1 Development of Clean Technology Concept

1.1 The Evolution from Local to Global Environmental Policy

The ecosphere is a closed system with the limited resources of energy and raw materials and inadequate ability to accumulate or assimilate the pollutants. Therefore uncontrolled exploitation of the water, air, and resources may lead to irreversible degradation, and even global catastrophe. Toxic substances such as organic chemicals (VOCs, PCBs, etc.), heavy metals, radioactive, and biological contaminants in water require the long-term and systematic policies that restrict more damaging production processes and induce safer alternatives. The way of thinking about these transboundary problems is changing rapidly from the local to global solutions of environmental problems. The social issues, i.e., health, comfort of life, job, etc. must also be taken into account. This was the reason why policymakers and stakeholders have accepted recently the global viewpoint and necessity of serious breakthrough from local to global environmental policies (see the appendix).

1

In 1970, US Congress enacted the three important acts, i.e., Clean Air Act 1970 [1], Clean Water Act 1972 [2], and Resource Conservation and Recovery Act, RCRA (1976) [3], which were the primary sets of federal regulations that governed water quality issues in the United States. Moreover, the international community approved the Conventions concerning the global pollution, e.g., acts on marine waters: in London 1972, Helsinki 1974, Paris 1974, Barcelona 1976 and 1982; Law of the Sea - the international agreement on resource preservation with 160 signatories. Ministerial Declaration on the protection of the North Sea was signed in London 1987 by eight countries. Some spectacular examples of international actions against air pollution were the ECE Convention on Long-Range Transboundary Air Pollution, which was agreed on November 1979 and entered into force in March 1983. This convention was signed by 34 countries and ratified by 24 countries. In 1985, the UNEP Convention for the Protection of the Ozone Layer was agreed in Vienna. The Helsinki Protocol was signed by 20 countries and entered into force in 1987 and the signatories reduce their national annual sulfur emissions by at least 30% by 1993. The Montreal Protocol from 1987 was added to this convention, in which (46) signatory countries agreed to halve their production of five chlorofluorocarbons (CFCs) and three halons by 2000. This

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was further agreed in London 1990 by about 100 countries. The protocol on nitrogen oxides was signed in October 1988 in Sofia and entered into force when ratified by 16 signatory countries which agreed to take measures against further increases of NO_x emissions so that national NO_x emissions did not increase beyond 1987 levels after 1994. Recent documents and guidelines, such as Kyoto protocol [4], Treaties of Maastricht and Amsterdam, Rio and Oslo accords, created the foundation of a global environmental policy. The European Climate Change Program (ECC) was established in June 2000 to help identify the most environmentally and cost-effective EU measures enabling the EU to meet its target under the Kyoto Protocol, e.g., an 8% reduction in greenhouse gas emissions from 1990 levels by 2008-2012. This corresponds to a reduction of 336 Mt CO₂ in 2010 with respect to 1990 [5]. The next step forward to global environmental policy was Basel Treaty to control international trade in hazardous waste, which was signed in March 1989 by 34 countries and the EC; the signatories agree in principle to prohibit and establish notification procedures for all trade in hazardous waste. The real integration and interaction between nations and companies toward Sustainable Development was commenced on U.N. Conference on Environment and Development UNCED "Earth Summit," which was held in Rio de Janeiro, Brazil, 1992 (Agenda 21 [6]).

1.2

Proactive Strategies Contra End-of-Pipe Technologies

Faucheux [7] and Fukasaku [8] presented the definitions of end-of-pipe technologies as added technologies that enable an ex-post control of pollution. Many authors [9,10] pointed out the conservative role of the end-of-pipe technologies that coincided with the strategic reorientation toward less polluting types of processes. They also [11,12,37] emphasized that the purely environmental innovations were not satisfactory strategies for environmental protection. The end-of-pipe technologies are considered as a negative pattern of outdated conservative way of waste minimization because they are supposed as being separate from the production process, while the clean technologies integrate environmental issues in the entire production process [13,14]. However, end-of-pipe technology equipment suppliers still play important role in industry and in some applications; they enjoy strong position such as municipal wastewater treatment.

Prevention approach means the avoidance of the pollutants, being released into the environment [15]. Proactive pollution prevention approaches are to achieve sustainable production capabilities, where environmental and economic systems are in balance. The waste minimization is one of the proactive approaches. As noted by Alvares, "The reduction of the water to be treated, as well as the minimization of the contamination load, implies a smaller waste water treatment plant, a lower consumption of chemical products, and less production of sludge that must be treated later and, finally, a rational use of water have been achieved" [16]. The main objective of proactive strategies is the development of clean technologies, defined by The Commission of the European Communities as "any technical measures taken at various industries to reduce or even eliminate at source the production of any nuisance, pollution, or waste, and to help save raw materials, natural resources, and energy" [17]. The difference between clean technologies and cleaner production concepts is that the former is proactive and well define the goals and the latter is very general involving nontechnical factors. However, both concepts are revolutionary compared to earlier end-of-pipe technologies.

