensate	- Adsorbent
			- Filter dust

Guaranteed performance data at rated load	- Emission levels: pollutants, sound pressure level (dB(A)) - Utility consumption, materials- Availability
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After this information has been obtained, the cycle time of the system must be determined. The overall size of the unit is determined primarily by economic considerations, balancing low operating costs against the capital costs (smaller system → shorter cycle time; bigger adsorber → long cycle time). The limiting factor for the adsorber diameter is normally the maximum allowable flow velocity under continuous operating conditions. The latter is related to the free vessel cross-section and, taking into account fluctuations in the gas throughput, selected such (0.1 to 0.5 m/s) that it is sufficiently below the disengagement point, i.e., the point at which the adsorbent particles in the upper bed area are set into motion. Once the adsorber diameter has been selected, the adsorber height can be determined from the required adsorbent volume plus the support tray and the free flow cross-sections to be provided above and below the adsorbent bed. The required adsorbent volume is dictated by the pollutant concentration to be removed per hour and the achievable adsorbent working capacity.

From the view point of adsorption theory, it is important that the bed be deeper than the length of the transfer zone which is unsaturated. Any multiplication of the minimum bed depth gives more than proportional increase in capacity. In general, it is advantageous to size the adsorbent bed to the maximum length allowed by pressure drop considerations. Usually fixed-bed adsorber has a bed thickness of 0.8 - 2 m.

22.1.4.2.2 Adsorber types

Adsorbers for solvent recovery¹⁻³ units (Figure 22.1.8) are build in several configurations:

- vertical cylindrical fixed-bed adsorber
- horizontal cylindrical fixed-bed adsorber
- vertical annular bed adsorber
- moving-bed adsorber
- rotor adsorber (axial or radial)

For the cleanup of high volume waste gas streams, multi adsorber systems are preferred. Vertical adsorbers are most common. Horizontal adsorbers, which require less overhead space, are used mainly for large units. The activated carbon is supported on a cast-iron grid which is sometimes covered by a mesh. Beneath the bed, a 100 mm layer of 5 - 50 mm size gravel (or Al₂O₃ pellets) is placed which acts as a heat accumulator and its store part of the desorption energy input for the subsequent drying step. The depth of the carbon bed, chosen in accordance with the process conditions, is from 0.8 to 2 m. Adsorbers with an annular bed of activated carbon are less common. The carbon in the adsorber is contained between vertical, cylindrical screens. The solvent laden air passes from the outer annulus through the outer screen, the carbon bed and the inner screen, then exhausts to atmosphere through the inner annulus. The steam for regeneration of the carbon flows in the opposite direction to the airstream. Figure 22.1.8 illustrates the operating principle of a counter-current flow vertical moving bed adsorber. The waste gas is routed in counter-current to the moving adsorbent and such adsorption systems have a large number of single moving beds. The discharge system ensures an uniform discharge (mass flow) of the loaded adsorbent. In this moving bed system adsorption and desorption are performed in a separate column or column sections. The process relies on an abrasion resistant adsorbent with good flow proper-

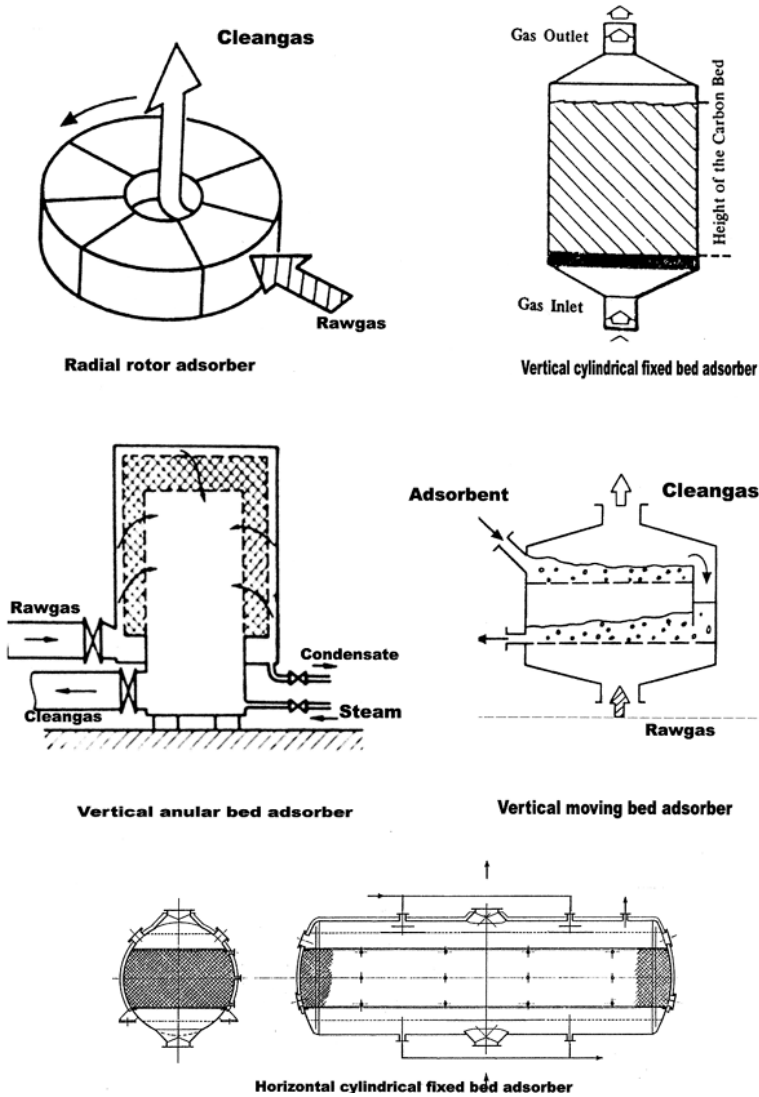


Figure 22.1.8. Adsorber construction forms.

ties (beaded carbon or adsorber resins). After the adsorption stage of a multi-stage fluidized-bed system, the loaded adsorbent is regenerated by means of steam or hot inert gas in a moving-bed regenerator and pneumatically conveyed back to the adsorption section.² When using polymeric adsorbents in a comparable system, desorption can be carried out with heated air because the structure-inherent faster kinetics of these adsorbents require desorption temperatures of only 80 to 100°C.

Rotor adsorbers allow simultaneous adsorption and desorption in different zones of the same vessel without the need for adsorbent transport and the associated mechanical stresses. Rotor adsorbers can be arranged vertically or horizontally and can be designed for

axial or radial gas flow, so that they offer great flexibility in the design of the adsorption system.

The choice of the rotor design^{2,27,33} depends on the type of adsorbent employed. Rotor adsorbers accommodating pellets or granular carbon beds come as wheel type baskets divided into segments to separate the adsorption zone from the regeneration zone. Alternatively, they may be equipped with a structured carrier (e.g., ceramics, cellulose) coated with or incorporating different adsorbents such as

- activated carbon fibers
- beaded activated carbon
- activated carbon particles
- particles of hydrophobic zeolite

The faster changeover from adsorption to desorption compared with fixed-bed adsorbers normally translates into a smaller bed volume and hence, in a reduced pressure loss. Hot air desorption is also the preferred method for rotor adsorbers. Hot air rates are about one tenth of the exhaust air rate. The desorbed solvents can either be condensed by chilling or disposed of by high-temperature or catalytic combustion.

In some cases, removal of the concentrated solvents from the desorption air in a conventional adsorption system and subsequent recovery for reuse may be a viable option. The structural design of the adsorber is normally governed by the operating conditions during the desorption cycle when elevated temperatures may cause pressure loads on the materials. Some solvents when adsorbed on activated carbon, or in the presence of steam, oxidize or hydrolyze to a small extent and produce small amounts of corrosive materials. As a general rule, hydrocarbons and alcohols are unaffected and carbon steel can be used. In the case of ketones and esters, stainless steel or other corrosion resistant materials are required for the solvent-wetted parts of the adsorbers, pipework and condensers, etc. For carbon tetrachloride and 1,1,1-trichloroethane and other chlorinated solvents, titanium has a high degree of resistance to the traces of acidity formed during recovery.

22.1.4.2.3 Regeneration

The key to the effectiveness of solvent recovery is the residual adsorption capacity (working capacity) after in-place regeneration. The basic principles of regeneration are given in Sections 22.1.2.4 and 22.1.4.1. After the adsorption step has concentrated the solvent, the design of the regeneration system^{1-3,13-16} depends on the application and the downstream use of the desorbed solvents whether it be collection and reuse or destruction. Table 22.1.8 may give some indications for choosing a suitable regeneration step.

Table 22.1.8 Basic principle of regeneration

Regeneration step	Basic principle	Typical application
Off-site reactivation	Transportation of the spent carbon to a reactivation plant. Partial gasification at 800-900°C with steam in a reactivation reactor. Reuse of the regenerated activated carbon	<ul style="list-style-type: none"> - low inlet concentration - odor control application - solvents with boiling points above 200 °C - polymerization of solvents

Regeneration step	Basic principle	Typical application
Steam desorption	Increasing the bed temperature by direct steaming and desorption of solvent. The steam is condensed and solvent recovered.	Most widely used regeneration technique for solvent recovery plants. Concentration range from 1-50 g/m ³
Hot air desorption	Rotor adsorber are often desorbed by hot air	Concentration by adsorption and incineration of the high calorific value desorbate
Hot inert gas desorption	Desorption by means of an hot inert gas recirculation. Solvent recovery can be achieved with refrigerated condenser	Recovery of partly or completely water soluble solvents. Recovery of reactive solvents (ketones) or solvents which react with hot steam (chlorinated hydrocarbons)
Pressure swing adsorption/vacuum regeneration	Atmospheric pressure adsorption and heatless vacuum regeneration. The revaporized and desorbed vapor is transported from the adsorption bed via a vacuum pump.	Low-boiling and medium-boiling hydrocarbon vapor mixes from highly concentrated tank venting or displacement gases in large tank farms. Recovery of monomers in the polymer industry.
Reduced pressure and low temperature steam desorption	Steam desorption at low temperature and reduced pressure.	Recovery of reactive solvents of the ketone-type. Minimizing of side-reactions like oxidizing, decomposing or polymerizing.

22.1.4.2.4 Safety requirements

Adsorption systems including all the auxiliary and ancillary equipment needed for their operation are subject to the applicable safety legislation and the safety requirements of the trade associations and have to be operated in accordance with the respective regulations.^{2,19}

Moreover, the manufacturer's instructions have to be observed to minimize safety risks. Activated carbon or its impurities catalyze the decomposition of some organics, such as ketones, aldehydes and esters. These exothermic decomposition reactions^{25,26} can generate localized hot spots and/or bed fires within an adsorber if the heat is allowed to build up. These hazards will crop up if the flow is low and the inlet concentrations are high, or if an adsorber is left dormant without being completely regenerated. To reduce the hazard of bed fires, the following procedures are usually recommended:

- Adsorption of readily oxidizing solvents (e.g., cyclohexanone) require increased safety precautions. Instrumentation, including alarms, should be installed to monitor the temperature change across the adsorber bed and the outlet CO/CO₂ concentrations. The instrumentation should signal the first signs of decomposition, so that any acceleration leading to a bed fire can be forestalled. Design parameters should be set so as to avoid high inlet concentrations and low flow. A minimum gas velocity of approximately 0.2 m/s should be maintained in the fixed-bed adsorber at all times to ensure proper heat dissipation.
- A virgin bed should be steamed before the first adsorption cycle. Residual condensate will remove heat.

- Loaded activated carbon beds require constant observation because of the risk of hot spot formation. The bed should never be left dormant unless it has been thoroughly regenerated.
- After each desorption cycle, the activated carbon should be properly cooled before starting a new adsorption cycle.
- Accumulation of carbon fines should be avoided due to the risk of local bed plugging which may lead to heat build up even with weakly exothermic reactions.
- CO and temperature monitors with alarm function should be provided at the clean gas outlet.
- The design should also minimize the possibility of explosion hazard
- Measurement of the internal adsorber pressure during the desorption cycle is useful for monitoring the valve positions.
- Measurement of the pressure loss across the adsorber provides information on particle abrasion and blockages in the support tray.
- Adsorption systems must be electrically grounded.

22.1.4.3 Special process conditions

22.1.4.3.1 Selection of the adsorbent

The adsorption of solvents on activated carbon¹⁻⁴ is controlled by the properties of both the carbon and the solvent and the contacting conditions. Generally, the following factors, which characterize the solvent-containing waste air stream, are to be considered when selecting the most well suited activated carbon quality for waste air cleaning:

for solvent/waste air:

- solvent type (aliphatic/aromatic/polar solvents)
- concentration, partial pressure
- molecular weight
- density
- boiling point, boiling range
- critical temperature
- desorbability
- explosion limits
- thermal and chemical stability
- water solubility
- adsorption temperature
- adsorption pressure
- solvent mixture composition
- solvent concentration by components
- humidity
- impurities (e.g., dust) in the gas stream

for the activated carbon type:

General properties:

- apparent density
- particle size distribution
- hardness
- surface area

- activity for CCl_4 /benzene
 - the pore volume distribution curve
- For the selected solvent recovery task:
- the form of the adsorption isotherm
 - the working capacity
 - and the steam consumption

The surface area and the pore size distribution are factors of primary importance in the adsorption process. In general, the greater the surface area, the higher the adsorption capacity will be. However, that surface area within the activated carbon must be accessible. At low concentration (small molecules), the surface area in the smallest pores, into which the solvent can enter, is the most efficient surface. With higher concentrations (larger molecules) the larger pores become more efficient. At higher concentrations, capillary condensation will take place within the pores and the total micropore volume will become the limiting factor. These molecules are retained at the surface in the liquid state, because of intermolecular or van der Waals forces. Figure 22.1.9 shows the relationship between maximum effective pore size and concentration for the adsorption of toluene according to the Kelvin theory.

It is evident that the most valuable information concerning the adsorption capacity of a given activated carbon is its adsorption isotherm for the solvent being adsorbed and its pore volume distribution curve. Figure 22.1.10 presents idealized toluene adsorption isotherms for three carbon types:

- large pores predominant
- medium pores predominant
- small pores predominant

The adsorption lines intersect at different concentrations, depending on the pore size distribution of the carbon. The following applies to all types of activated carbon: As the toluene concentration in the exhaust air increases, the activated carbon load increases.

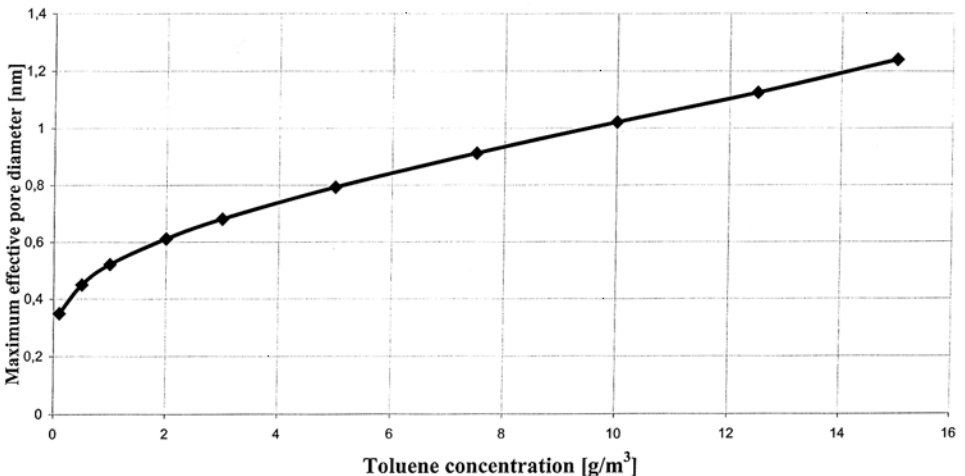


Figure 22.1.9. Relationship between maximum effective pore diameter and toluene concentration.

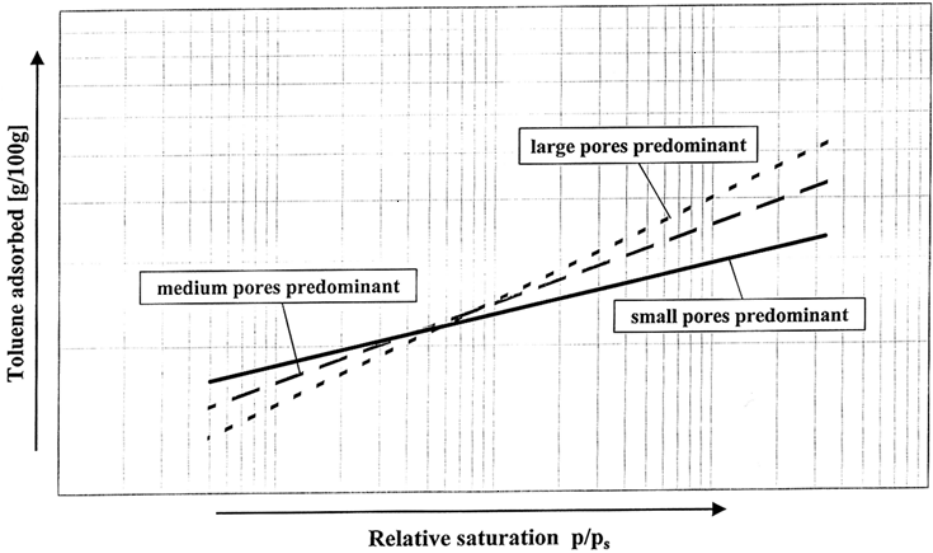


Figure 22.1.10. Idealized toluene adsorption isotherms.

