

CONTROL OF GASEOUS EMISSIONS

A. Buekens, K. Schroyens

Department of Chemical Engineering – CHIS 2, Vrije Universiteit Brussel, Belgium

S. Oleszek

IMRAM, Tohoku University, Sendai, Japan

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Summary

This chapter gives a survey of the treatment methods available for removing gases and vapors from air, off-gas, and flue gas. It touches also upon smell problems and indoor pollution.

Gaseous emissions may be controlled either by physical and physicochemical means of **separation** or by **chemical conversion**, including thermal or catalytic combustion and chemical oxidation or reduction.

Three important separation processes are:

- Absorption, i.e. dissolving the compounds to be separated from the flow to be treated in an auxiliary liquid.
- Adsorption onto suitable solid adsorbents.
- Condensation of vapors,

Depending on the nature of the forces at hand either **absorption** or **adsorption** may be purely physical or at least partly chemical. However, both types are difficult to distinguish, since the methods of implementation are practically identical in both cases.

Heat transfer is the controlling factor in vapor condensation. Mass transfer generally controls the rate of both absorption and adsorption. Mass transfer in absorption has been described by the two-film theory, the surface renewal theory and the penetration theory. In adsorption, distinction is to be made between external and internal diffusion; depending on the case, internal diffusion can best be described as molecular diffusion, Knudsen diffusion and surface or adsorbed-state diffusion.

Thermal and catalytic **combustion** are frequently used in order to remove organics from off-gas. Thermal treatment requires high temperatures so that optimal fuel economy is imperative. Its catalytic counterpart operates at much lower temperatures (300 – 500° C), but depends on ensuring both the activity and longevity of an expensive catalyst that

is easily poisoned or sintered.

Chemical oxidation and other processes are more expensive than oxidation with air or oxygen, hence highly specific and only occasionally treated in this topic.

1. Atmospheric Pollution

1.1. Survey

Natural processes, such as

- the surf of the sea projecting brine particles,
- the desert wind hauling fine sand over huge distances,
- forest fires emitting Products of Incomplete Combustion (PICs),
- volcanic activity causing sulfur dioxide and mercury pollution,
- the digestion of autumn leaves, or even
- pollen, isoprene and terpenes emitted from trees and plants,

all create pollution. Table 1 shows the composition of the atmosphere. Table 2 lists the prefixes used in SI units. Anthropogenic pollution is mostly attributed to industry and traffic. In the past, enterprise followed and authorities tolerated a strategy of high chimneys. However, especially with respect to **acidification** this tolerance merely displaces and generalizes the problem. Swedish lakes have fallen victim to imported pollution. Some compounds are subject to **Global Distillation**, i.e. they volatilize in industrial areas, and again condense in cold polar areas, creating pollution problems at a distance. Starting in the 1970s numerous countries established air pollution **monitoring networks**, featuring a double approach, on the one hand establishing the spatial distribution of major air pollutants as it varies in time, on the other of overseeing the sources of specific air pollutants, such as sulfur and nitrogen oxides, lead, cadmium, or fluorine and their effects on their short range surroundings. Monitoring networks also allow imposing measures in case of pollution episodes, e.g. converting towards cleaner fuel, or traffic restrictions.

	Chemical Formula	Percent
Permanent Gases:		
Nitrogen	N ₂	78.1
Oxygen	O ₂	20.9
Noble Gases:		
Argon	Ar	0.9
Neon	Ne	0.002
Helium	He	0.0005
Krypton	Kr	0.0001
Hydrogen	H ₂	0.00005
Variable Gases:		
Water vapor	H ₂ O	0 to 4
Carbon Dioxide	CO ₂	0.03 – 0.04
	CH ₄	0.0002

Methane Ozone	O ₃	0.000004
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[Source: <http://www.met.fsu.edu/explores/atmcomp.html>. *ATMOSPHERIC COMPOSITION*]