1.3 Cleaner Production Concept

There are several definitions of cleaner production, from which it is clear that CP was a tool for the pollution prevention strategy and which concerned the combination of reduction of emissions with energy recovery (CLEANER (Combining Lower Emissions And Networked Energy Recovery). EPA had introduced the cleaner production concept [18] in 1988. The definition of Bass [19] from 1990 is: "cleaner production is the conceptual and procedural approach to production that demands that all phases of the life-cycle of a product or of a process should be addressed with the objective of prevention or the minimization of short and long term risks to humans and the environment." The second definition of this author was closer to idea of sustainable development, i.e., "Cleaner production is an effective approach to understanding the best ways of fostering the development of a paradigm shift toward sustainable production and service organizations and products." Huisingh [20] also put a main stress of cleaner production onto the preventive approach, saying that: "cleaner production approach is an ongoing process involving technical as well as attitudinal, motivational, and other non-technical factors that are essential for corporations to benefit from the preventative approach." The CP strategy was adjoined to PP by UNEP [21]: "cleaner production is the continuous application of an integrated preventive strategy to process products and services and/or to make efficient use of raw materials, including energy and water, to reduce emissions and wastes, and to reduce risks for humans and the environment." The definition of the cleaner production presented by Barbiroli [22] is very general stating, "Cleaner Production is the efforts of industry to improve the environmental performance of its production cycles."

In 1994, a study commissioned by the UNEP to the Toxic Use Reduction Institute in Lowell, Massachusetts proposed a classification of "cleaner production" in four different types based on their general characteristics.

- Business-driven technologies, i.e., sophisticated production systems, improving production quality and/or efficiency, improving competitiveness, and reducing costs. Such technologies improve eco efficiency within overall performance improvement and are highly beneficial.
- Clean technologies, i.e., fairly sophisticated production systems, developed and adopted for the primary purpose of improving environmental performance; they are marginally beneficial.

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 - 3. Appropriate technologies [23,24], i.e., simple production systems that improve environmental performance, but are adopted primarily for economic development purposes.
 - 4. "Low-fruit" technologies, i.e., simple production systems that modify existing ones to improve environmental performance (e.g., waste heat recovery/recycling with special furnaces in aluminum smelting.

However, this classification did not determine which quantitative criterions should be used as the basis. As pointed by Geiser [25], one problem with this classification is that it does not follow any objective or systematic approach but merely classifies the kinds of technologies on a quantitative basis into four rather general categories. However, UNEP already prepared more than 500 concise reports contained in the International Cleaner Production Information Clearing house (ICPIC) database [26].

1.4

Sustainable Chemistry Concept

Sustainable (named "green") chemistry was introduced by EPA in 2002 [27]. The idea of *Green Chemistry* is to develop new products, reaction media, conditions, and/ or utility of materials [28,29]. More specifically, green chemistry is the design of chemical products that reduce or eliminate the use or generation of hazardous substances by offering environmentally friendly alternatives. Sustainable chemistry technologies can be categorized into the following three focus areas, e.g., the use of alternative synthetic pathways, the use of alternative reaction conditions, and the design of safer chemicals that are less toxic than current alternatives or inherently safer with regard to accident potential. There are equally dozen principles of green chemistry, e.g.,

- 1. prevent waste, by design chemical syntheses to avoid waste to treat or clean up;
- 2. design safer chemicals and products to be fully effective, with no toxicity;
- 3. design less hazardous chemical syntheses through use and generate no toxic substances to humans and the environment;
- use renewable rather than depleting feedstocks. Renewable feedstock is usually made from agricultural products or the wastes whereas depleting feedstock is made from fossil raw materials;
- 5. use catalysts rather than stoichiometric reagents, which are used in excess and work only once, to minimize waste,
- avoid chemical derivatives by using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste;

- maximize atom economy. Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be minimum wasted atoms;
- 8. use safer solvents and reaction conditions;
- 9. increase energy efficiency at ambient temperature and pressure whenever possible;
- design degradable chemicals and products to break down to harmless substances after use to avoid their accumulation in the environment;
- 11. analyze by real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts to prevent pollution;
- minimize the potential for accidents by designing safer chemicals to minimize the potential for chemical accidents, explosions, fires, and releases to the environment.