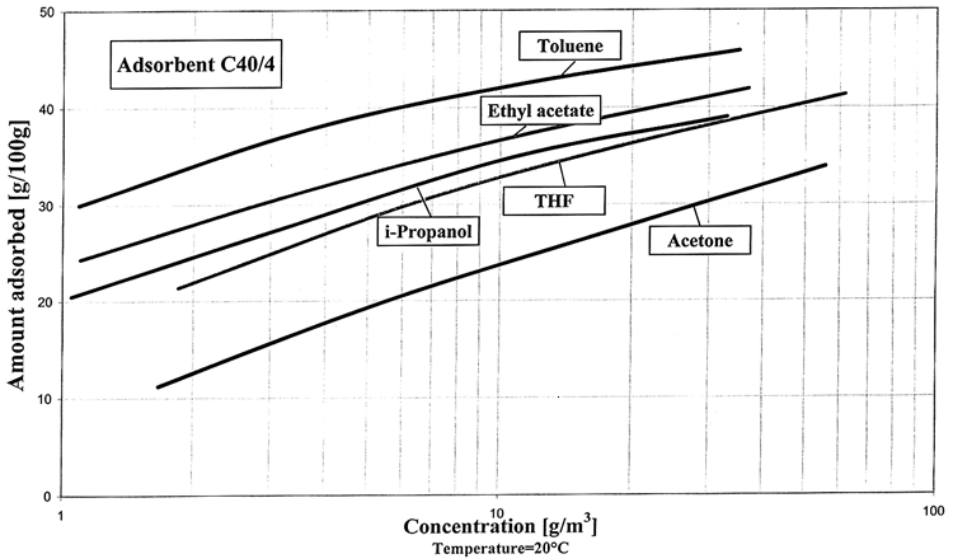


Figure 22.1.11. Adsorption isotherm of five typical solvents (After reference 13).

From the viewpoint of adsorption technology, high toluene concentration in the exhaust air is more economic than a low concentration. But to ensure safe operation, the toluene concentration should not exceed 40% of the lower explosive limit. There is, however, an optimum activated carbon type for each toluene concentration (Figure 21.1.10).

The pore structure of the activated carbon must be matched to the solvent and the solvent concentration for each waste air cleaning problem. Figure 22.1.11 shows Freundlich

adsorption isotherms of five typical solvents as a function of the solvent concentrations in the gas stream. It is clear that different solvents are adsorbed at different rates according to the intensity of the interacting forces between solvent and activated carbon.

Physical-chemical properties of three typical activated carbons used in solvent recovery appear in Table 22.1.9.

Table 22.1.9. Activated carbon pellets for solvent recovery (After reference 13)

AC-Type	C 38/4	C 40/4	D 43/4
Appearance	cylindrically shaped		
Bulk density (shaken), kg/m ³	380±20	400±20	430±20
Moisture content, wt%	<5.0	<5.0	<5.0
Ash content, wt%	<6.0	<6.0	<5.0
Particle diameter, mm	4	4	4
Surface area (BET), m ² /g	>1250	>1250	>1100
Carbon tetrachloride activity, wt%	80±3	75±3	67±3

Producers¹³ of activated carbon are in the best position to provide technical advice on

- selecting the right activated carbon type
- contributing to the technical and economical success of a solvent recovery plant

22.1.4.3.2 Air velocity and pressure drop

In solvent recovery systems, air velocity rates through the bed should be between 0.2 to 0.4 m/s. The length of the MTZ is directly proportional to the air velocity. Lower velocities (<0.2 m/s) would lead to better utilization of the adsorption capacity of the carbon, but there is a danger that the heat of adsorption not be carried away which would cause overheating and possibly ignition of the carbon bed.

The power to operate the blowers to move waste air through the system constitutes one of the major operating expenses of the system. Pressure drop (resistance to flow) across the system is a function of

- air velocity
- bed depth
- activated carbon particle size

Small particle size activated carbon will produce a high pressure drop through the activated-carbon bed. Figure 22.1.12 compares the pressure drop of cylindrically-shaped activated carbon pellets with activated-carbon granulates. The activated carbon particle diameter must not be excessively large, because the long diffusion distances would delay adsorption and desorption. Commercially, cylindrical pellets with a particle diameter of 3 to 4 mm have been most efficient.

22.1.4.3.3 Effects of solvent-concentration, adsorption temperature and pressure

For safety reasons the concentration of combustible solvent vapors should be less than 50 % of the lower explosive limit. The adsorption capacity of adsorbents increases as the concentration of the solvents increases. But the length of the MTZ is proportional to the solvent concentration. Because of the adsorption heat, as the adsorption front moves through the

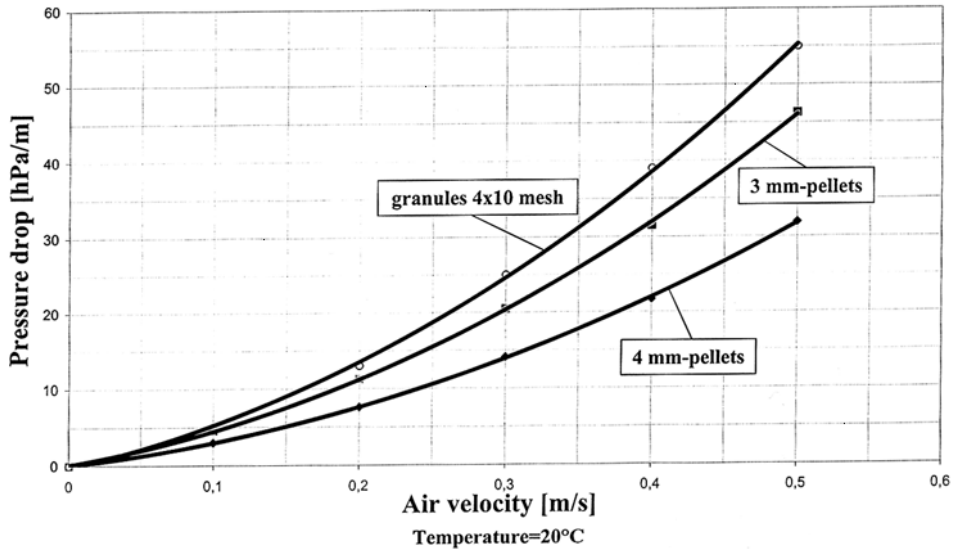


Figure 22.1.12. Pressure drop for various activated carbon types.

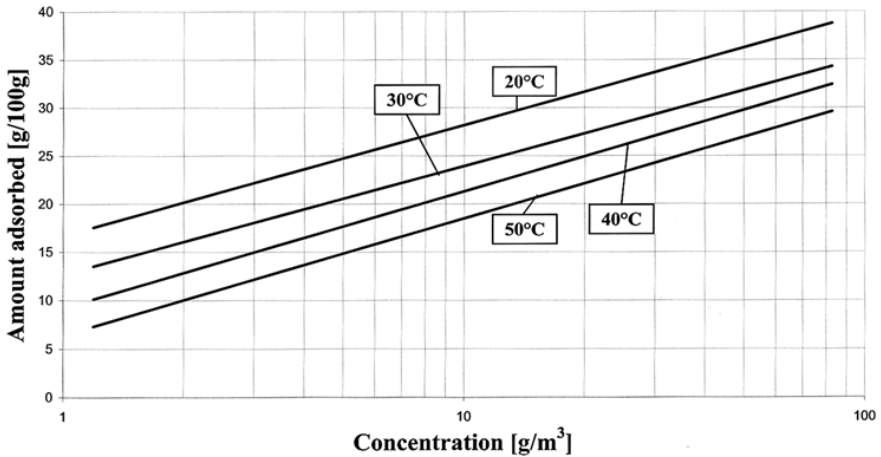


Figure 22.1.13. Adsorption isotherm of tetrahydrofuran for several temperatures.

bed also a temperature front follows in the same direction. To deal with the adsorption heat the inlet solvent concentration is usually limited to about 50 g/m^3 .

The adsorption capacity of the adsorbent increases with pressure because the partial pressure of the solvent increases. An increase in adsorbent temperature causes a reduction in adsorption capacity. Because the equilibrium capacity is lower at higher temperatures, the dynamic capacity (working capacity) of the activated carbon adsorbent will also be lower. To enhance adsorption, the inlet temperature of the adsorbent should be in the range of $20\text{--}40^\circ\text{C}$. In Figure 22.1.13 the adsorption isotherms of tetrahydrofuran on activated carbon D43/3 for several temperatures are shown.¹³

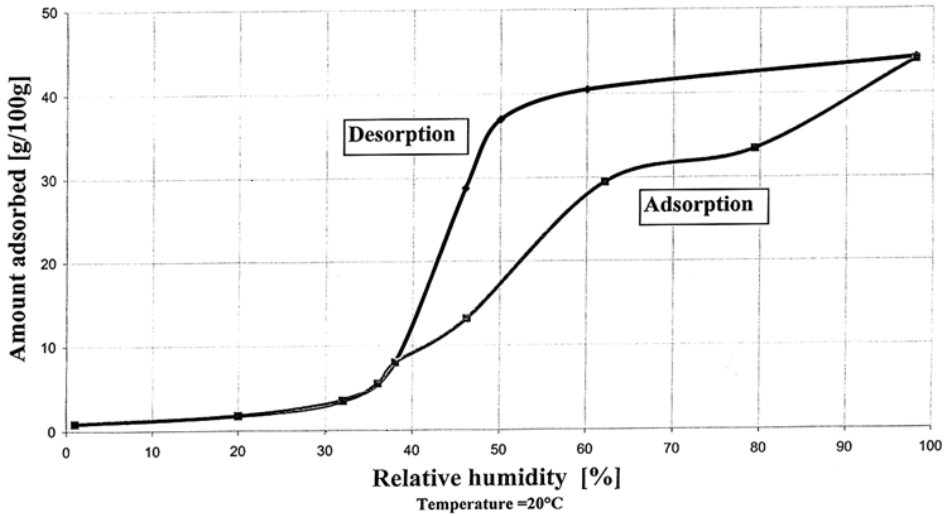


Figure 22.1.14. Water isotherm on activated carbon D43/4.

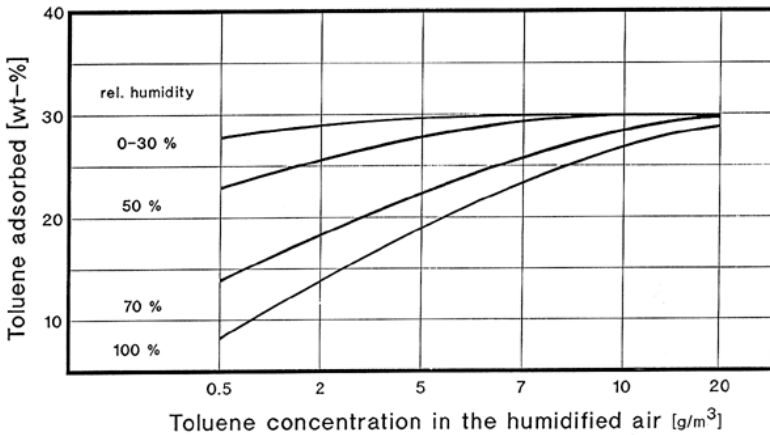


Figure 22.1.15. Dynamic toluene adsorption from humidified air (after reference 24).

22.1.4.3.4 Influence of humidity

Activated carbon is basically hydrophobic; it adsorbs preferably organic solvents. The water adsorption isotherm (Figure 22.1.14) reflects its hydrophobic character. Below a relative gas humidity of about 40% co-adsorption of water can be neglected in most applications. However, higher humidity of the waste gases may affect the adsorption capacity of the activated carbon. Figure 22.1.15 demonstrates, using toluene as an example, how the relative humidity of the exhaust air influences the activated carbon loads.

Experimental work²⁴ has shown that

- relative humidity rates below 30% will neither reduce the adsorption capacity nor the adsorption time,
- relative humidity rates above 70% substantially reduce the adsorption capacity,
- the humidity of the gas will affect the adsorption capacity much more with low toluene concentrations than with high concentrations,
- with toluene concentrations between 10 and 20 g/m³ the negative influence of the humidity is small.

The water content of the activated carbon after desorption may constitute another problem. The purification efficiency of each activated carbon is the better the less water is present after desorption. Unfortunately, the desorbed activated carbon in the vicinity of the adsorber walls usually contains high proportions of water (approx. 10 to 20%). With such a high water content it is difficult to remove all the water even when drying with hot-air over longer periods. The wet and poorly-regenerated activated carbons in these zones frequently lead to higher solvent concentrations in the purified air, and this is even at the beginning of the adsorption cycle. Some proposals for improvement include:

- good insulation of the adsorber walls,
- sufficient drying after each regeneration cycle,
- cycle the desorption steam and the drying air counter-current to the direction of the adsorptive stream.

22.1.4.3.5 Interactions between solvents and activated carbon

The majority of solvents are effectively recovered by adsorption on activated carbon and, when this is the case, the operation of the plant is straightforward. But some solvents may decompose, react or polymerize when in contact with activated carbon during the adsorption step and the subsequent steam desorption.^{19,25,26}

Chlorinated hydrocarbon solvents can undergo hydrolysis to varying degrees on carbon surfaces, resulting in the formation of hydrogen chloride. Each activated carbon particle which is in contact with a metal screen or other constructional component may then act as a potential galvanic cell in the presence of moisture and chloride ions.

Carbon disulfide can be catalytically oxidized to sulphur which remains on the internal surface of the activated carbon.

Esters such as ethyl acetate are particularly corrosive because their hydrolysis results in the formation of e.g. acetic acid.

Aldehydes and phenol or styrene will undergo some degree of polymerization when in contact with hot activated carbon.

During the adsorptive removal of ketones such as methyl ethyl ketone or cyclohexanone a reduced adsorption capacity has been measured. Corrosion problems were also apparent and in some cases even spontaneous ignition of the activated carbon occurred.

Activated carbon acts, in the presence of oxygen, as a catalyst during adsorption and even more frequently during desorption because of higher temperature.^{25,26} Figure 22.1.16 shows that the catalytic reactions occurring with cyclohexanone are predominantly of the oxidation type. Adipic acid is first formed from cyclohexanone. Adipic acid has a high boiling point (213°C at a 13 mbar vacuum). Further products identified were: cyclopentanone as a degradation product from adipic acid, phenol, toluene, dibenzofuran, aliphatic hydrocarbons and carbon dioxide. The high-boiling adipic acid cannot be desorbed from the activated carbon in a usual steam desorption. Consequently the life of the activated carbon becomes further reduced after each adsorption/desorption cycle.

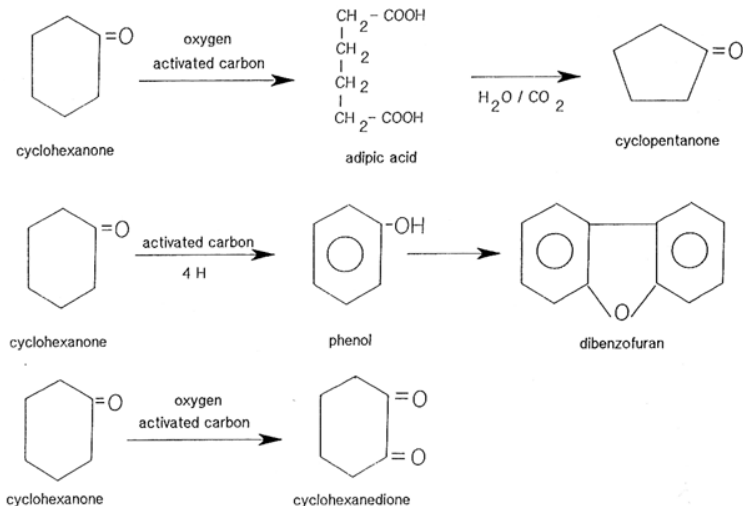


Figure 22.1.16. Surface reaction of cyclohexanone on activated carbon (After reference 25).

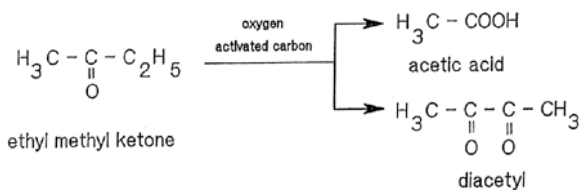


Figure 22.1.17. Surface reaction of methyl ethyl ketone on activated carbon (After reference 25).

During adsorption of methyl ethyl ketone in the presence of oxygen, some catalytic surface reactions occur (Figure 22.1.17). The reaction products are acetic acid, di-acetyl, and presumably also di-acetyl peroxide. Di-acetyl has an intensive green coloration and a distinctive odor. Important for the heat balance of the adsorber is

that all of the reactions are strongly exothermic.

Unlike the side products of cyclohexanone, acetic acid the reaction product of the MEK (corrosive!) will be removed from the activated carbon during steam desorption. Adsorption performance is thus maintained even after a number of cycles.

Operators of ketones recovery plants should adhere to certain rules and also take some precautions²⁵

- Adsorption temperature should not be higher than 30°C (the surface reaction rates increase exponentially with temperature).
- The above requirement of low-adsorption temperatures includes:
 - a) adequate cooling after the desorption step;
 - b) a flow velocity of at least 0.2 m/s in order to remove the heat of adsorption.

Since ketones will, even in an adsorbed state, oxidize on the activated carbon due to the presence of oxygen, these further precautions should be taken:

- keep the adsorption/desorption cycles as short as possible,
- desorb the loaded activated carbon immediately at the lowest possible temperatures,
- desorb, cool and blanket the equipment with inert gas before an extended shut down.

22.1.4.3.6 Activated carbon service life

Activated carbon in solvent recovery service will have a useful service life of 1 to 10 years, depending on the attrition rate and reduction in adsorption capacity.