Table 1: Percent Composition of the Atmosphere

Factor	Name	Symbol
10 ¹⁵	Peta-	P
10 ¹²	Tera-	T
10 ⁹	Giga-	G
10 ⁶	Mega-	M
10 ³	Kilo-	k
10 ²	Hecto-	h
10	Deca-	da
10 ⁻¹	Deci-	d
10 ⁻²	Centi-	c
10 ⁻³	Milli-	m
10 ⁻⁶	Micro-	μ
10 ⁻⁹	Nano-	n
10 ⁻¹²	Pico-	p
10 ⁻¹⁵	Femto-	f

[Source: <http://physics.nist.gov/cuu/Units/prefixes.html>. *The NIST Reference on Constants, Units, and Uncertainty, International System of Units, SI Prefixes*]

Table 2: Prefixes used with SI units

Emissions are **guided**, i.e. leaving through a stack, or **fugitive**, i.e. arising in a diffuse manner, through small leaks, evaporation, or from mobile sources. Emissions eventually spread and are picked up by the wind, dispersed and diluted, distributed over phases (air and contained dust and droplets, water surfaces, soil) and also transformed on their pathway from the source of emission towards the receptor. Since pathways are variable and unpredictable in space and time much depends on local and atmospheric factors (topography, wind speed and direction, atmospheric stability); the resulting immission often varies over orders of magnitude with conditions. Hence, numerical values strongly depend on whether a yearly, monthly, daily, hourly... average, or a 5, 50, 90, or 99 percentile value is considered. Pollutants are quite often photochemically transformed, into either innocuous products, such as water or carbon dioxide, or secondary pollutants.

Immissions may be described as the sum of obnoxious effects exerted on humans, animals, plants, or goods by air pollutants.

1.2. Air Pollution Control Methods

The chapters on this subject viz., *Control of Gaseous Emissions, Condensation, Control of Carbon Monoxide and Volatile Organic Compounds, Adsorption of Gaseous Pollutants, Adsorbents and Adsorption Processes for Pollution Control, Control of Sulfur Oxides, Control of Nitrogen Oxides, Odor Control, and Indoor Air Quality Monitoring and Control* give a brief explanation of the underlying principles as well as

the field of application, possibilities and limitations of each technique considered, in brief the engineering side of environmental management. There is also a more fundamental, scientific side to the problem and the question arises: what are the particles, aerosols, vapors, gases, or smells, creating air pollution, and what are their main health, safety and environmental effects? A comprehensive analysis of such environmental, health, and sometimes safety hazards serves to establish limit values regarding tolerable emission (or immission) values. In reality, however, it is often unpractical to establish safe limits and also the borderline between a minor nuisance and a major hazard cannot always be well established. Hence, pollution control progresses stepwise in a partly haphazard fashion.

1.3. Pollution Prevention Pays

In most cases the best pollution control strategy is **prevention**.

Selecting appropriate Air Pollution Control Technology should start by data collection and analysis. Measures for reducing Air Pollution should be devised in the following order:

1. Prevention or Reduction, i.e. reducing the flow to be treated and/or the amount of pollutants.
2. Treatment, i.e. reducing pollutant loads below some limit or target values, and
3. Dispersion of emissions in the atmosphere

Prevention strategies can be classified, according to their area of application, into:

- Cleaner Combustion techniques.
- Cleaner Products.
- Avoiding Products- Hazardous, Persistent and accumulating in the food chain.
- Greenhouse and Ozone Depleting Compounds.

Prevention is the only possible method to reduce fugitive emissions. These are omnipresent, e.g. at piping flanges and valves, pump shafts, instrument connections etc. as opposed to the much more important guided emissions, escaping from a stack, or a vent, and depend on the quality of both preventive and curative maintenance, equipment specifications, and on the selection and quality of gaskets, seals, and packing. Systematic sniffing programs periodically monitoring pipe, equipment, or instrument connections address such fugitive emissions. Depending on the properties of the liquid, vapor, or gas handled in the system, sniffing may be sensorial or, more probably, founded on various types of instruments (see *Odor Control*). Other possible prevention measures include the use of welded rather than flanged connections, of double rather than single packing around shafts, or of special, leak-proof equipment, such as *canned pumps*. Prevention of 'fugitive emissions' is of tremendous importance when producing or processing highly toxic or (sometimes worse with respect to public perception) extremely smelly compounds, such as mercaptans or alkylamines (see *Control of Sulfur Oxides* and *Odor Control*).