The green chemistry concept solves the pollution prevention problem at the molecular level by focusing on chemicals whereas clean technologies deals mainly with processes such as separation for recycling, recovery, conservation, and rational use of raw materials, water and energy, optimization of production processes, disposal or recycling of unavoidable waste. In this sense green chemistry is complementary to clean technologies which is based on chemical engineering rather than pure chemistry.

1.5 Earlier Concepts of Sustainable Development

Sustainable development stems from the earlier concepts based on similarities between biological and industrial systems such as industrial ecosystem, industrial metabolism, and industrial symbiosis. There are many concepts of preventative strategies including industrial ecology [30], ecologically conscious management [31], life cycle analysis, and design for the environment, dematerialization, and design for efficient longevity, and sustainable product development [14]. The so-called industrial ecology focuses largely on the physical flows of substances and the physical transformation processes. The concept of industrial ecology has been introduced by Elster [32], who made observation that industry is similar to biological systems applying the principles of natural systems because the process of variation, selection, and reproduction (in short, adaptation) runs faster than the change in the environment. In addition, Frosch and Gallopoulos [30] used the analogy with the ecosystem and industry stating that industrial system should approximate the ideal closed system. Tibbs [33] pointed out the connections between man-made ecosystems and the natural global ecosystem. Ayres [34] also developed the concept of industrial metabolism taking into account the material flows. The industrial metabolism was defined as the whole integrated collection of physical

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processes that convert raw materials and energy, plus labor, into finished products and wastes under a more or less steady-state condition. Tibbs [35] defined the industrial ecosystem as a system "in which the consumption of energy and materials is optimized and the effluents of one process serve as the raw material for another process." Tibbs, Graedel [36,37], and Ayres [38] pointed out longer term vision of production within a living system: "to manage the earth's resources in such a way as to approach and maintain a global carrying capacity for our species which is both desirable and sustainable over time, given continued evolution of technology and quality of life." [39] Industrial ecology takes the pattern of the natural environment as a model for solving environmental problems [40]. Industrial ecology goes beyond a company's internal production optimally identifying environmental management as system oriented and covers a longer period and the whole manufacturing system [41,42], involving reducing waste, reusing industrial byproducts, and choosing low-impact and safer materials [25,43].

1.6 The Principles of Sustainable Development

The policy of sustainable development points out that "sustainability must integrate ecological integrity, economic efficiency, and social equity" [44]. This concept is already accepted by majority of countries since the debate of the World Conservation Strategy in 1980, the report ("Our Common Future"), of the World Commission on Environment and Development in 1987 and Agenda 21 in 1992. A strategy for sustainable development was agreed upon in Göteborg in June 2001 (see the appendix): "EU sustainable development strategy is based on the principle that economic growth, environmental protection and social inclusion should go hand in hand." Brundtland Commission defined the goal of the state sustainability within the ecosphere: "to meet the needs of the present without compromising the ability of future generations to meet their own needs." [45] The system in which the sustainability is planned to be achieved comprises societies and the surrounding ecosystems. Ecosystem includes whole ecosphere, which occupies the full space above the lithosphere (Earth's crust) to the outer limits of the atmosphere. Principles of sustainable development must be based on real assumptions and physical (conservation laws) and biological laws; the biogeochemical cycles; the ecological interdependences of species; the anthropogenic influence on the ecosphere [46]. The main postulates (so-called system conditions) of sustainability are as follows:

- Eliminate our contribution to systematic increases in concentrations of substances from the Earth's crust by substituting certain minerals that are scarce in nature with others that are more abundant, using all mined materials efficiently, and systematically reducing dependence on fossil fuels.
- 2. Eliminate our contribution to systematic increases in concentrations of substances produced by society by systematically substituting certain persistent and unnatural compounds with those that are normally abundant or break down

more easily in nature ("green chemistry"), and using all substances produced by society efficiently.

- 3. Eliminate our contribution to the systematic physical degradation of nature through overharvesting, introductions, and other forms of modification. This means drawing resources only from well-managed ecosystems, systematically pursuing the most productive and efficient use both of those resources and land, and exercising caution in all kinds of modification of nature.
- 4. Contribute as much as we can to fulfill human needs in our society and worldwide, over and above all the substitution and dematerialization measures taken in fulfilling the first three objectives. This means using all of our resources efficiently, fairly, and responsibly so that the needs of all people on whom we have an impact, and the future needs of people who are not yet born, stand the best chance of being fulfilled.