Attrition rates are usually less than 1-3% per year. The actual rate will depend on carbon hardness. Particle abrasion and the resulting bed compaction leads to an increased pressure loss after several years of service. After 3-5 years of service screening to its original size is necessary.

Adsorption capacity can be reduced by traces of certain high-boiling materials (resins, volatile organosilicone compounds) in the waste air which are not removed during the desorption cycle. Some solvents may decompose, react or polymerize when in contact with activated carbon and steam (Section 22.1.4.3.5).

This gradual loading will decrease the carbon's activity. While carbon can remain in service in a reduced capacity state, it represents a non-optimal operation of the system that results in

- reduced amount of solvent removed per cycle
- increased steam consumption
- higher emissions
- shorter adsorption cycles

Eventually, recovering capacity will diminish; it is more economical to replace carbon than continue its use in a deteriorated state. In replacing spent activated carbon there are two options:

- Replacing with virgin carbon and disposal of the spent carbon.
- Off-site reactivation of the spent carbon to about 95% of its virgin activity for about one-half of the cost of new carbon

Some activated carbon producers offer a complete service including carbon testing, off-site reactivation, transportation, adsorber-filling and carbon make-up.¹³

22.1.5 EXAMPLES FROM DIFFERENT INDUSTRIES

Some examples of solvent recovery systems in different industries show that reliable and trouble-free systems are available.

22.1.5.1 Rotogravure printing shops

Process principle

Absorptive solvent recovery with steam desorption and condensation units with gravity separator and a stripper have become a standard practice in modern production plants. The solvents-laden air (toluene, xylene) is collected from emission points, e.g., rotogravure printing machines, drying ducts by means of a blower and passed through the recovery plant.

Design example³⁰

In 1995, one of Europe's most modern printing shops in Dresden was equipped with an adsorptive solvent recovery system (Supersorbon[®] process (Figure 22.1.18.)).

Design data

(First stage of completion)	
Exhaust air flow rate	240,000 m ³ /h
(expandable to	400,000 m ³ /h)
Solvent capacity	2,400 kg/h (toluene)
Exhaust air temperature	40°C
Toluene concentration in clean air	max. 50 mg/m ³
(half-hour mean)	

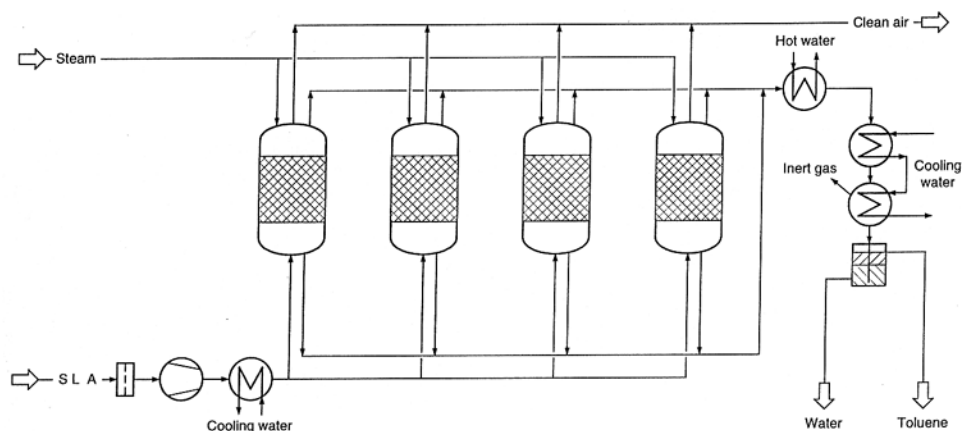


Figure 22.1.18. Supersorbon[®] process for toluene recovery (After reference 30).

Solvent-laden air is exhausted at the three rotogravure printing presses by several fans operating in parallel and is routed in an upward flow through four adsorbers packed with Supersorbon[®] activated carbon. The solvent contained in the air is adsorbed on the activated carbon bed. Adsorption continues until breakthrough, when the full retentive capacity of the adsorbent for solvent vapors is used up.

The purity of the clean exhaust air complies with the regulation for emission level of less than 50 mg/m³. Regeneration of the adsorbent takes place by desorbing the solvent with a countercurrent flow of steam. The mixture of water and toluene vapors is condensed and the toluene, being almost insoluble in water, is separated by reason of its different density in a gravity separator. The recovered toluene can be re-used in the printing presses without further treatment. Very small amounts of toluene dissolved in the wastewater are removed by stripping with air and returned to the adsorption system inlet together with the stripping air flow. The purified condensate from the steam is employed as make-up water in the cooling towers.

Operating experience

The adsorption system is distinguished by an extremely economical operation with a good ratio of energy consumption to toluene recovery. Solvent recovery rate is about 99.5 %.

22.1.5.2 Packaging printing industry

In the packaging printing industry solvents like ethyl acetate, ethanol, ketones, tetrahydrofuran (THF), hexane and toluene are used in printing. The solvent laden air generally contains between 2 and 15 g/m³ of solvent and, depending on the season, 5-18 g/m³ of water.

Adsorptive recovery with steam desorption was widely used for many years but its disadvantage is that the solvents are recovered in various mixtures containing large amounts of water. The recovery of solvents is complicated because most solvents produce azeotropes with water which are not easily separated and, consequently, the waste water fails to meet the more stringent environmental regulations. In the last 10 years the adsorbent regen-

eration with hot inert gas has become the more favored process in the packaging printing industry.

22.1.5.2.1 Fixed bed adsorption with circulating hot gas desorption^{31,32}

Activated carbon preferentially adsorbs non-polar organic solvents, while adsorbing relatively little water. Thus activated carbon allows the passage of 95-98 % of the water while retaining the solvents from the gas stream. During the adsorption step solvent laden air or gas is delivered to the bed through the appropriate valves. As adsorption starts on a fresh bed, the effluent gas contains traces of solvent. Through time, the solvent level increases and when it reaches a predetermined value, the adsorption is stopped by closing the feed gas valves. The adsorption step usually lasts for 4-16 hours. An example of a solvent recovery plant with 5 activated carbon beds and hot gas desorption is shown in Figure 22.1.19.

If necessary, feed air is cooled to 35°C and sent by the blower V-1 to the main heater 6 from which it enters 4 beds simultaneously, while one bed is being regenerated. The cleaned air is collected in header 7 and vented.

After the adsorption step, the air is displaced from the bed by an inert gas such as nitrogen. A circulating inert gas at 120-240°C serves for heating and stripping the solvent from the carbon. The solvent is recovered by cooling and chilling the circulating gas. The optimum chilling temperature depends on the boiling point of the solvent. Generally, chilling temperatures are between +10 and -30°C.

During the heating step, the temperature of the effluent gas gradually increases until a predetermined value (for example, 150°C) is reached, after which the heater is bypassed and the bed is cooled down by cold gas. Typical solvent recovery plants will have from 2 to 8 beds. All beds go through the same adsorption, inertization, heating and cooling steps but each at different time.

Referring to the flow sheet in Figure 22.1.19 the regeneration gas is circulated by blower V-2 to the gas heater, the header 8 to the bed being regenerated. The effluent gas is passed to the header 9, cooler, molecular sieves (or water condenser), to the chiller for sol-

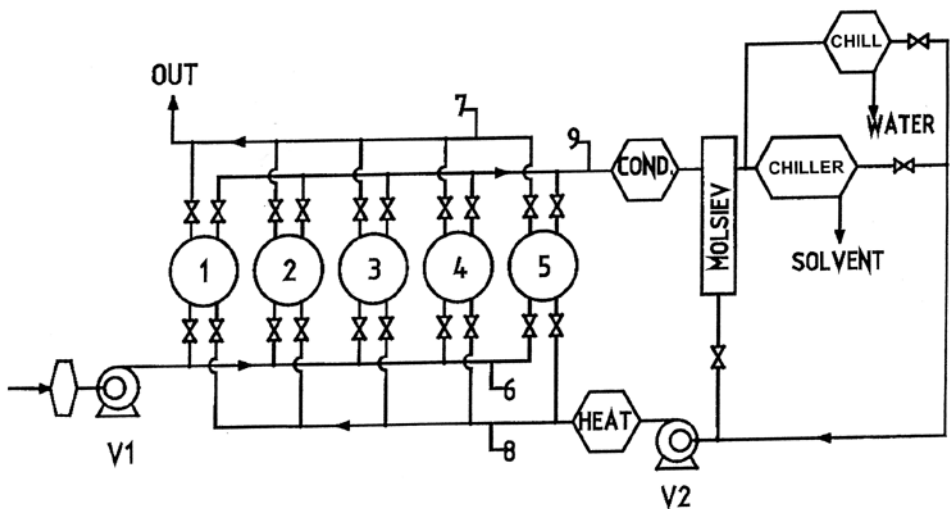


Figure 22.1.19. Fixed bed adsorption with circulating hot gas desorption (After references 31,32).

vent condensation and back to the blower V-2. At the end of the adsorption step the bed contains 10-30% solvent and 1-2% water.

There are various ways to remove the water separately and to recover a solvent containing between 0.1 and 1.5 % water (Table 22.1.10).

Table 22.1.10. Process conditions and water content in the solvent (After references 32,33)

	Water in the raw solvent	Investment cost, %	Heat needed, kWh/kg S	Power, kWh/kg S
Basic process with molsieve beds	0.1	100	2.2	1.0
Chiller instead of molsieve	1.5	91	1.5	1.0
Chiller and 1 carbon bed	0.4 - 1.0	93	1.1	1.0
Chiller, and 1 carbon bed molsieve	0.1	96	1.1	1.0

Using molecular sieves

Beds of molecular sieves are used to recover a solvent with 0.1%. This process requires around 2-2.5 kWh heat/kg of recovered solvent. Regeneration loop pressure drops are high, because of the additional molsieve beds and valves.

Separate condensation of water

Initially, when regenerative heating of the bed starts, very little solvent is desorbed, but much of the water (about 87%) is desorbed. The circulating gas is first passed through a cooler and then a separate chiller for the condensation or freezing of the water. Subsequently the gas is passed to the chiller where the water is condensed or frozen. From 1 to 1.8% water is recovered. This process is simpler than the molecular sieves process.

Two separate chillers

Two separate chillers are used in another adsorption process which offers further substantial improvements. A third activated carbon bed is added so that while two of the beds are being regenerated one of these is being cooled and transferring its heat to the other bed which is being heated. This not only gives excellent heat recovery but also provides a means of reducing the water content of the recovered solvent. The cooled bed absorbs the water vapor from the gas stream coming from chiller. This dry gas stream is transported to the bed which is being heated and the desorbed solvent from the heated bed remains dry. Solvents recovered at this stage contain only 0.4 to 0.5% water. Solvent which is removed from the bed being cooled is re-adsorbed on the bed being heated.

The process, which is patented, brings important benefits of regeneration gas flow rates. Such low flow rates mean that the process requires less heat, less refrigeration and a lower cost regeneration loop. The overall efficiency is high because the low residual solvent loading of the regenerated beds leads to increased solvent recovery.

Two separate chillers plus molecular sieve bed

A two chiller system with a molecular sieve bed has to be regenerated only about once per week, since most of the water is removed in the chiller and re-adsorbed on the cooled carbon bed. This process offers a high solvent recovery rate giving a solvent with only 0.1 % water at greatly reduced heat consumption, lower investment, and higher solvent recovery rate.

Key plants with all the above mentioned processes are offered by special engineering companies.^{31,32} The investment cost for a typical recovery plant with hot gas regeneration can be estimated by the following equation:

$$\text{COST (in 1000 Euro)} = 200 + 0.4 \times A^{0.7} + 15 \times S^{0.7}$$

where:

A	feed air rate in Nm ³ /h
S	solvent flow rate in kg/h

22.1.5.2.2 Solvent recovery with adsorption wheels

Adsorption wheels³³ are used for the continuous purification of large volumes of exhaust air containing relatively low solvent concentrations.

The adsorption wheel consists of a number of identical chambers arranged axially around a vertical axis. All chambers contain adsorbent. The wheel rotates and each chamber passes in sequence over an exhaust air duct and solvent molecules are adsorbed. As wheel continues to rotate the chamber in which adsorption had occurred now moves into a desorption position in which hot air is passed through the chamber and over the adsorbent. This removes the adsorbed solvent. The hot air flow in the desorption sector is at relatively low flow rate compared to that of contaminated gas stream. The number of chambers in the desorption zone is much greater than the number in the absorption zone so the desorption stream is many times more concentrated in solvent than was the exhaust stream. At this higher concentration, the desorption stream can now be economically treated in one of the ways:

- The adsorption stream is purified by means of recuperative or regenerative oxidation. This approach is advantageous in painting applications with solvent mixtures that cannot be reused in production.
- For solvent recovery by condensation, the desorption stream is cooled down in a cooling aggregate and the liquid solvent is recovered for reuse. Water contents below 1% can be achieved without further purification.

Example:

A manufacturer who specializes in flexible packaging, i.e., for confectionary, always adds the same solvent mixture (ethanol, ethyl acetate, ethoxypropanol) to his printing ink.

Adsorptive solvent removal of the solvent-mixture by use of an adsorption wheel (Figure 22.1.20) and solvent recovery via condensation proved the technically and cost effective. 10,000 to 65,000 Nm³/h of exhaust air from printing machines and washing plants at a temperature maximum of 45°C and a maximum solvent loading of 4.6 g/m³ is to be cleaned. Depending on the air volume two adsorption wheels with a capacity of 26,000 Nm³/h and 39,000 Nm³/h and separate desorption circuits are used either alternatively or together. The total desorption air of max. 11,000 Nm³/h is being concentrated to max. 27 g/m³, which corresponds to 50% of the lower explosion limit. The condensation unit for the solvent recovery process is gradually adjusted to small, medium or large exhaust air volumes. The recovered solvents are stored and returned to the production process.

22.1.5.3 Viscose industry

In plants which produce viscose fibre (stable fibre), viscose filament yarn (rayon) and viscose film (cellophane), large volumes of exhaust air contaminated with carbon disulfide

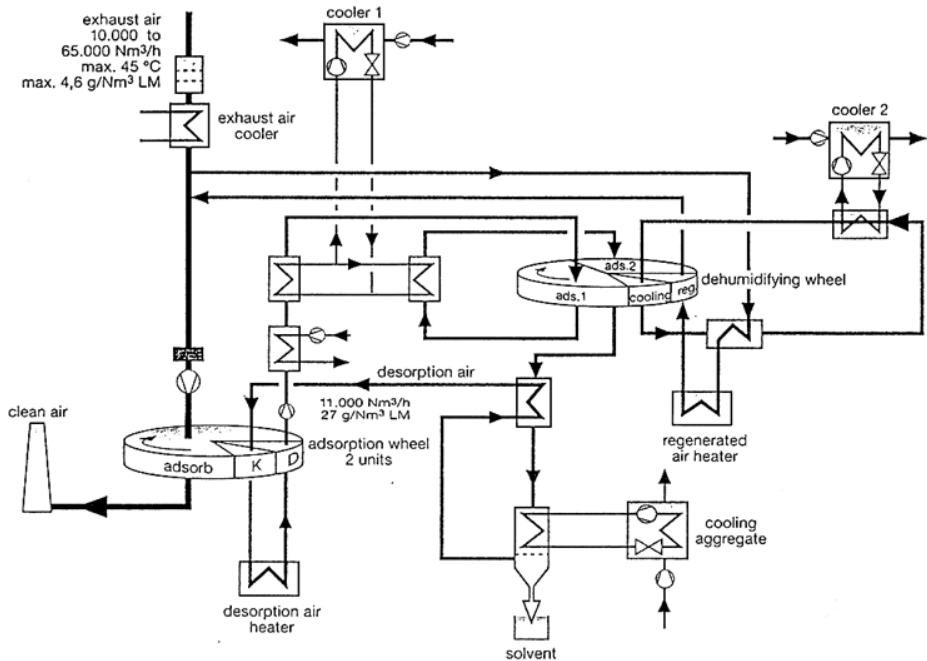


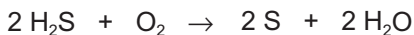
Figure 22.1.20. Adsorption wheel for solvent recovery in packaging printing (After reference 33).

(CS₂) and hydrogen sulphide (H₂S) have to be cleaned. Typical waste gas volumes and concentration of CS₂ and H₂S are given in Table 22.1.11.

Different cleaning/recovery processes are available for the removal of each of the two sulfur containing compounds:^{2,17,34,35}

Hydrogen sulfide

- Absorption of H₂S in a NaOH-scrubber
- Catalytic oxidation of H₂S to elemental sulphur on iodine impregnated activated carbon (Sulfosorbon-process)



The sulphur is adsorbed at the internal surface at the carbon-catalyst.

Table 22.1.11. Waste gas in the viscose industry (After reference 35)

Product	Spec. waste gas volume, m ³ /t	Concentration (mg/m ³)	
		H ₂ S	CS ₂
Rayon	400,000 - 700,000	60 -130	300 - 800
Staple fibre	50,000 - 90,000	700 -1800	2300 - 4000
Viscose fibre	100,000 -150,000	280 - 400	1000 - 3000

Carbon disulfide

Adsorptive removal on activated carbon and recovery by steam desorption. For simultaneous H_2S and CS_2 removal the Sulfosorbon-process uses adsorbers packed with two different activated carbon types

- Iodine impregnated wide-pore activated carbon for H_2S oxidation in the bottom part (gas inlet) of the adsorber
- Medium-pore activated carbon for the adsorption of CS_2 in the upper layer of the fixed bed.

As soon as the CS_2 concentration in the treated air approaches the emission limit, the exhaust air stream is directed to a regenerated adsorber. After an inert gas purge, the carbon disulfide is desorbed with steam at 110 to 130°C. The resulting CS_2 /steam mixture is routed through a condenser and cooler, before entering a gravity separator where phase separation occurs.