1.3.1. Combustion

As a rule, combustion produces scores of pollutants, more in particular of a generic group of Products of Incomplete Combustion, airborne ash particles, not to mention particles generated by the wear of engines, tires, brake linings, or seats, a few examples arising when traffic is considered.

Fuels are rarely entirely devoid of hetero-atoms, mainly oxygen, sulfur, nitrogen, sometimes halogens, and combustion is the major source of acidification, responsible for extinction of all life in some poorly buffered Swedish lakes, irremediable damage to invaluable historic heritage, corrosion of metals, and respiratory disorders in humans.

1.3.2. Cleaner Products

Prevention is highly topical in product preparation and formulation. Numerous commodities, such as inks, paints, varnishes, lacquers, coatings, and glues, are traditionally formulated on a solvent basis. During product application and also afterwards, during drying and hardening, the solvents evaporate, contributing to the local atmospheric VOCs burden and possibly occupational diseases. Newer formulations gradually but surely favor a water basis.

Similarly, **residual monomers** are eliminated from polymers, e.g. vinyl chloride monomer (VCM) from polyvinyl chloride resin powder (PVC), by steam stripping in a contacting tower, reducing the original monomer content from typically 500 – 2000 ppm to very low residual values, below 1 ppm. Elimination of monomer became an absolute necessity, when (in 1973) Goodrich physicians discovered that VCM is carcinogenic, after routine scrutiny of death causes amongst its workforce.

Polyurethane glues and foams may liberate suspect amines. Epoxy resin compounds cause highly individual allergies and those afflicted have no other chance than looking for another job. Particleboard panels, widely used in building and furniture, contain formaldehyde-based glues that can slowly liberate this toxic chemical and formerly did so to a sometimes-sizeable extent. Developing new formulations is the best way out of such problems, albeit some substitutes may show other shortcomings.

1.3.3. Hazardous, Persistent, and Bio-accumulating Products

Chlorinated solvents were considered appropriate in numerous technical and domestic applications, because of superior dissolution power for fats and greases and a safe, low or negligible flammability. Today, they are much more restricted in their use, because of a mix of environmental and occupational hazards, such as ozone depletion potential, persistence, and toxicity.

Pesticides, such as DDT, one day could claim the merit of almost having overcome malaria. Many pesticides, however, are persistent, lipophilic and thus bioaccumulating. The latter enrich in the food chain, due to a combination of fat tissue/aqueous phase distribution and inadequate biodegradation. The deleterious effects of chlorinated environmental pollutants on the procreation of, in particular, seagoing birds and mammals, have not yet been observed.

The problem with hazardous, persistent, and bioaccumulating products is one of chain management, rather than intrinsic unsuitability or a lack of quality. Two of the more objectionable pollutants, PCBs and asbestos based materials both were introduced with vigorous support from insurance companies, (rightly) pointing at their superior fire safety. And indeed, the worst ever catastrophe in Belgian coal mining history (Marcinelle, 1952) would never have occurred if a duct of hydraulic oil would have contained PCBs, rather than a flammable oil.

1.3.4. Greenhouse and Ozone Depleting Compounds

Ozone Depleting Chemicals	Industrialized Countries	Developing Nations
Chlorinated Fluorocarbons		
CFCs	100% reduction by 1996	100% reduction by 2006
Halons	100% reduction by 1994	100% reduction by 2006
HCFCs	35% reduction by 2004	35% reduction by 2014
	65% reduction by 2010	65% reduction by 2020
	90% reduction by 2015	90% reduction by 2015
	99.5% reduction by 2020	99.5% reduction by 2030
	100% reduction by 2030	100% reduction by 2040
Methyl bromide CH ₃ Br		
Fumigant uses	Freeze in 1995 at 1991 levels	
From auto exhaust	Eliminate between 2000 and 2005	
From biomass burning	50% reduction between 2010 and 2040	

[Source: http://www.mpcfakulty.net/mark_bishop/Ozone_CFCs.htm. *Ozone and the Stratosphere - The Copenhagen Amendment to the Montreal Protocol*]

Table 3: Ozone depleting chemicals

CFCs were unanimously considered as an almost ideal non-flammable, non-toxic group of compounds, used as a fluid in thermodynamic cooling cycles, a thermal insulating gas in closed foams, and an excellent extinguishing agent, until it was found to attack the ozone layer slowly but surely.