During the 2000 Seville Conference, industry representatives proposed Integrated Pollution Prevention and Control (IPPC) Directive with the requirements for Best Available Techniques (BATs). The "best" means most effective in achieving a high general level of protection of the environment as a whole [47]. As stated in BAT reference documents the directive should be descriptive rather than prescriptive [48,49]. Paragraph 11 in Article 2 of the IPPC Directive defines "Best Available Technique" as "the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing in principle the basis for emission of limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole." Article 2(11) defines techniques as follows: "techniques" include both the technology used and the way in which the installation is designed, built, maintained, operated, and decommissioned. Available techniques are those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced. The purpose of the Directive is to achieve integrated prevention and control of pollution arising from the activities (listed in the appendix), leading to a high level of protection of the environment as a whole. Its implementation should also take account of other community objectives such as the competitiveness of the community's industry thereby contributing to sustainable development. Essential to this approach is the general principle given in Article 3 that operators should take all appropriate preventative measures against pollution, in particular through the application of best available techniques enabling them to improve their environmental performance [50].

The IPPC Directive specifically deals with the following forms of environmental pollution:

- 1. acidification resulting from emissions into the air;
- 2. soil and water eutrophization resulting from emissions to air or water;

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 - 3. diminution of oxygen in water;
 - 4. global warming;
 - 5. depletion of the ozone layer;
 - 6. emission of particles into the air, especially micro particles and metals;
 - 7. formation of photochemical ozone;
 - discharge of persistent, bioaccumulative, and toxic substances into water or into the soil;
 - 9. generation of waste, in particular hazardous waste;
 - 10. vibrations, noise, and odors;
 - 11. overexploitation of raw material and water resources.

Thus clean technologies contribute under all system conditions of sustainable development on a strictly technological level.

1.7 Clean Technologies

The Commission of the European Communities put the definition of clean technologies as a main objective of proactive strategies: "any technical measures taken at various industries to reduce or even eliminate at source the production of any nuisance, pollution, or waste, and to help save raw materials, natural resources, and energy" [17].

Kemp *et al.* [51] stressed that environmental protection problems should be solved at the source and the main elements of clean technologies (CT) concern simultaneously, emissions, raw materials, and natural resources, i.e., "clean technologies techniques, processes, and products that make it possible to avoid or to reduce atthe-source pollutant emissions and/or the use of raw materials, natural resources, and energy." Definition of clean technologies given by Getzner [56] is very general, i.e., "clean technologies: fairly sophisticated production systems, developed and adopted for the primary purpose of improving environmental performance"; however he mentioned skeptically that "they are marginally beneficial." Fukasaku noted that [8] "clean technologies as the technological solutions that are most likely to sustain environmental preservation over the long run."

Agence de l'Environnement et de la Maýtrise de l'Energie (ADEME) [52] introduced and emphasized internal recycling to the definition of clean technologies: "clean technologies are techniques that enable the recycling of water and waste, or which allow pollutants to be viewed as secondary raw materials." The ADEME also stressed that CT "reduce pollution at the source since polluting emissions are regenerated during the production process." Faucheux accepted the same criterion for clean technologies [7]: "clean technologies reduce pollutant emissions 'at the source' instead of capturing them only after they have been generated." Alvares [16] says, "...a big effort must be taken by industrial leaders to incorporate clean technologies into their productive processes such as technologies with less consumption of natural resources and with less generation of waste. So, it is necessary to strike a balance between the increasing production without exhausting the resources, while generating less waste and recovering and reusing aqueous solutions as much as possible."

Clean technologies were recently officially adjoined (ADEME 1998 [53]) to sustainable development policy: this was changed following the European Community's adherence to the concept of sustainable development. State authorities had been trying to encourage firms to adopt clean technologies since the early 1980s. Now this attitude has finally become official. ADEME [53] distinguish between three types of clean technologies, i.e.,

- 1. optimization of the existing process, leading to an abatement in the emission of pollutants, thanks to additional equipment and resources;
- process modification, corresponding to situations where the overall process principle remains the same, and where one simply adds one or several step(s) that enable the recovery or replacement of certain resources;
- 3. process change, this being the situation that is the most difficult in investment and risk terms since it involves a modification of the nature of the production process.

Marie-Claude Belis-Bergouignan [54] identified four types of clean technologies:

- 1. substitution and savings in inputs;
- pollution prevention and control technologies to integrate into the production process a new technology or a new type of equipment that makes it possible to diminish or to treat pollutant emissions;
- recovery or internal recycling involving the recovery, recycling, or regeneration of raw materials and/or of certain substances, leading to a reduction at the source of the polluting emissions of the production process;
- radically new clean process to completely modify production process and adopt a new and cleaner process that generally involves radical innovations.