At the usual CS_2 and H_2S concentrations in viscose production exhaust air, the CS_2 adsorption/desorption cycles can be run for a prolonged periods before the first layer loaded with elemental sulphur has to be regenerated.

The regeneration process of the sulphur loaded activated carbon involves the following steps:

- washing out of sulphuric acid with water
- extraction of elemental sulphur with carbon disulfide
- desorption of carbon disulfide with steam
- air drying and cooling of activated carbon

The elemental sulphur present in the carbon disulfide in dissolved form can be separated by distillation and recovered as high-purity sulphur.

Design example³⁴

In the production of viscose filament yarn a Supersorbon[®]-system combined with a NaOH-scrubber system (Figure 22.1.21) has been in use since 1997. A very high standard of safety engineering is implemented in the treatment system owing to the flammability of the CS_2 and the toxic nature of the constituents to be removed from the exhaust air.

System concept

First treatment stage:

Absorption of H_2S in two NaOH jet scrubbers and one water-operated centrifugal scrubber.

Second treatment stage:

Fixed-bed adsorption for purification of exhaust air and CS_2 recovery.

Treated air stream

Exhaust air from viscose filament yarn plant.

Design data:

Exhaust air flow rate	12,000 Nm ³ /h
Solvent capacity	27 kg CS_2 /h and 7.5 kg H_2S /h
Exhaust air temperature	15 - 30°C
Clean air solvent concentration	
CS_2 : max.	100 mg/Nm ³ (24-hour mean)
H_2S : max.	5 mg/Nm ³ (24-hour mean)

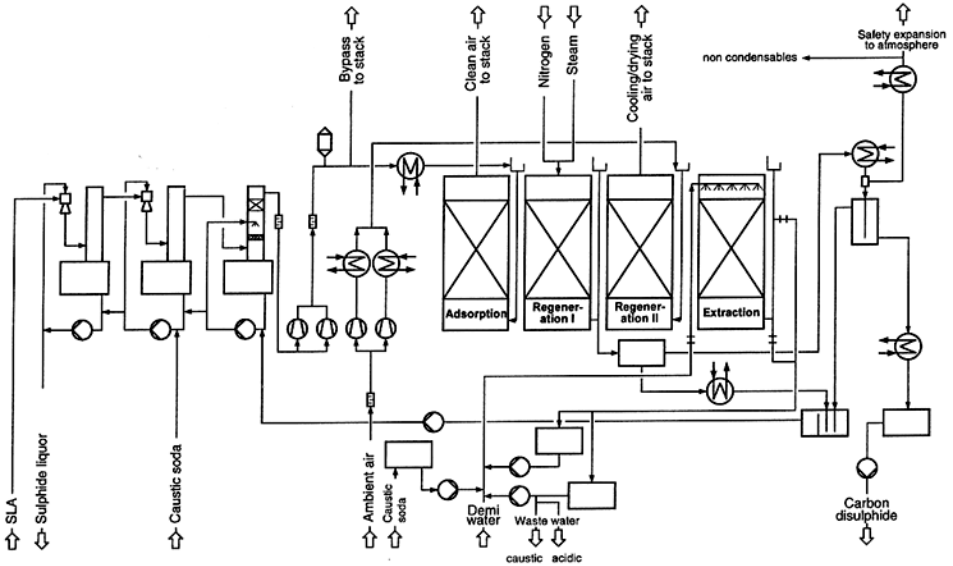


Figure 22.1.21. H_2S and CS_2 removal in the filament yarn production (After reference 34).

H_2S -removal

The exhaust air, saturated with water vapor, is first treated in an absorption unit for removal of H_2S by routing it through two successive jet scrubbers working with dilute caustic soda solution. Downstream of these, a centrifugal scrubber is installed as an entrainment separator. The sulphide-containing solution rejected from the scrubbers is used to precipitate zinc in the waste water treatment system of the production plant. By products adsorbed on the activated carbon, such as sulphuric acid and elemental sulphur, are removed periodically by water and alkaline extraction.

CS_2 -removal and recovery

The pre-cleaned airstream containing carbon disulphide vapors passes through two or three parallel adsorbers, in which the CS_2 is absorbed on a bed of Supersorbon[®] activated carbon. As soon as the adsorbent is saturated it is regenerated by desorbing the solvent with a countercurrent flow of steam. The resulting mixture of water and CS_2 vapors is condensed and separated in gravity settlers. The recovered CS_2 is returned to the viscose production without further treatment. The condensed steam is stripped of residual CS_2 in the centrifugal scrubber and used as dilution water for operation of the jet scrubbers.

Operating experience

The specified purity of the treated exhaust air is reliably achieved with the Supersorbon[®] process³⁴ with respect to both CS_2 and H_2S . The CS_2 recovery rate is about 95%. The purity of the recovered solvent meets viscose production specifications. A widely varying CS_2 concentration in the exhaust air has not adversely affected operation of the adsorption system.

22.1.5.4 Refrigerator recycling

Condensation process

Condensation processes are especially suitable for the cleaning of low flow highly concentrated streams of exhaust gas.³⁶ The entire waste gas stream is cooled below the dew point of the vapors contained therein, so that these can condense on the surface of the heat exchanger (partial condensation). Theoretically, the achievable recovery rates depend only on the initial concentration, the purification temperature and the vapor pressure of the condensables at that temperature. In practice however, flow velocities, temperature profiles, the geometry of the equipment, etc. play decisive roles, as effects such as mist formation (aerosols), uneven flow in the condensers and uncontrolled ice formation interfere with the process of condensation and prevent an equilibrium concentration from being reached at the low temperatures.

The Rekusolv Process³⁷ uses liquid nitrogen to liquefy or freeze vapors contained in the exhaust gas stream. In order to reduce the residual concentrations in the exhaust to the legally required limits, it is often necessary to resort to temperatures below minus 100°C. The Rekusolv process is quite commonly used in the chemical and pharmaceutical industry and at recycling plants for solvent recovery.

Example of solvent recovery in refrigerator recycling^{36,37}

In refrigerator recycling plants R11 or pentane is released from the insulating foam of the refrigerator during shredding. Figure 22.1.22. shows the Rekusolv process as it is used by a refrigerator recycling company. At this plant around 25 refrigerators per hour are recycled thereby generating 8 kg/h of polluting gases. The Rekusolv plant is capable of condensing almost all of this. The unit is designed to operate for 10 to 12 hours before it has to be defrosted. The plant is operated during the day and is automatically defrosted at night. The concentration of pollutants in the exhaust gas is reduced from 20 to 40 g/m³ to 0.1 g/m³ - a recovery rate of more than 99.5%.

22.1.5.5 Petrochemical industry and tank farms

Vapor recovery units are installed at petrochemical plants, tank farms and distribution terminals of refineries. Tank venting gases are normally small in volume, discharged intermittently at ambient temperature and pressure and loaded with high concentrations of organic vapors.²

Processes used for the cleanup of such waste air streams with organic vapor up to saturation point are often combined processes:^{2,38,39}

- absorption and pressure-swing adsorption
- membrane permeation and pressure-swing adsorption
- condensation and adsorption

Adsorption on activated carbon and vacuum regeneration

Figure 22.1.23 represents the basic principle of the systems which are used to recover vapors displaced from tank farms and loading stations and blend them back into the liquids being loaded. The plant consists of two fixed-bed adsorbers packed with activated carbon which operate alternatively. The vapor pressure gradients required as a driving force for desorption is generated by vacuum pumps. As the raw gas entering the adsorber is saturated with hydrocarbon vapors, the heat of adsorption causes local heating of the well insulated adsorbent bed. The higher temperature of the spent activated carbon supports subsequent desorption as the pressure is being lowered by means of a vacuum pump.

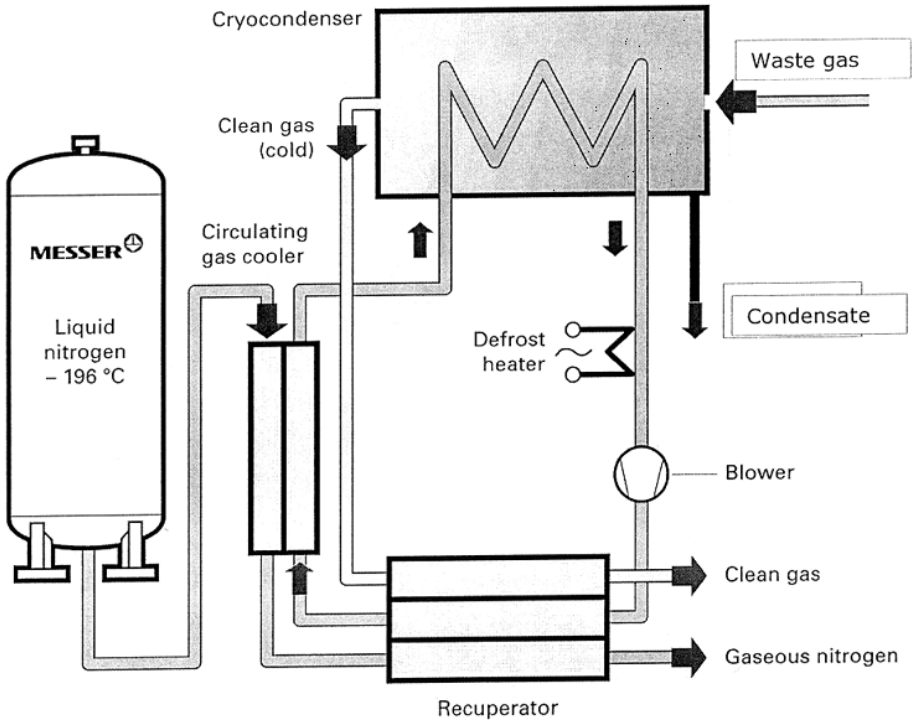


Figure 22.1.22. Block diagram of the Rekusolv process (After references 36,37).

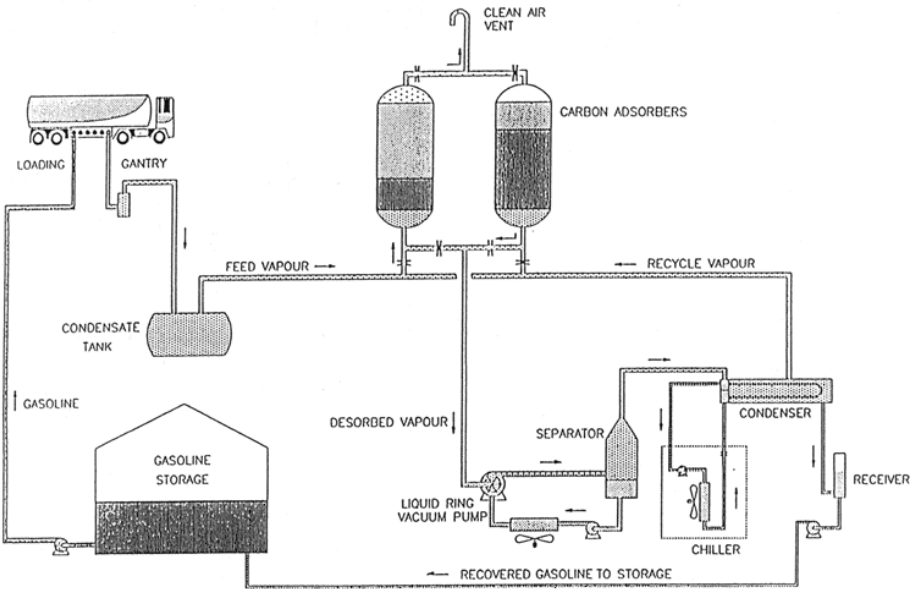


Figure 22.1.23. Vapor recovery by adsorption and vacuum regeneration (After reference 39).

The desorbed vapor is transported from the adsorption bed via a vacuum pump. A liquid ring pump using water for the seal fluid is normally applied for safety purposes in operations where air is allowed to enter the adsorbers.

The desorption stream is processed through a cooler and absorber. The absorber uses gasoline (or the recovered solvent) as a sorbent and serves as a hydrocarbon reduction stage for the entire system. Loading facilities with the inlet vapor concentrations of over 10% by volume can demonstrate recovery efficiencies of over 99%.

22.1.5.6 Chemical industry

In the chemical industry a variety of solvents and solvent mixtures are in use. For many gas cleaning operations special adsorption processes are required.

Two-stage adsorption⁴⁰

In many cases, a two-stage process offers significant advantages. This process makes use of two adsorbers that are operating alternately in series. Four-way reverse valves ensure safe change-over. During operation, the air passages of the valves are always open so that any blocking of the flow is impossible. Solvent laden air first passes into one of the adsorbers. Purified air is released into the atmosphere only during the time when the second adsorber is being steamed. During this phase of the process, the on-line adsorber is only slightly charged with solvent which means that it will be completely adsorbed. In general the time required for steaming an adsorber is at most 50% of the time provided for adsorption.

After the adsorber has been steamed, the outlet valve is switched over. The steamed adsorber is then dried with solvent-free air taken from the laden adsorber. A feature of this process is that the steamed adsorber is always dried with solvent-free air. An advantage of this two-stage process is that the laden adsorber can be loaded beyond the breakthrough capacity since the second adsorber is unladen and can therefore accept any excess solvent.

The condensation phase and reprocessing of the desorbate are carried out in the same manner as described for the single-stage plant. For example, a two-stage adsorption plant for the recovery of dichloromethane is able to clean a gas stream of 3000 m³/h to a residual solvent content of less than 20 mg/m³.

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22.2 SOLVENT RECOVERY

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22.2.1 ACTIVATED CARBON IN FLUIDIZED BED ADSORPTION METHOD

This section discusses a solvent recovery process developed by Kureha Engineering Co. Ltd., Japan.¹ In this continuous process, spherical particles of activated carbon (AC) circulate in the adsorption and desorption columns by fluidization. In the adsorption column, the particles form fluidized beds on multi-trays to adsorb the solvent in counter-current contact with the feed gas. The cleaned gas is released from the top of the adsorption-column to the atmosphere.

The carbon absorber with adsorbed solvent is electrically heated (150-250°C) at the upper part of the desorption column and solvent is desorbed by nitrogen, which is supplied from the bottom of the desorption column. Nitrogen is continuously recycled in the desorption column. The solvent in the carrier gas is fed to a condenser for its recovery.

Features of the process:

- Atmospheric condensate is the only waste product because nitrogen (or air) is used as the carrier gas.
- High flow rate per unit area because the process is conducted by fluidization.
- Low thermal energy loss because both the adsorption and desorption are conducted at constant temperature.
- Low electric energy consumption because the fluidization needs less blower driving power.

Figure 22.2.1 shows the process diagram and Table 22.2.1 shows application data.

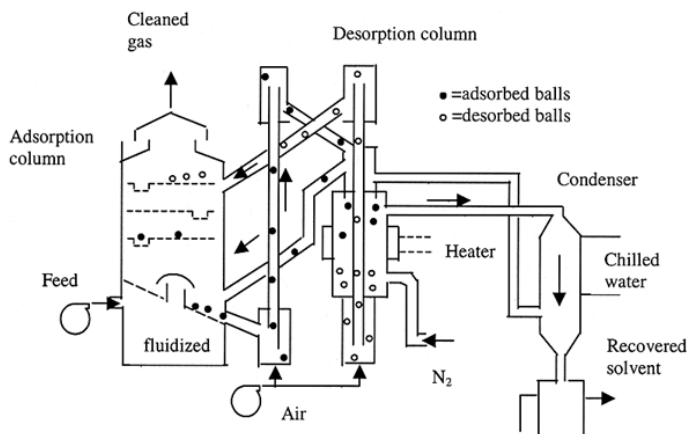


Figure 22.2.1. Flow diagram of the process.

Table 22.2.1. Application data. Activated carbon fluidized bed adsorption process

Solvents	Manufacturing plants	Flow rate, m ³ /min	Feed conc., ppm
phenol, naphthalene	semiconductors	50	100*
curry odor	food processing	240	4,000
IPA, phenol, acetone, ethanol	electronics	120	220
terpineol	IC	300	30
dichloromethane	semiconductors	80	500
IPA, xylene	semiconductors	150	110
IPA	semiconductors	80	200
manure odor	fertilizers	600	3,000*
phenol, formaldehyde, ammonia	shell mold casting	2,000	4
butyl acetate, IPA, etc.	semiconductors	420	50
terpineol	IC	300	30
butyl acetate, etc.	solvents	550	50

*odor concentration

22.2.2 APPLICATION OF MOLECULAR SIEVES

Molecular sieves is a term synonymous in this context to aluminosilicate hydrate also called zeolite. The zeolite is applied to deodorization, gas separation and some other processes. Since this material is, unlike activated carbon, non-combustible, it has increasingly been applied to concentrate volatile organic compounds, VOC. The concentration process discussed here applies to the “VOC concentrator” developed by Seibu Giken Co. Ltd. Japan.² The element referred to here as the VOC concentrator is non-combustible and has a honeycomb structure. The key features are summarized below.

Key features of honeycomb rotor concentrator

- Hydrophobic zeolite is embedded into a calcinated ceramic honeycomb substrate with an inorganic binder and recalcinated at high temperature to improve the compatibility of zeolite with the ceramic substrate.
- Various types of VOCs can be efficiently purified and concentrated.
- The most suitable zeolite and composition are selected for application.
- Absorption medium is non-combustible
- Heat resistance up to 500°C
- Desorption temperature: 150 - 220°C

Functions of the VOC concentrator

(1) Purification - The VOC laden exhaust air stream is purified by zeolite or other adsorbent while passing through the rotor, and the purified air stream is vented into the atmosphere.