Their interference in stratospheric photochemical reactions was proven to remove the natural protective quality of the stratospheric layers enriched in ozone against incoming U.V.-rays, thus exposing an increasing part of the Southern Hemisphere to skin cancer, and due to their extreme atmospheric stability accumulation was inevitable. The use of this unexpectedly dangerous generic group of chemicals was phased out at the Montreal Conference, even before the causes were fully understood or the extent of the potential damage precisely assessed.

1.3.5. Fugitive Emissions

Preventive measures are the only ones possible for reducing fugitive emissions. These emissions are omnipresent in any process plant and located, e.g. at piping flanges and valves, pump shafts, instrument connections, as opposed to the much more important, guided emissions, escaping from a stack, or a vent. Their magnitude depends on the selection and quality of gaskets, seals, and packing, on equipment specifications and on the quality of both preventive and curative maintenance.

1.3.6. Outlook

Anthropogenic and, in some cases, even natural pollution processes may exceed the possibilities and capacity of the self-cleaning processes in the atmosphere. These include dry and wet deposition (sedimentation and rainfall) and photochemical oxidation as most important atmospheric cleaning mechanisms. Very small particles tend to coalesce, after being brought in contact through the Brownian movement. Airborne dust particles settle out or form nuclei for aerosol particles and eventual raindrops. For numerous chemical elements and compounds a global balance was made over the entire atmosphere or one of its strata, to study input/output data, and decide whether both are in equilibrium, or not. In some cases secondary pollutants are formed, that are more dangerous even than their predecessors, e.g. SO_2 is converted into SO_3 , NO into NO_2 , car exhaust gases (i.e. hydrocarbons, NO) are converted into peroxyacetal nitrate.

New problems first need adequate publicity to attract attention and stimulate necessary measures to be taken, often against powerful lobbying work minimizing their still incompletely explored impact. An example of a potential pollutant, that is still being largely ignored, is laughing gas (N_2O), a product arising in the low temperature combustion of sewage sludge and biomass.

That air pollution may have serious effects upon health of man, animals, trees or plant is beyond dispute. Pollution also creates material damage, by destroying cultural heritage, accelerating corrosion of metals, or the ageing of rubber and other polymers. Also the meteorological conditions may deteriorate and atmospheric visibility may be impaired. Due attention should be given to the ultimate fate of emission and stack dispersion of polluting plumes, their eventual fate in the atmosphere, e.g. photochemical oxidation, spreading according to the bi-Gaussian dispersion model, settling, dry and wet deposition, accumulation, etc.

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Biographical Sketches

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).

Kathleen Schroyens graduated in Industrial Engineering in Chemistry (1998) at KAHO – Ghent.

Since 1999 she has been working as scientific collaborator at the Chemical Engineering Department of Vrije Universiteit Brussel, contributing to the European Union projects MINIDIP and Haloclean and to a comprehensive inventory of all waste or product streams, derived from thermal processes that are contaminated with dioxins, dressed by order of The Flemish Government, AMINAL. She assisted in preparing process descriptions, monitoring effluents, performing (succinct) risk analysis and devising preventive and curative measures required to control such streams. She fulfilled numerous assignments

concerning the study and characteristics of dioxins emissions from MSWI and other industrial plants worldwide and supervised preparations of all chapters under the titles: Control of Particulate Matter in Gaseous Emissions, Control of Gaseous Emissions, and Pollution Control through Efficient Combustion Technology.

Sylwia Oleszek-Kudlak, born and educated in Poland, received her M.Sc. (1999) in Chemical Engineering from Wroclaw University of Technology. From 2000 she started work as a research assistant at the Institute of Environmental Engineering of the Polish Academy of Sciences in Poland. From 2001 she is Ph.D. student at the Tohoku University of Sendai in Japan (Scholarship of Ministry of Education, Science, Sports and Culture, Government of Japan (Monbukagakusho)). Her research interest is in the area of physical-chemical properties for organic compounds of environmental concern.

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