(2) Concentration - The VOC laden exhaust air stream is adsorbed in the process zone and desorbed in the desorption zone into a heated desorption air stream with much less air volume than that of process air stream. The VOC is concentrated nearly equal to the air volume ratio (5-15) of the process and desorption (QP/QD).

Basic design of VOC concentrator

VOC concentrator consists of a VOC rotor, a rotor driving device, a rotor casing with a set of seals, a pair of chambers (front/rear) with a zone partition wall, and a desorption heater as shown in Figure 22.2.2.

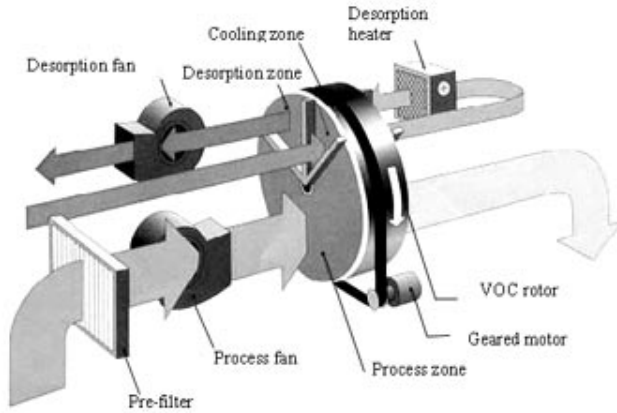


Figure 22.2.2. VOC concentrator.

Advantages

VOC concentrators, outstanding in their purifying and concentrating efficiency, have been used worldwide as a high-quality and safe product owing to material engineering expertise. By being combined with oxidizers, and other recovery equipment, the initial investment and running cost of the total system can be drastically diminished. Even for such VOCs as cyclohexane/MEK/ammonia/methyl alcohol/ethyl alcohol/styrene/formaldehyde/isophorone/phenol, which have been found unsuitable for the existing technology using activated carbon, due to economic or safety concerns, the VOC concentrator is cost-effective and safe.

- *Non-combustible components* - The development of non-flammable rotors has been achieved by engineering the appropriate materials for the honeycomb substrate, the adsorbent, and the binder and by application of special material processing technique.
- *Treatment of VOCs which have high boiling point* - Taking advantages of zeolite rotors, non-combustible component, and high heat resistance, concentrators can use adsorption air at high temperatures. Accordingly, VOCs that could not be treated by carbon material due to its desorption temperature limit have turned out to be easily treated.
- *Inertness* - VOCs that can easily polymerize, such as, styrene, cyclohexanone, etc., can be effectively treated by hydrophobic zeolite.
- *Cleaning and reactivation* - Zeolite rotors can be calcinated under high temperature, due to their all inorganic content (including binder). The rotors can be easily washed. Zeolite rotors can be reactivated by heat treatment.

Table 22.2.2 shows the typical applications of the VOC concentrator.

Table 22.2.2. Typical applications of the VOC concentrator

Industry	Facilities	Treated VOCs
Automobile, Steel structure manufacturing	Painting booth	Toluene, xylene, esters, alcohols
Steel furniture	Painting booth, oven	Toluene, xylene, esters, alcohols
Printing	Dryer	Toluene, xylene, esters, alcohols
Adhesive tape Hook and loop fastener	Coating process Cleaning unit	Ketones (MEK, cyclohexanone, methyl isobutyl ketone, etc.)
Chemicals	Oil refinery, reactors	Aromatic hydrocarbons, organic acids, aldehydes, alcohols
Synthetic resin adhesive	Plastics Plywood manufacturing process	Styrene, aldehydes, esters
Semiconductor	Cleaning unit	Alcohols, ketones, amines

22.2.3 CONTINUOUS PROCESS FOR AIR CLEANING USING MACROPOROUS PARTICLES AS ADSORPTION AGENTS

In the photoresist segment of the semiconductor process a very low concentration of VOC is generated. These low concentration VOCs can be removed by a concentration step followed by a catalytic oxidation process. The industrial application of this method is discussed below. Dilute VOC is fed to the rotating zeolite concentrator discussed in Section 22.2.2 (honeycomb rotor) where it is concentrated to 10 times of the original concentration and burned on catalysts at relatively low temperature. This saves fuel cost. The VOC is a mixture of IPA, acetone, MEK, toluene, ethyl acetate, n-hexane, propylene glycol monoethyl ether, propylene glycol monoethyl ether acetate, and tetramethyl ammonium hydroxide. The mix-

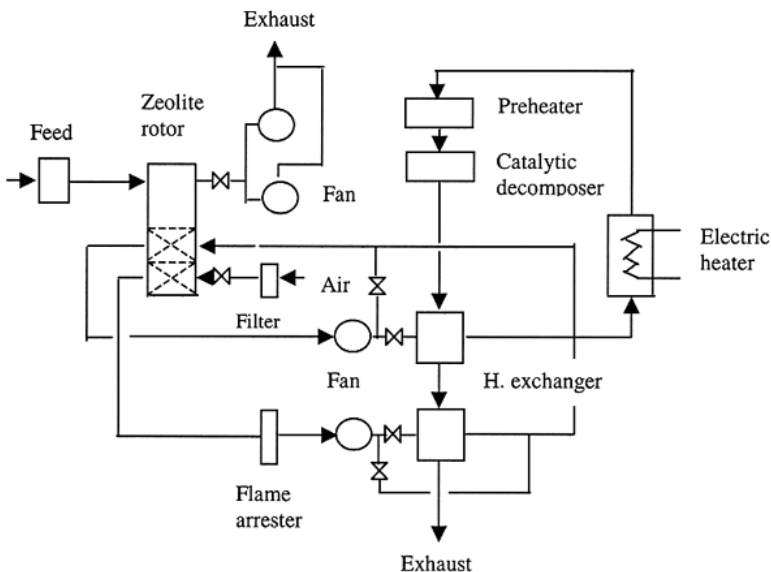


Figure 22.2.3. Flow diagram of continuous air cleaning process by zeolite concentrator.

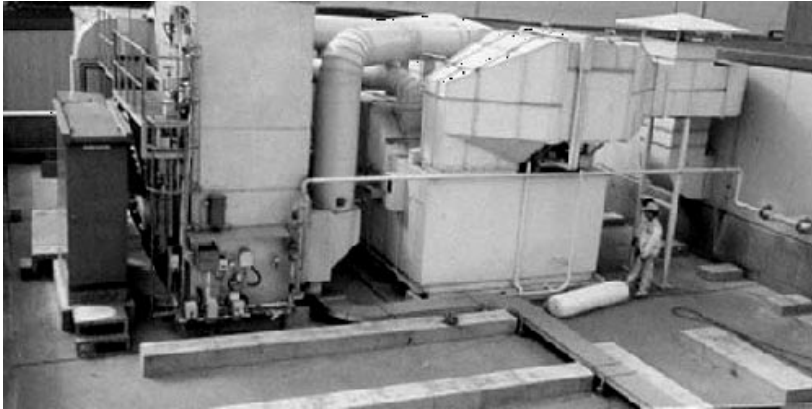


Figure 22.2.4. Continuous air cleaning unit by zeolite concentrator.

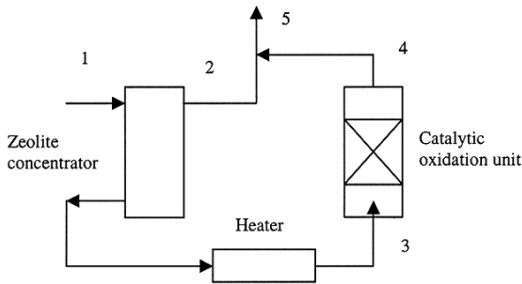


Figure 22.2.5. Block diagram. Continuous air cleaning process by zeolite concentrator.

ture is exhausted from the photoresist at approximately $100 \text{ Nm}^3/\text{min}$, 20°C and 60% RH. Figure 22.2.3 shows the process flow diagram. The VOC laden feed gas (exhausted from the photoresist) is pre-treated by filters in two steps, first by a bag filter and then by activated carbon. The former removes dusts and the latter removes any readily polymerizable vapors such as, acrylic acid, organic silicon compounds e.g. hexamethylene disilazane (HMDS), phosphorous-compounds and halogen-compounds which are all

catalyst poisons. The pretreated gas is fed to the zeolite honeycomb rotor for concentration. (Figure 22.2.4)

Table 22.2.3 shows measurements at the designated points in the block diagram (see Figure 22.2.5). VOC removal reached 91 % at outlet of the rotor and 98 % at outlet of the catalytic oxidation unit.

Table 22.2.3. Measurements according to block diagram (Figure 22.2.5). Continuous air cleaning process by zeolite concentrator

No.	Point of detection	Temp., $^\circ\text{C}$	Conc., ppm	Flow rate, Nm^3/min
1	Concentrator, inlet	26	430	102
2	Concentrator, outlet	33	40	116
3	Cat. oxidation, inlet	450	3,700	
4	Cat. oxidation, outlet	490	83	
5	Exhaust		39	

22.2.4 SOLVENT RECOVERY FROM HAZARDOUS WASTES

Table 22.2.4. Properties of cycloparaffins as a cleaning solvent

Property	Value
Appearance	transparent
Color (Seibolt)	+30
Specific gravity	0.839
Viscosity, 40°C Cst	1.6
Flash point, °C	76
Aniline point	58
Cycloparaffins content, %	80
Alkylbenzene content, %	10
Aromatics content, %	1

Table 22.2.5. Cleaning performance of solvents

Cleaning solvent	Oils	Residual oil, mg/cm ²
cycloparaffins	press oil	0.0017
	fan press oil	0.0015
	bender oil	0.0017
trichloroethane	press oil	0.0021
	fan press oil	0.0013
	bender oil	0.0013

The process was previously used for chlorine compounds represented by perchloroethylene and trichloroethylene and for fluorine compounds used for cleaning of press stamped metal parts. However, these compounds are now prohibited for use and production by environmental regulations. The current replacements include emulsions, organic and inorganic solutions, etc. Cycloparaffins originating from petroleum products were quali-

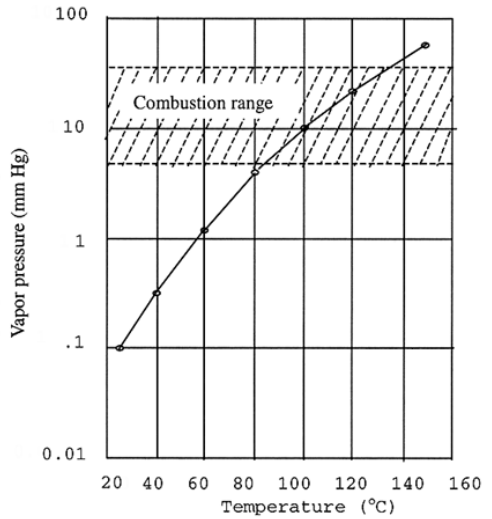


Figure 22.2.6. Vapor pressure and combustion range of cycloparaffins.

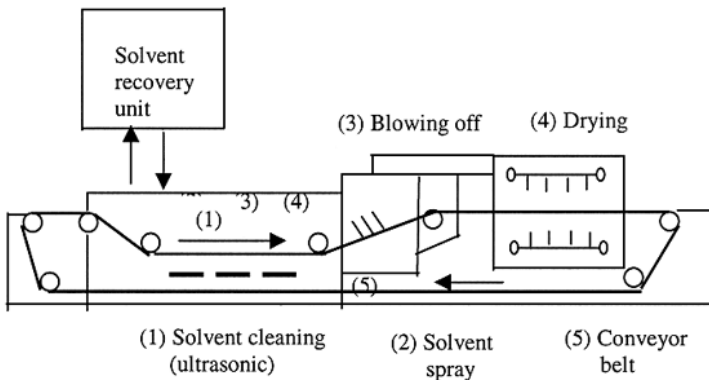


Figure 22.2.7. Metal parts cleaning employing cycloparaffins.

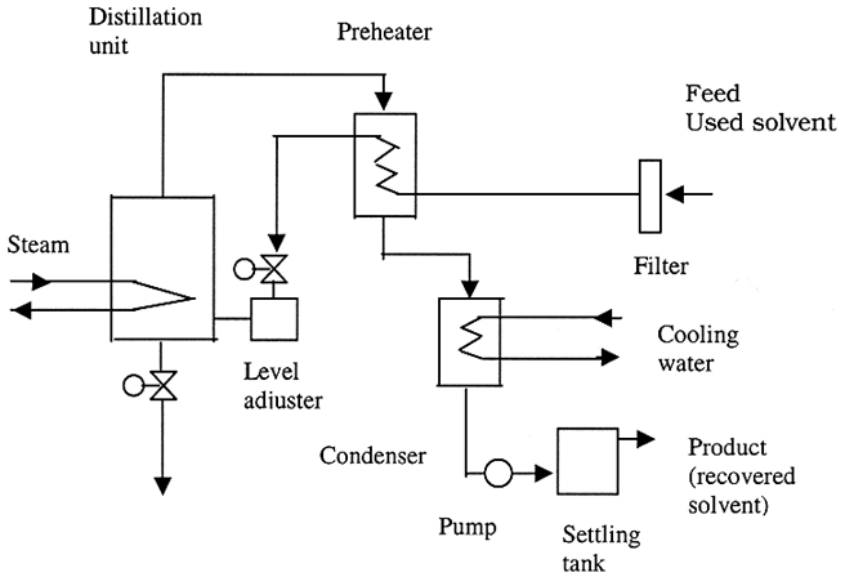


Figure 22.2.8. Flow diagram of solvent recovery process.

Table 22.2.6. Brief specification of the cycloparaffins recovery unit

Item	Specification
Solvent	cycloparaffins
Capacity	70 l/min
Dimensions	1,050 x 533 x 1,355 mm
Weight	250 kg (approx.)
Steam pressure	6.0 MPa
Steam consumption	25 kg/h
Cooling water	<30°C, >2MPa, >20 l/min

fied as a good cleaning solvent (see Table 22.2.4).

Table 22.2.5 shows the cleaning performance of the solvent. Figure 22.2.6 shows the vapor pressure and combustion range of the solvent. Figure 22.2.7 shows a process diagram of cycloparaffins solvent use in cleaning stamped metal parts. The solvent is recycled after recovery by distillation. Combining the cleaning and the distillation process gives a continuous process.

Figure 22.2.8 shows a schematic diagram of distillation process. Table 22.2.6 shows specification of the recovery unit.

22.2.5 HALOGENATED SOLVENT RECOVERY

22.2.5.1 Coating process

A process to recover ethylene dichloride, EDC, and methylene dichloride, MDC, using activated carbon fibers, ACF, is discussed in this section. The gas at approximately 50°C, containing EDC and MDC is received from a painting process. It is pretreated by a filter to remove dusts and passed through a heat exchanger to cool it down to approximately 30-40°C. The pre-treated gas is fed to adsorption columns filled with ACF where the gas is cleaned sufficiently for it to be safely released to atmosphere.

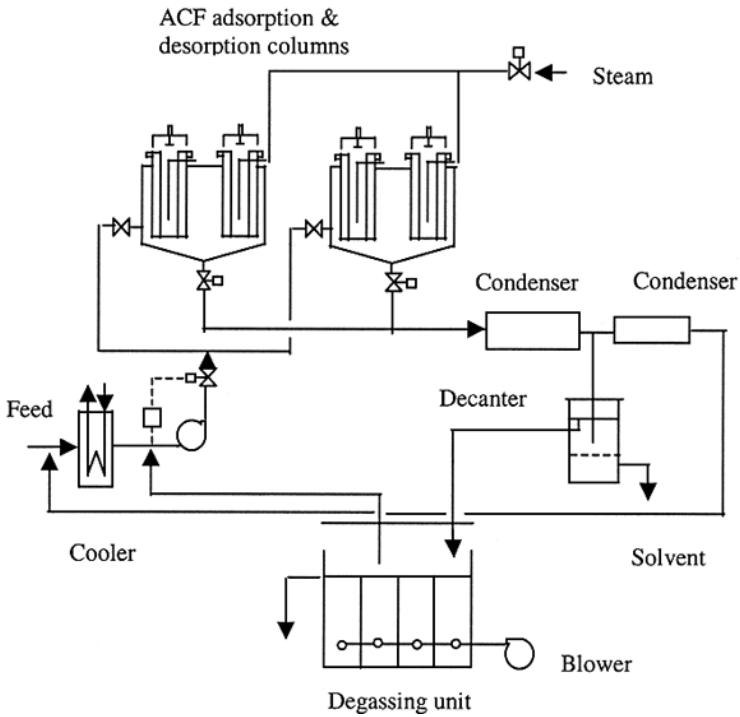


Figure 22.2.9. Flow diagram of ACF solvent recovery process.



Figure 22.2.10. ACF solvent recovery unit.

Figure 22.2.9 shows the process flow diagram. The process consists of two (or more) adsorption columns to ensure a continuous run of adsorption and desorption cycles. Figure 22.2.10 shows an industrial application of the system.

Table 22.2.7. Performance data for the ACF solvent recovery unit

Item	Operational & performance data
Flow rate	100 m ³ /min, 20°C
Solvent	
EDC	46.7 l/h
MDC	23.3 l/h
Gas concentration	
Inlet	2,900 ppm
Outlet	58 ppm
Adsorption efficiency	98 %
ACF specific surface area	900 - 2,000 m ² /g
Adsorption & desorption cycle	10 min

The desorption is done by steam. The desorbed stream is fed to a series of two condensers in which both the steam and solvent are condensed. The condensate is fed to a decanter to separate water and solvent by gravity. Water containing approximately 1-2% solvent is fed to a degassing unit and the vaporized solvent is joined to the feed. The decanted solvent is refined, stored in a tank, analyzed, and adjusted to its appropriate EDC/MDC ratio. The refined solvent is recycled for painting.

Water from the degassing unit contains solvent in a concentration relative to the solvent's solubility. For example, if the solubility of perchloroethylene in water is designated as 1, the relative solubility of EDC in water would be 58 and of MDC in

water would be 88. In degassing at 60°C and 180 l/min x 30 min the residual EDC content in water is brought below 0.01 ppm (the environmental standard limit is 0.04 ppm) but in the case of MDC it remains a problem to reach to the environmental standard of 0.2 ppm. A treatment by activated carbon may be one of the solutions. Table 22.2.7 shows performance data in the industrial application.

The performance of the ACF solvent recovery process can be summarized as follows: Since ACF has larger surface area and smaller bulk density than particulate activated carbon, PAC, ACF's filling density becomes 1/10 of PAC's.

Advantages:

- *High recovery rate* - The solvent recovery rate of the ACF process is higher than that of the PAC, especially in the case of lower boiling point solvents, such as, MDC, benzene, trichloroethane, etc.
- *High quality* - ACF has low catalytic activity and a short adsorption and desorption cycle time (approx. 10 min). The solvent is less decomposed in the process. In the recovery of chlorine-containing solvents, it produces less acids as decomposition products. Thus it is less corrosive to the materials of construction. Also, the recovered solvent is of better quality.
- *Broader application* - It is applicable to polymerizing monomers and high boiling point compounds.
- *Light weight, compact and safe* - The process unit can be compact because of the short adsorption and desorption cycles and it is safer because there is less heat accumulation.
- *Energy savings* - The process needs less steam consumption in the adsorption and desorption.

Disadvantages:

- *Less flexibility regarding capacity* - ACF's filling volume cannot be readily changed.

- *Difficult in decreasing outlet temperature* - The short cycle in adsorption and desorption makes the cooling process difficult to synchronize.
- *Expensive* - ACF are more expensive than PAC, thus the unit modification cost is more expensive.

22.2.5.2 Tableting process of pharmaceutical products

In a process which produces tablets, a mixture of solvents, containing MDC and methanol and binders is used. Solvents are emitted from the tableting unit. The following process is used to recover the emitted solvent.

Feed gas at 50°C from the tableting process is pre-treated by a filter to remove dusts and by a rotary wet scrubber to absorb mainly methanol. During the scrubbing MDC also dissolves in water, although at low concentration. This water is treated in two steps, by a degassing unit at room temperature and by an activated carbon filter so that the concentration of residual solvents is decreased below that of the environmental standard. The gas from the degassing unit is joined to the feed gas at the outlet of the demister of the MDC recovery unit. The gas, the pretreated feed, and gas from the degassing are cooled down to 30 - 40°C before feeding to the MDC recovery unit which consists of at least two columns for adsorption and desorption cycles. After processing the gas is released to the atmosphere.

Because little methanol is vaporized at room temperature, the water stream is fed to another degassing unit heated to 65°C to vaporize methanol. For safety purposes, the degassing air flow rate is controlled at 10 m³/min. The methanol laden gas from the heated degassing unit is fed to a catalytic oxidation unit where methanol is decomposed before exhausting the gas stream to the atmosphere. Table 22.2.8 shows the process performance.

Table 22.2.8. Performance of the solvent recovery in the tableting process

Item	Performance
Flow rate at rotary scrubber	1,000 l/min
Feed concentration	MeOH 10,000 ppm MDC 2,000 ppm
Exhaust concentration	MeOH 150 ppm MDC 3 ppm
Catalytic oxidation flow rate	10,000 l/min
Feed concentration	MeOH 8,500 ppm MDC 1 ppm
Exhaust concentration	MeOH 10 ppm

This is a unique example of a process in which the recovery and the catalytic oxidation steps are combined. In addition to its use in the pharmaceutical industry, the adsorption is a suitable method for the separation of chlorine-containing solvents. Figure 22.2.11 shows the process flow diagram.

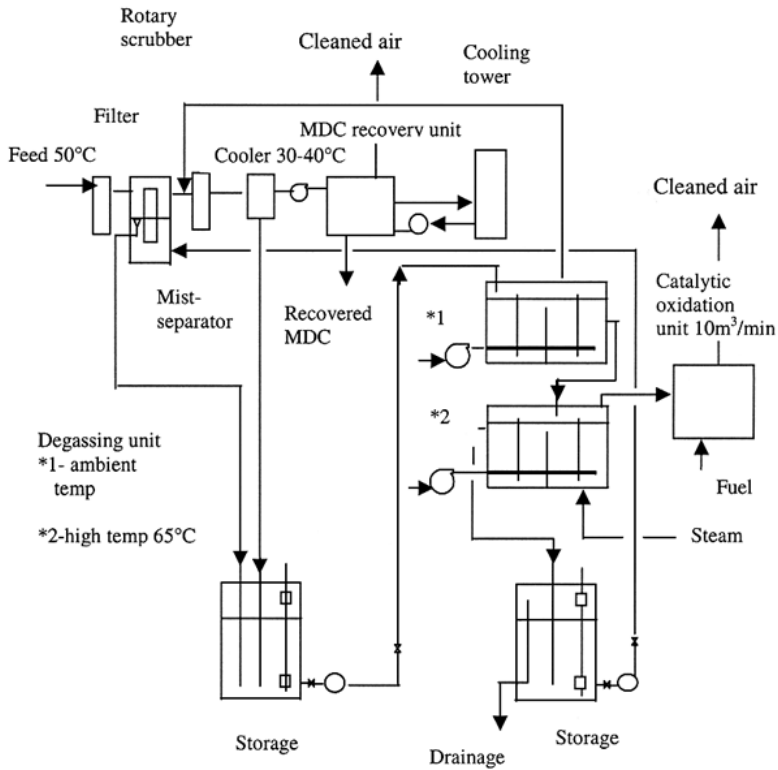


Figure 22.2.11. Flow diagram of tablet binder recovery process.

22.2.6 ENERGY RECOVERY FROM WASTE SOLVENT

Table 22.2.9. Specifications of the VOC oxidation unit

Type of unit	Direct firing
Total gas flow rate	2,000 kg/h
Solvent flow rate	160 kg/h
Solvent	Acetone, methanol, IPA
Feed temp.	60 - 100°C
Oxidation temp.	800 °C
Performance, THC meter	97 %
Supplemental fuel	Heavy oil, max170 l/min

Table 22.2.10. Specifications of the waste heat boiler

Type of unit	Horizontal, multi-tube
Use for	Steam as heating medium
Waste gas flow rate	5,000 Nm ³ /h
Temp., waste gas	Inlet: 800, outlet: 350°C
Supply water temp.	20°C
Steam generated	1,300 kg/h

It is not always economically justified to recover solvents if they are at very low concentrations and in mixtures. It may be more economical to burn the solvent blend in a boiler to save fuel. Tables 22.2.9 and 22.2.10 contain the specifications of industrial combustion units.

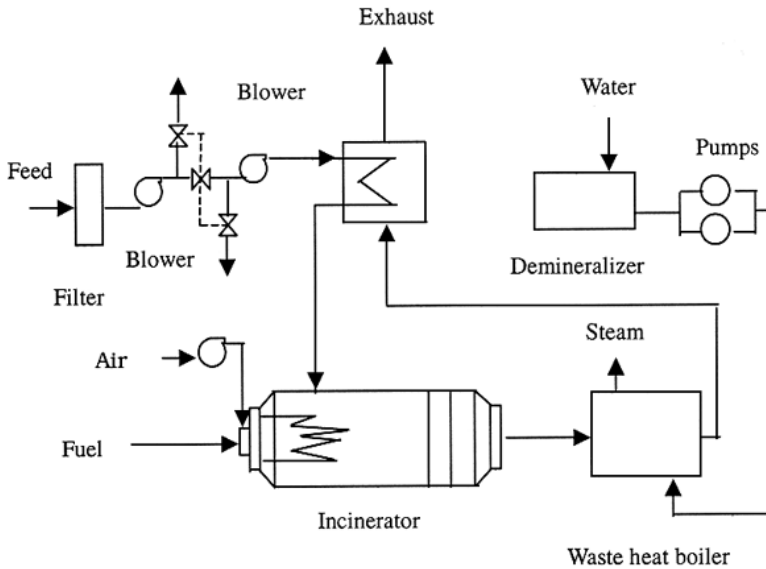


Figure 22.2.12. Flow diagram of energy recovery process.

Savings of energy

The net calorific values for acetone, methanol and IPA is 6,962, 5,238 and 7,513 kcal/kg, respectively, and the simple mean value of their mixture is 6,600 kcal/kg. Let us assume that solvents are generated from a process at a maximum rate of 160 kg/h. The total heat generation of the VOC oxidation unit is as follows:

$$6,600 \times 160 = 1,056 \times 10^3 \text{ kcal/h}$$

Heavy oil = 10,200 kcal/kg; specific gravity of heavy oil = 0.86

The saved energy is as follows:

$$1,056 \times 10^3 / 10,200 = 103.5 \text{ kg/h}$$

$$103.5 / 0.86 = 120 \text{ l/h [1]}$$

If no solvent is supplied, the required heavy oil is 170 l/h [2]

If solvent is supplied at max. rate, the required heavy oil is only 50 l/h.

$$[1] - [2] = 50 \text{ l/h}$$

Thus, energy saving performance is 71% ($[1]/[2] \times 100 = 71\%$)

Figure 22.2.12 shows the process flow diagram and Figure 22.2.13 shows an industrial application of the energy recovery unit.

The VOC laden gas from a painting plant is supplied through a filter and is blown to a heat exchanger and then to succeeding units. The fan drive motors are controlled by inverters to adjust the flow rate. In the heat exchanger the feed is preheated with a waste heat boiler's off gas, at a temperature of 350°C, to 60 - 100°C before it is fed to a VOC oxidation unit. In the oxidation unit, heavy oil and VOC are mixed and burnt. At approximately 800°C, VOC is burnt out with yield of more than 97%. The off gas at 800°C is fed to a waste heat boiler where it generates 1,300 kg/h steam at 8 MPa. The heat transfer gas at 350°C is used for the preheating the feed gas.



Figure 22.2.13. Energy recovery unit.

REFERENCES

- 1 T.Takahashi and S.Ito, *Kogyo Toso*, No. **150**, 75-79, 1998.
- 2 Seibu Giken's Catalog. VOC Concentrator (1997).

22.3 SOLVENT TREATMENT IN A PAINTS AND COATING PLANT

DENIS KARGOL

OFRU Recycling GmbH & Co. KG, Babenhausen, Germany

The Swiss coating manufacturer Karl Bubenhofer AG was planning to acquire various wash plants for cleaning batch, mixing and multi-trip containers efficiently. The contaminated solvents obtained during the wash process were then to be treated automatically by distillation. The distillation plant had to have a suitable output, operate continuously and be simple to operate. Another requirement was the ability to combine this plant with the wash plants in a new building complex. A distillation plant suitable for this purpose was supplied by OFRU Recycling in Babenhausen/Germany.

Karl Bubenhofer AG, known by the name, "Kabe-Farben", is regarded as one of the largest paint and coating producers in Switzerland and has been producing coating materials since 1926. The product range covers architectural paints and plasters, powder coatings and industrial liquid paints. The company's wide range of customers includes industrial, commercial and contract paint companies as well as resellers at home and abroad.

Kabe offers a special service in cooperation with regional painters' associations. For a small charge customers and painters can offload their waste paints and contaminated solvents to Kabe in special multi-trip containers. About 160 tonnes per year of spent solvents



Figure 22.3.1. Soiled multi-trip container.

are obtained by way of this disposal system. Even before the planning phase, these contaminated spent solvents were treated with the company's own small distillation plant.

Until now, manual cleaning of these multi-trip containers and large batching and mixing vessels from production was particularly inconvenient and labor-intensive for Kabe. A wash plant for mobile large containers (250-1800 l volume) and for small drums/pails (about 80-100 per day) would obviate the unpleasant manual cleaning task in the future. A combination of container wash following by distillation therefore seemed very practicable. The treated clean solvent would feed the wash plants and ensure thorough cleaning. The company was also interested in further processing a part of the distillate for Kabe products.

When the solvent requirement of the container wash plant and the customers's spent solvent quantities were added together, the total was about 200 tonnes of contaminated solvents per year. Solvents such as toluene, ketones, esters, ethyl acetate, xylene, glycol and petroleum spirits were to be separated almost completely from solids such as alkyd, 2-pack, epoxy and polyester resins.

The solvent recovery plant had to meet the following requirements:

1. Combination with wash plants and storage tanks
2. Distillation with a high rate of recovery
3. Continuous operation (24 hour)
4. Distillation output of 200-400 l/h
5. Low maintenance
6. Minimum operating and control times
7. Residue to be contaminated only slightly with residual solvent

Kabe-Farben found the solution Rio Beer, a wash plant producer from Switzerland. Rio Beer supplied not only the wash plant design but also integrated OFRU Recycling from Babenhausen in Germany with its solvent recovery plants. OFRU Recycling provided the necessary expertise from the paints and coatings sector.

Kabe-Farben visited the OFRU pilot plant in Babenhausen and was able to recover 224 kg of clean solvent within a few hours from 300 kg of contaminated solvent. A quantity of 76 kg of solid paint slurry was then discharged from the distillation unit. An analysis afterwards showed that the residue contained only 5.5% solvent. More than 74% of the solvent could therefore be recovered in the first instance.

The solution

Kabe decided in favor of a vacuum evaporator with an integrated stirrer. The ASC-200 model together with three solvent tanks stand together in an explosion-proof room. The cus-

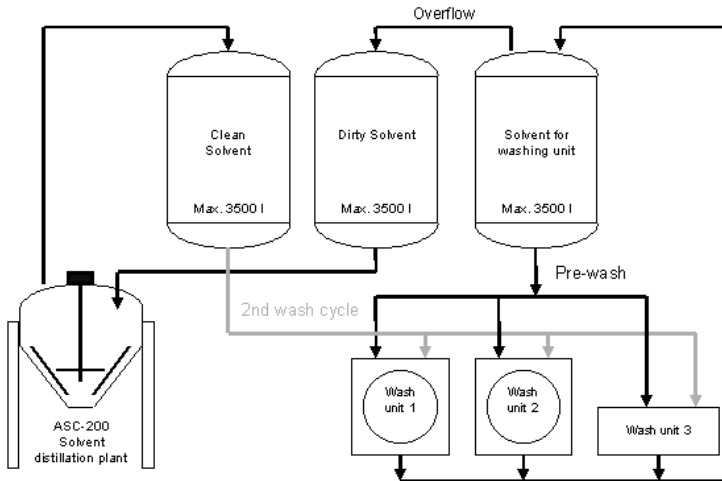


Figure 22.3.2. Solvent circuit and treatment.



Figure 22.3.3. Wash plant for mixing vessels.

tomers' contaminated spent solvents are poured in through a large sieve by means of a drum tilting device. Twin diaphragm pumps then convey the contaminated solvent to the first soiled solvent tank. In view of the large proportion of paint in the solvent (5-20 vol.%), the solvent is kept homogeneously in motion in the tank by means of the stirrer. Another soiled solvent tank is connected up to the wash circuit and supplies the solvent for pre-washing.

The ASC-200 model used by Kabe operates entirely under vacuum. A considerable increase in capacity is achieved by means of the vacuum equipment; moreover, distillation is milder and residue is largely solvent free.

The contaminated product is introduced automatically by suction into the evaporator by means of a magnetic valve and the vacuum until it reaches the height of a capacitive level controller, which keeps the solvent level constant during continuous operation. The filling operation is adjusted in such a way that no excessive cooling or interruption in the distillation process takes place.

The solvent is usually heated by means of a double jacket with its own thermal oil facility. Kabe, on the other hand, operates a catalytic waste air purification plant. The solvent-air mixture obtained in the plant is converted catalytically to heat and stored as an energy store. A small portion of the heat thereby obtained is absorbed in our case by a thermal oil system and released to the distillation plant.

A stirrer is fitted inside the ASC-200 distillation plant. Its scrapers rotate inside the inner wall of the vessel. They keep the heat transfer surface free from encrustation and guarantee uniform heat transfer into the boiling solvent. The stirrer keeps the liquid in motion



Figure 22.3.4. ASC-200 distillation plant in the explosion-proof room.

days. Distillation of the bottom product takes place independently afterwards. After the residue has been thickened to a predetermined viscosity, the equipment shuts down automatically. The still is drained by means of a discharge valve at the bottom of the cone. The 200-300 kg of compact greyish residues are transferred to 20 completely empty 20 liter plastic pails and then fed to an inexpensive solid waste incineration process. No further cleaning operations are required at the plant so the stirred distillation unit is ready for use again immediately.

The plant used at Kabe treats about 200 liters of solvent per hour. At about 200 tonnes per year it is therefore being used to 60-70% of its capacity at present. Since its installation, the distillation plant has been operating for 5 days per week with very little maintenance. A few mechanics maintain the plant twice a year without external support.



Figure 22.3.5. Residue transferred to PE pail.

and thereby promotes evaporation of the solvent. Finally, the solvent vapor reaches a water-cooler tubular condenser provided with a cooling water control unit. The condensed, clean distillate is pumped from here to the distillate tank. This tank has a level control and now feeds the clean solvent directly into the wash plant for a second wash. The distillation process takes place fully automatically and lasts about 2

22.4 APPLICATION OF SOLAR PHOTOCATALYTIC OXIDATION TO VOC-CONTAINING AIRSTREAMS

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22.4.1 SOLVENT DEGRADATION BY PHOTOCATALYTIC OXIDATION

Photocatalytic solvent oxidation had been demonstrated at the pilot scale in two recent field tests located at McClellan Air Force Base (AFB) in Sacramento, California and at the Fort Carson U. S. Army Installation in Colorado Springs, Colorado (Watt et al., 1999; Magrini et al., 1998). The objective of the tests was to determine the effectiveness of solar-powered photocatalytic oxidation (PCO) treatment units for destroying emissions of chlorinated organic compounds (trichloroethylene and dichloroethylenes) from an air stripper at ambient temperature and destroying paint solvent emissions (toluene and MEK) from a painting facility at higher temperatures. Goals for field testing these solar-driven systems were to gather real-world treatability data and establish that the systems maintained performance during the duration of the testing.

The photocatalytic oxidation process can effectively destroy hazardous organic pollutants in air and water streams. Although treatment systems will vary depending on the type of stream being treated, the basic process remains the same. The key ingredient is the photoactive catalyst titanium dioxide (TiO_2), which is an inexpensive, non-toxic material commonly used as a paint pigment. When TiO_2 is illuminated with lamps or natural sunlight, powerful oxidizing species called hydroxyl radicals form. These radicals then react with the organic pollutant to tear it apart and ultimately form carbon dioxide (CO_2) and water (Phillips and Raupp, 1992). When halogenated organics are treated, dilute mineral acids like HCl form. The process works at both ambient and mildly elevated temperatures ($>200^\circ\text{C}$) (Fu et. al., 1995; Falconer and Magrini, 1998).

Researchers throughout the world have been investigating PCO as an advanced oxidation technology for treating air and water streams contaminated with a variety of organic and inorganic compounds (Blake, 1996; Cummings et al., 1996). The susceptibility of an organic species to complete oxidation is typically reported in terms of photoefficiency, defined as the number of molecules of contaminant oxidized to carbon dioxide, water, and simple mineral acids divided by the number of photons incident on the catalyst. These values vary widely, depending on the reactor design, catalyst geometry and the compound of interest.

Much of the work on photocatalytic oxidation focuses on treating the halogenated organics trichloroethylene (TCE) and perchloroethylene, contaminants commonly found in ground water sources. These compounds and other chlorinated ethylenes typically react rapidly with TiO_2 and photons at efficiencies greater than 100%. These rates are likely due to chain reactions propagated by chlorine radicals (Luo and Ollis, 1996; Nimlos et. al. 1993; Yamazaki-Nishida, 1996). Paint solvent emissions generally consist of toluene, xylenes, ketones and acetate vapors. Measured photoefficiencies for benzene and other aromatic compounds like toluene are typically less than 5% (Gratson et. al., 1995; d'Hennezel

and Ollis, 1997). Besides exhibiting low photoefficiencies, aromatic species tend to form less reactive, nonvolatile intermediates during gas phase PCO. These intermediates build up on the catalyst surface and block or inhibit the active catalytic sites for further reaction (Larson and Falconer, 1997). The addition of heat and small amounts of platinum to the TiO_2 catalyst overcome these problems (Falconer and Magrini, 1998; Fu *et al.*, 1996). Oxygenated organics such as ethanol and acetone have photoefficiencies typically around 1%-10% (Peral and Ollis, 1992).

Several field demonstrations of PCO using sunlight to treat groundwater contaminated with TCE have been reported (Mehos and Turchi, 1993; Goswami *et al.*, 1993). These field tests found that nontoxic constituents in the water can non-productively react with or "scavenge" the photogenerated hydroxyl radicals and reduce the rate of the desired reaction. Common scavengers such as humic substances and bicarbonate ions increase treatment costs for the technology (Bekbolet and Balcioglu, 1996). Turchi and co-workers, (1994) found that by air stripping the volatile contaminants from the water stream, the regulated compounds at many contaminated sites could be transferred to the air, leaving the radical scavengers behind. The water can then be safely discharged and the air effectively treated with PCO. The improved photoefficiency reduces treatment costs and more than offsets the added cost of air stripping these contaminants from water. Read *et al.*, (1996) successfully field tested a lamp-driven, PCO system on chloroethylene vapors from a soil vapor extraction well located at DOE's Savannah River Site. Magrini *et al.*, 1996, and Kittrell *et al.*, 1996, both used modified TiO_2 catalysts and lamp-driven reactors to treat VOCs representative of semiconductor manufacturing and contact lens production, respectively. 1,2-dichloroethane, stripped from contaminated groundwater, was successfully treated in a pilot scale PCO demonstration at Dover AFB (Rosansky *et al.*, 1998).

The second field test assessed PCO to treat paint solvent vapors. Painting operations for military and civilian vehicles are conducted in ventilated enclosures called paint booths. Filters in the exhaust ducts trap paint droplets from the paint overspray while the VOC-laden air is typically exhausted through roof vents. The vent emissions can contain several hundred parts per million (ppm) of the paint solvents, which continue to evaporate from the vehicle after painting is complete. Most types of paint generally contain significant amounts of VOCs such as toluene, a suspected carcinogen, as well as other hazardous solvents such as methyl ethyl ketone, methyl isobutyl ketone, hexanes, xylenes, n-butyl acetate, and other components in lesser amounts.

Current technologies for treating these emissions include catalytic combustion of the vapors over supported Cu and Cr-oxides at temperatures of 350°C (Estropov *et al.*, 1989); air-flow reduction and recirculation strategies (Ayer and Darvin, 1995); and regenerative thermal oxidation at near incineration temperatures (Mueller, 1988). The use of platinumized TiO_2 and temperatures of 180-200°C provide significant energy savings in treating these emissions. Our goals for testing the paint booth emissions was to gather real-world treatability data and establish that the system maintained performance during the duration of the testing.

22.4.2 PCO PILOT SCALE SYSTEMS

22.4.2.1 Air stripper application

Figure 1 shows a schematic of the pilot-scale system used at McClellan AFB. This system, scaled from an optimized laboratory reactor, was fabricated by Industrial Solar Technology

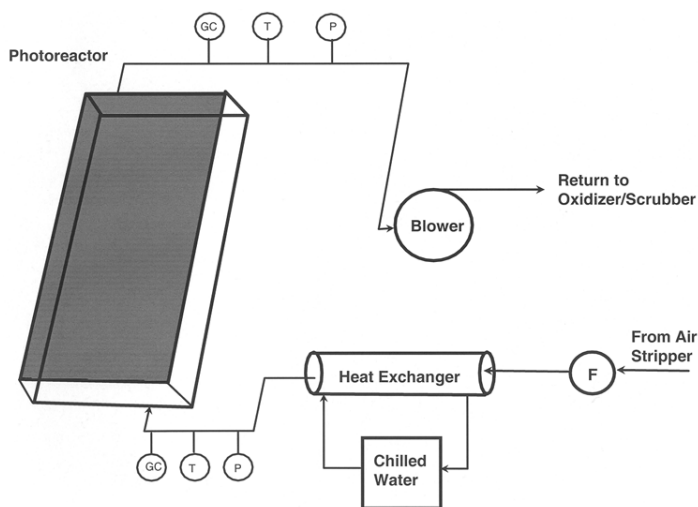


Figure 22.4.1. Schematic of the 10 SCFM solar photoreactor system used at McLellan AFB.

Corporation (Golden, CO). The reactor, 1.22 m wide by 2.44 m, consisted of a fiberglass-reinforced plastic I-beam frame. A transparent fluoropolymer film, treated to accept adhesives, formed the front and back windows of the reactor. The film windows were attached to the reactor frame with foam tape coated on both sides with an acrylic adhesive. The catalyst, titanium dioxide (Degussa P25), was coated onto a structured, perforated polypropylene tubular packing commonly used in oil-water separators. The TiO_2 was suspended in water as a slurry and sprayed onto the tubular supports with a new paint sprayer until the supports were opaque. Fluid modeling of airflow through the reactor showed that a 5.1 cm PVC manifold, located at the inlet and outlet of the reactor, would provide an even flow distribution. Small (0.6 cm) holes, drilled into the manifold at one inch intervals, provided the even flow distribution required for efficient contact of the contaminated air with the catalyst.

A two-inch diameter pipe from the outlet of the air stripper supplied the contaminated air stream to the reactor. The air stream was first passed through to a tube-in-shell heat exchanger for partial dehumidification. A chiller circulated 2°C ethylene glycol through the tube side of the heat exchanger. Chilling, which reduced the relative humidity of the air stream from near saturation to less than 20% at 20°C, was required because high humidity reduces the TCE destruction rate, likely because of competitive adsorption between moisture and TCE molecules at the catalyst surface (Fan and Yates, 1996). By lowering the humidity to less than 20% (@ 20°C), the reaction rate was sufficient to ensure complete TCE destruction. This effect was observed by Hung and Marinas (1997) in a lamp-illuminated annular reactor in which TCE conversion was not affected by relative humidity up to 20%; conversion deteriorated as the humidity level reached saturation. Laboratory tests of the system demonstrated that at TCE concentrations of near 100 ppmv, less than 15% of the TCE in the airstream transferred to the condensate formed in the heat exchanger. The condensate (approx. 1-2 liters per day) could be fed back into the air stripper for treatment.

On the reactor, GC sample ports and temperature and pressure sensors provided monitoring of reactor inlet and outlet VOC concentrations and temperature and pressure drop throughout the system. A portable gas chromatograph provided on-line VOC organic anal-

ysis of the inlet and outlet air streams. A portable light intensity monitor was used to measure the global horizontal light intensity at the surface of the photoreactor. The calibrated radiometer was mounted on the reactor framework which faced south at an angle of 40° to the horizon. Two blowers in series were used to draw contaminated air into the system. The blowers were located at the end of the air handling system so that the entire system was maintained under slight negative pressure. Because TCE oxidation can produce intermediates such as phosgene, (Nimlos *et. al.*, 1993; Read *et. al.*, 1996; Fan and Yates, 1996), keeping the system under vacuum prevented release of any toxic vapors. The exhaust gases from the blower were returned for final treatment by a caustic contacting tower. Any hydrochloric acid and phosgene formed from TCE oxidation were neutralized and hydrolyzed respectively by the caustic scrubber.

The contaminated airstream provided by the air stripper unit contained volatile organic compounds as analyzed from Summa canister tests by Air Toxics, Ltd. using EPA method TO-14. These compounds, listed in Table 22.4.1, consisted primarily of trichloroethylene and trace quantities of dichloromethane, 1,1-dichloroethene, cis-1,2-dichloroethane, chloroform, carbon tetrachloride, and benzene. The other compounds present in the outlet presumably formed during treatment.

Table 22.4.1. Results from the Summa canister tests of inlet and outlet reactor air streams during the McClellan tests. The two inlet and two outlet samples were taken sequentially and represent approximately replicate samples

Compound	Inlet 1, ppbv	Inlet 2, ppbv	Outlet 1, ppbv	Outlet 2, ppbv	Detection limit, ppbv
Chloromethane	ND	ND	4.8	4.1	1.5-30
Dichloromethane	36	36	30	32	1.5-30
1,1-Dichloroethane	ND	ND	17	17	1.5-30
1,1-Dichloroethene	200	200	ND	ND	1.5-30
cis-1,2-Dichloroethane	220	240	6	2.2	1.5-30
Chloroform	250	260	280	280	1.5-30
Carbon tetrachloride	700	730	790	790	1.5-30
Benzene	170	190	120	110	1.5-30
1,2-Dichloroethane	ND	ND	12	ND	1.5-30
Trichloroethylene	13000	13000	660	280	1.5-30
Acetone	ND	ND	84	69	9.8-120
1,4-Dioxane	ND	ND	10	ND	9.8-120

22.4.2.2 Paint booth application

For the paint solvent application, a slipstream of a paint booth vent located at Fort Carson was analyzed to determine the components present with rapid scan gas chromatograph. On any operational day, several paint types are sprayed. The solvent emissions content thus varies during painting operations. In general, the amounts and types of solvent emissions from the Fort Carson paint booth are listed in Table 22.4.2.

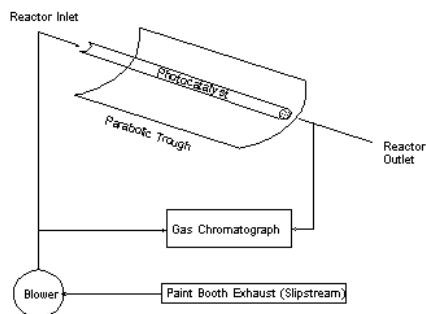


Figure 22.4.2. Schematic of the 10 SCFM parabolic trough, solar photoreactor system used at Fort Carson U. S. Army Installation.

Table 22.4.2. Breakdown of solvent emissions from painting operations at Fort Carson in 1994. VOC refers to volatile organic compounds, HAP to hazardous air pollutants, MEK to methyl ethyl ketone, and MIBK to methyl isobutyl ketone

Paint Type	Total usage, l/yr	VOC, lbs/yr	HAP, lbs/yr	MEK, lbs/yr	Toluene, lbs/yr	MIBK, lbs/yr	Xylene, lbs/yr
Solvent base	19,656	110,074	5405	3931	491	0	983
Thinner	983	7235	722	552	0	174	0

A small field test system, consisting of a photoreactor packed with Degussa TiO₂-coated glass beads, was used to assess treatability of the slipstream and provide design data for the pilot scale system. The small reactor operated with a flow rate of 20 liters/minute provided by a pump connected to the paint booth exhaust vent line and variable reactor temperature (ambient to 200°C). Inlet and outlet VOC concentrations were simultaneously measured by two gas chromatographs directly connected to both lines. This arrangement provided real time monitoring of the inlet and outlet VOC concentrations during painting operations.

The resultant treatability data was used to size a 5-SCFM pilot-scale system (Figure 22.4.2) also built by Industrial Solar Technologies. This system consists of a parabolic trough reflector to focus incident sunlight onto a receiver tube containing the catalyst. The trough has a 91 cm aperture width and is 243 cm long. The reflective surface is covered with SA-85 (3M Company), a polymer film that reflects greater than 90% of the incident radiation onto the catalyst tube, providing both heat and light for reaction. The catalyst-containing receiver tube is a 3.81 cm I.D. borosilicate tube packed with 1.9 cm ceramic berl saddles coated with 2.0 wt% platinum on TiO₂. A higher weight loading of platinum was used in the field test because of the variable VOC composition of the paint booth stream. Operating temperatures of 200°C were obtained, depending on cloud cover, during most of the day. Note that a thermally heated, lamp-illuminated system will provide similar performance as the solar-based system described here. The reflective trough rotates around the fixed receiver tubes by means of a gear motor. A control and photodiode arrangement activate the gear motor, permitting the trough to track the sun throughout the day. Paint booth emissions were sampled directly from the exhaust stream via 10.1 cm aluminum ducting. On-line analysis of the inlet and outlet concentrations was provided by sample lines connected to the MTI gas samplers. Reactor temperature and inlet flows were measured continuously.

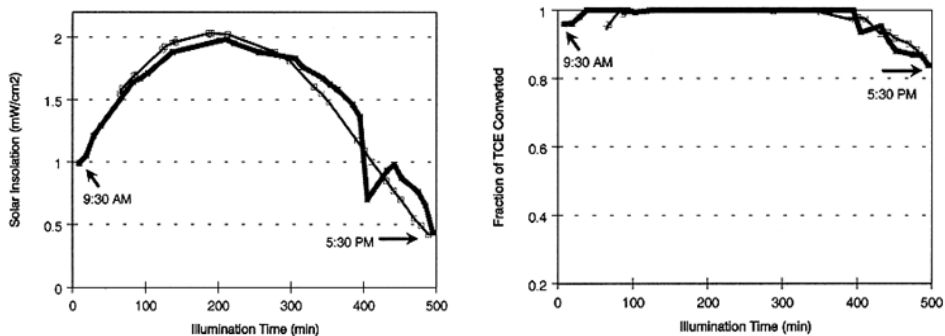


Figure 22.4.3. Solar insolation (left) and fractional TCE conversion (right) versus illumination time. Flow rate and relative humidity of the incoming air stream was 10 SCFM at 20% RH. Data taken on April 8-9, 1997.

22.4.3 FIELD TEST RESULTS

22.4.3.1 Air stripper application

The field test at McClellan AFB took place during a 3-week period in April, 1997. System operating conditions included two flow rates (10 and 20 SCFM) and variable light intensity. The photoreactor system, designed to perform optimally at 10 SCFM with natural sunlight, was also operated at 20 SCFM to challenge the system. Because of varying solar illumination levels during the day, the system can operate for longer periods at lower flow rates. Residence times in the reactor at 10 and 20 SCFM were 0.50 sec and 0.25 sec, respectively.

Figure 22.4.3 shows TCE conversion and UV intensity versus illumination time at 10 SCFM for two days of operation. UV intensities were measured with a UV radiometer (UHP, San Gabriel, CA, Model UHX). TCE inlet concentrations varied from 10-15 ppmv. Detection limits for the gas chromatograph were measured at 0.5 ppmv. Figure 22.4.3 indicates that conversions greater than 95% at 10 SCFM are achieved with UV intensities at or greater than 1.5 mW/cm². At 10 SCFM, continuous destruction greater than 95% was achieved for at least 6 hours per day on two clear days in April at this latitude (37°N). The length of operation for a solar-driven system will vary with time of year, latitude, and altitude due to the effect each parameter has on available solar-UV intensity.

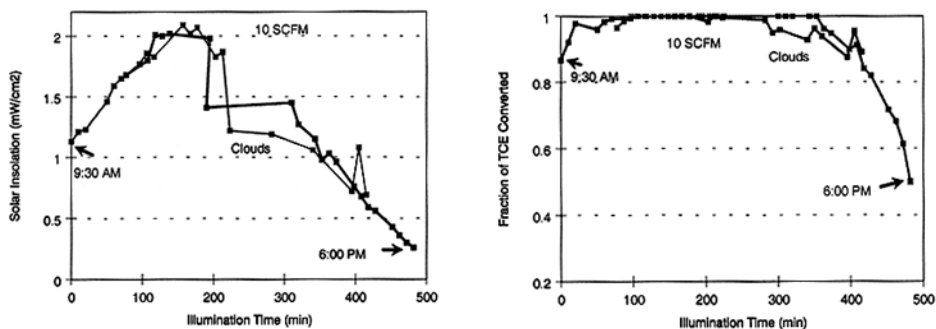


Figure 22.4.4. Solar insolation (left) and fractional TCE conversion (right) versus illumination time during periods of partial cloud cover. Flow rate and relative humidity of the incoming stream was 10 SCFM and 20% RH. Data taken on April 7 and April 16, 1997.

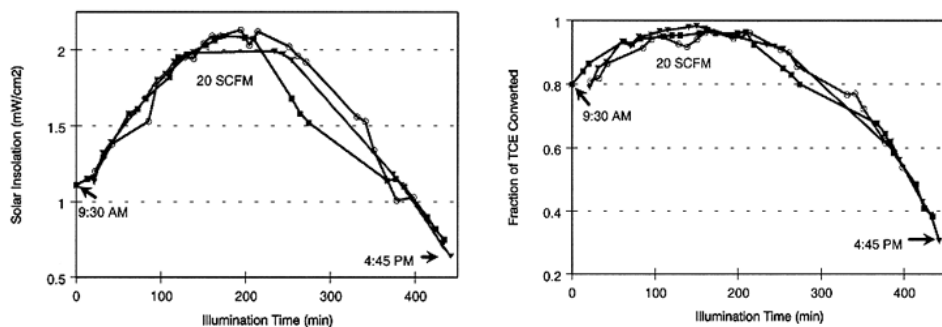


Figure 22.4.5. Solar insolation (left) and fractional TCE conversion (right) versus illumination time. Flow rate and relative humidity of the incoming air stream was 20 SCFM at 20% RH. Data taken on April 10, 14, and 15, 1997.

Figure 22.4.4 shows the effect of clouds on solar insolation (left) and TCE conversion (right) as a function of illumination time at 10 SCFM for two separate days. Again TCE conversions greater than 95% were obtained when the insolation levels were greater than 1.5 mW/cm². In general, clear skies had UV intensities of 2 mW/cm² or better. Haze and high clouds reduced the intensity to 1.5 mW/cm², and thicker clouds reduced available intensity to about 1 mW/cm². Conversions greater than 90% were still achievable during periods of significant cloud cover due to the photoreactor's ability to use global horizontal (diffuse) UV illumination.

TCE conversion versus solar insolation for three days of operation at 20 SCFM is shown in Figure 22.4.5. Doubling the flow rate halves the residence time of the gas in the photoreactor. Conversions greater than 95% are achieved with UV intensities greater than 2.0 mW/cm². The reproducibility of TCE conversion indicates that the little or no catalyst deactivation occurred during the three weeks of testing.

Pooling all of the data taken at the two flow rates provides a relation between TCE conversion and UV intensity (Figure 22.4.6). Significant scatter, which exists for both flow rates, is likely due to the rapidly varying UV intensity levels during cloud events. The variable illumination makes it difficult

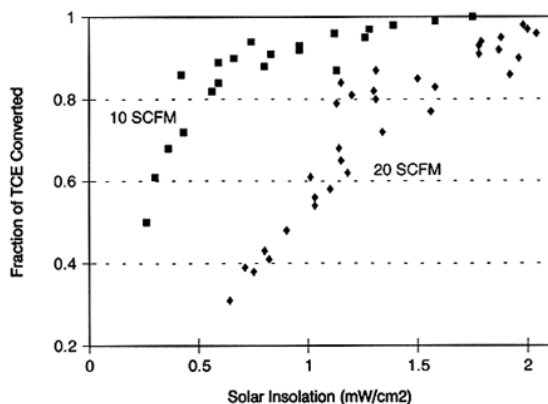


Figure 22.4.6. Pooled UV intensity versus TCE conversion data for all 10 SCFM and 20 SCFM runs.

to establish a precise correlation between an isolated UV measurement and the UV exposure received by the gas as it flows through and reacts with the photocatalyst bed. The 10 SCFM data suggests a square root relationship between UV intensity and conversion. The square root dependence was observed in a continuous flow reactor when TCE concentrations were less than 60 ppmv (Nimlos et. al., 1993). Higher concentrations yielded an approximately linear dependence.

On the last day of testing, grab samples were collected in Summa canisters and delivered to a local analytical laboratory (Air Toxics, Ltd., Folsom, CA) for TO-14 analysis to confirm the analyses provided by the MTI gas chromatographs and to provide outlet TCE concentrations that were below our GCs detection limits. Replicate samples were reported as 13000 ppbv for TCE in inlet air, and 280 and 660 ppbv TCE in the outlet (Table 22.4.1). This corresponds to 97.8% and 94.9% removal of TCE.

The reactor outlet airstream contained most of the dichloromethane and carbon tetrachloride present in the inlet stream. This result was expected, as single carbon haloorganics do not easily photo-oxidize (Jacoby *et al.*, 1994). Nearly all of the 1,1-dichloroethene and *cis*-1,2-dichloroethane were destroyed (destruction efficiencies of 97.3% and 99.1% respectively). This too was expected, as dichlorinated ethanes and ethenes photooxidize almost as rapidly as TCE.

Small amounts (<20 ppbv) of chloromethane, 1,1-dichloroethane, 1,2-dichloroethane and acetone, and 1,4-dioxane appeared in the reactor outlet and are likely reaction intermediates from TCE oxidation.

About 40% of the benzene in the inlet stream did not come out of the reactor. This result is in line with recent results in which benzene was oxidized with a sol-gel TiO₂ catalyst (Fu, X. *et al.*, 1995). Though not all of the benzene reacted, that which did formed only CO₂ and H₂O. Adding platinum to the TiO₂ sol significantly improved benzene oxidation. Transient reaction studies of benzene and Degussa TiO₂ thin films indicate that benzene oxidizes rapidly at 300K to form strongly bound surface intermediates that oxidize very slowly (Larson and Falconer, 1997). Other work with thin films of TiO₂ and benzene shows that benzene does not form intermediates when water vapor is present. In the absence of water, acetone forms and the catalyst becomes coated with a durable brown material (Sitkiewitz, S. and Heller, A., 1996). Because these tests were run at an average of 20% RH and the catalyst exhibited stable activity, it is likely that benzene was oxidized. Thus, since the catalyst activity did not deteriorate over the course of testing, it may be possible that low concentrations of aromatic species can be tolerated and treated in a solar photocatalytic reactor. It is also possible that the benzene was absorbed by the catalyst support material.

22.4.3.2 Paint booth application

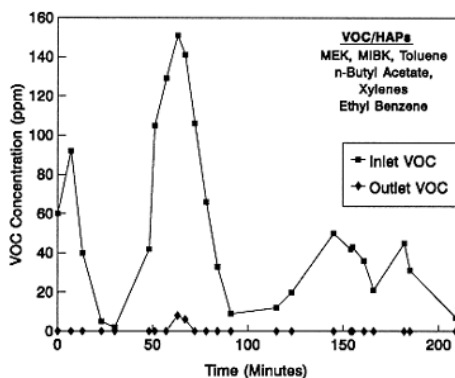


Figure 22.4.7. Inlet and outlet VOC concentrations from the Fort Carson paint booth using the small, lamp-driven, field test reactor.

Figure 22.4.7 shows the real time test results using the lamp-driven, small field scale reactor for treating VOC emissions from painting operations at Fort Carson. The inlet and outlet VOC concentrations are given in ppm. Test data begins at 8:10 AM on June 25, 1996 and ended at 11:55 for this run. The painting operations are conducted in a batch mode. Vehicles are placed in the paint booth, painted, then removed from the booth to the parking area, where they dry. The mixture of VOCs emitted from the aliphatic polyurethane green military paint being sprayed consisted of methyl ethyl ketone, methyl

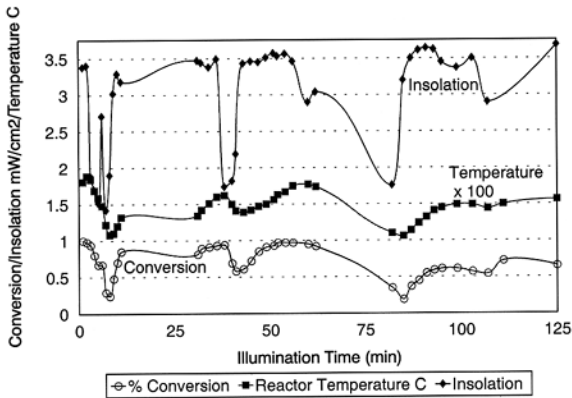


Figure 22.4.8. The effect of sunlight fluctuations on the photothermal destruction of methyl ethyl ketone in the parabolic trough, photothermal reactor. MEK conversion, insolation level, and reactor temperature are plotted as a function of continuous outdoor illumination time.

5-SCFM thermal photoreactor system was tested with methyl ethyl ketone (MEK), a paint solvent surrogate. Figure 22.4.8 shows the results of on-sun testing with this system. The Y-axis plots three factors: temperature in $^{\circ}\text{C} \times 100$ MEK, conversion as a fraction with 1 equaling 100% conversion, and solar insolation as mW/cm^2 . The X-axis plots illumination time in minutes. This test was performed on a hazy day with numerous clouds to evaluate the system under challenging conditions. Though conversion and reactor temperature parallel the insolation, they do so in a less than 1:1 ratio. This is likely due to the square root dependence of reaction rate on light intensity and to the heat transfer (insulative) characteristics of the ceramic support. 100% conversion was achieved when insolation levels were above $3.5 \text{ mW}/\text{cm}^2$ and reactor temperatures above 175°C .

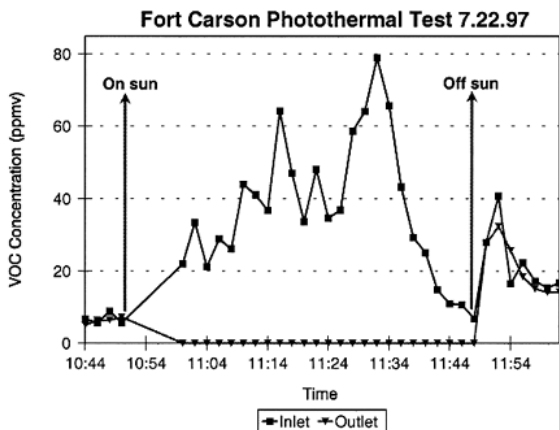


Figure 22.4.9. VOC concentration from paint solvents as a function of illumination time during photocatalytic treatment with a concentrating, parabolic trough, solar photoreactor.

isobutyl ketone, toluene, n-butyl acetate, xylenes, and ethyl benzene.

When the reactor reached an operating temperature of 170°C , complete VOC destruction was achieved for the entire run except for a period of peak VOC emissions beginning at 9:30 and ending at 9:45. Thus, during this four hour period, the PCO process destroyed virtually all of the VOCs in the slip stream from the paint booth exhaust. The total time averaged conversion is estimated to be greater than 95%. These data were used to design the solar-driven, photothermal reactor system.

Based on the lamp tests, the photothermal reactor was tested with methyl ethyl ketone (MEK), a paint solvent surrogate. Figure 22.4.8 shows the results of on-sun testing with this system. The Y-axis plots three factors: temperature in $^{\circ}\text{C} \times 100$ MEK, conversion as a fraction with 1 equaling 100% conversion, and solar insolation as mW/cm^2 . The X-axis plots illumination time in minutes. This test was performed on a hazy day with numerous clouds to evaluate the system under challenging conditions. Though conversion and reactor temperature parallel the insolation, they do so in a less than 1:1 ratio. This is likely due to the square root dependence of reaction rate on light intensity and to the heat transfer (insulative) characteristics of the ceramic support. 100% conversion was achieved when insolation levels were above $3.5 \text{ mW}/\text{cm}^2$ and reactor temperatures above 175°C .

The photothermal reactor was tested in July, 1997 for three weeks on paint booth emissions using natural sunlight. A representative data set for July 22, 1997 is shown in Figure 22.4.9 in which the total VOC concentration for the inlet and the outlet of the parabolic trough, photothermal reactor is plotted against illumination time. The solvent stream, which varied with time, generally contained about 140 ppmv of toluene, methyl ethyl ketone, methyl isobutyl ketone, xylenes, butyl acetate and ethyl benzene. The oper-

ating temperature was from 190 to 208°C, dependent on available illumination. On-sun refers to turning the concentrating receiver into the sun, which initiates heating and photoreaction. Off-sun refers to turning the receiver away from the sun (photoreaction and heating stops). Inlet and outlet VOC concentrations, which matched closely when the reactor was off-sun, were taken to ensure that thermal reaction as the reactor cooled and adsorption of contaminants onto the catalyst surface were not significant. No attempt was made to decouple photoreaction from thermal reaction because of rapid temperature changes when the trough was rotated off-sun and the difficulty of thermally heating the catalyst.

The results of 3 weeks of testing demonstrated that the photothermal treatment system has destruction and removal efficiencies (DREs) in excess of 95% under conditions where incident UV irradiation provided operating temperatures from 150 to 200°C. No loss of performance of the catalyst occurred.

Significant results from these pilot-scale field tests:

- A non-tracking, ambient-temperature, solar-powered photocatalytic reactor consistently achieved greater than 95% destruction of 10-15 ppmv TCE for 4 to 6 hours of operation per day during April at a latitude of 37°N. Catalyst performance remained constant during three weeks of testing.
- 95% destruction was achieved at 10 SCFM with UV intensities greater than 1.5 mW/cm² and at 20 SCFM at UV intensities greater than 2.0 mW/cm².
- Greater than 95% destruction of a variable paint solvent stream (140 ppm total VOC) was achieved with a concentrating solar photoreactor operated with ambient sunlight at temperatures of 180-200°C. These operating temperatures were achievable for 4-8 hours of operation per day in July at a latitude of 39.5°N. Catalyst performance remained constant during three weeks of testing.

22.4.4 COMPARISON WITH OTHER TREATMENT SYSTEMS

The design and fabrication of the photocatalytic reactor system used in the McLellan field test was provided by NREL engineers and the Industrial Solar Technology Corporation (IST), Golden, CO. IST estimates that the cost for a 200-SCFM system is about \$14,000.00, depending on the site requirements for hours of operation per day and the site solar potential. Costs to construct the reactors could be significantly reduced through economies of scale and large scale production likely could reduce reactor costs by half.²¹ Other purchased equipment costs for the photoreactor include a condenser/chiller and an instrumented blower/scrubber skid system for air handling. The level of instrumentation on the skid directly affects cost. The system described here was instrumented more than would be required for a commercial system. Equipment and installation costs for comparably sized carbon adsorption and thermal oxidation systems were calculated using EPAs HAPPRO v.2.1 software. Thus, total direct costs for the three systems are very close and range from an estimate of \$131K for thermal oxidation, \$119K for PCO, to \$97K for carbon adsorption. Indirect costs were estimated using a factor of 0.28 x total purchased equipment cost. This value includes engineering, construction fee, and start-up costs. (Vatavuk, 1994) Total capital required for all three systems is approximately equal and ranges from \$121K to \$164K. Operating costs are also similar and range from \$23 to \$28K and total annual costs range from \$37K for thermal oxidation to nearly equivalent values for carbon adsorption and PCO at \$32K and \$33K, respectively. No fuel is required for PCO and carbon adsorption. Details of the calculations are provided in the footnotes following Table 22.4.3.

Table 22.4.3. Comparison of estimated costs for similarly sized PCO, carbon adsorption, and thermal oxidation VOC treatment systems

Direct Costs	Solar PCO non-concentrating	Carbon Adsorption	Thermal Oxidation
Purchased Equipment (PE)			
Photoreactor ¹			
Condenser/Chiller ²	14,000		
Instrumented	10,625		
Blower/Scrubber Skid ³	60,000		
Total PE (TPE) ⁴	91,395	74,500 ⁵	100,500 ⁵
Installation	27,419	22,350	30,150
Total Direct Costs	118,814	96,850	130,650
Indirect Costs			
Indirect Installation Costs ⁷	29,923	24,391	32,904
Total Capital Required ⁸	148,736	121,241	163,554
Operating Costs ⁹			
Electricity	2,880	1,440	1,440
Fuel ¹⁰	0	0	5,000
Maintenance, Labor and Material	20,376	19,308	20,952
Direct Annual Costs	23,256	25,748	27,392
Indirect Annual Costs	8,664	7,063	9,527
Total Annual Costs	31,920	32,811	36,919
Levelized Cost ¹²	56,135	25,549	63,456
Levelized Cost/CFM	281	263	318

¹IST Corp., Golden, CO. Non-concentrating reactor cost is current and estimated price reductions anticipated from economies of scale at higher production levels.

²Peters and Timmerhaus, 1991.

³Zentox Corp., Ocala, FL. Concentrating vs. non-concentrating is primarily a function of instrumentation level.

⁴Includes 0.08 x PE for taxes and freight (Vatavuk, 1994).

⁵Calculated using EPAs HAPPRO v.2.1 software.

⁶0.38 x PE (Vatavuk, 1994).

⁷0.28 x TPE, including engineering costs, construction fee, and start-up costs (Vatavuk, 1994)

⁸Includes 6% contingency.

⁹Based on \$0.08/kWh, 10 kW blower and chiller costs.

¹⁰Based on \$0.33/ccf natural gas.

¹¹0.06 x Total Capital Required for taxes, insurance, and administration.

¹²Based on 10% interest rate, 10 year depreciation.

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