The European Commission [47] defined clean technologies as follows: "clean technologies are new industrial processes or modifications of existing ones intended to reduce the impact of production activities on the environment, including reducing the use of energy and raw materials." To support the definition the main attributes of clean technologies were precisely formulated:

- 1. conservation of raw materials,
- 2. optimization of production processes,

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 - 3. rational use of raw materials,
 - 4. rational use of energy,
 - 5. rational use of water,
 - 6. disposal or recycling of unavoidable waste,
 - 7. accident prevention,
 - 8. risk management to prevent major pollution, and
 - 9. restoring sites after cessation of activities.

The important social impacts of clean technologies are also economic, employment, and safety issues. Getzner [56] pointed out the positive effect of clean technologies on economy:

However, positive ecological impacts are only one side of the 'sustainability triangle'. The other two cornerstones are economic viability and social issues. Much work has been done on the economic impacts of clean technologies, which are again very different from end-of-pipe technologies. While the adoption of end-of-pipe technologies leads to higher investments and higher labor, operating and maintenance costs for companies which in turn decrease the productivity of the company (lower output per unit of inputs), clean technologies can lead to an increase in productivity due to cost savings and rationalization effects in the production process.

Getzner [56], Kanatschnig [57], and Tietenberg [58] documented the economic advantages of clean technologies in quantitative and qualitative terms. The systematic studies on the impact of clean technologies on economy from the perspective of companies that have adopted them were presented by Eder [59], based on the questionnaire, which was sent to 126 potential experts by participating in a workshop organized by the OECD in October 1998. The empirical basis for the results stems from a report to the European Commission in 2001 [60].

There are also many papers discussing the impact of clean technologies on employment and job conditions. Getzner [55] also took into consideration quantitative and qualitative terms: "in terms of the impact of clean technologies, the social part of sustainability considers the quantitative and qualitative impact of these technologies on employment. Within such an approach, the impact on the number of jobs in companies adopting clean technologies is only one important aspect." The positive impact is mentioned in the paper of Pfeiffer [61]: "a wide range of other topics have to be considered, like the quality of the work, environment, job security, stress, and other 'soft' factors of working relations and job satisfaction." Only very recently have a number of publications appeared which deal with these issues, in particular among them Progress Report 1992–1998 due to Agenda 21 from Poland [62]. The document states that in the long-term (25–30 years) employment of environmentally friendly production processes will be compulsory, and that clean technologies would be preferable.

1.8 Importance of Membranes in Clean Technologies

Membrane processes are actually the most effective separation processes and they are still in rapid development creating new prospects of their applications in clean technologies. The recent achievements in polymer chemistry, material science, nanotechnology, and process engineering opened the new applications for membrane processes. Especially the separation of large streams of diluted mixtures, heterogenic and homogenous, by means of membranes and membrane-based hybrid processes seems to be very effective, promising, and profitable. They serve practically unlimited selectivity of separation, which is essential for the clean technologies. Based on the recent definition of clean technologies almost all attributes may be fulfilled by using membrane processes.

Conservation and rational use of raw materials is possible by recovery, reuse, and recycling of unreacted substrates, water, and production media such as catalysts, solvents, surfactants, adsorbents, cooling agents etc. Membrane processes open new unexploited sources of raw materials. Diluted metal ions may be gained from waste streams, mining waters, tailings, leachates, seawaters, etc. Diluted organic compounds may be concentrated during pervaporation or membrane distillation, which additionally take advantages and utilize a waste heat. Biosorption enables us to join the water decontamination with the utilization of waste materials.

Membranes may play an important role in the optimization of the production process and rational use of energy in many ways, e.g., by the substitution of less energy consuming membrane alternatives (distillation by pervaporation or membrane distillation) or combination with conventional unit processes which are called hybrid processes. Membranes also open new prospects in new energy sources as fuel cells (catalytic membranes and ion selective membranes), new fuels (such as bio-fuels, bio-diesels based on membrane reactors for transestrification of fatty acids with alcohols. Pervaporation (PV) and vapor permeation (VP) enable dewatering of alcohols as substitutes of gasoline. Membranes may contribute in huge energy savings thanks to new solutions of work, pressure, and energy recovery systems.

Rational use of water during industrial processes may be attained by means of removal of all types of contaminants, e.g., suspended solids (MF), colloids (UF), soluble components (ED, LM, SLM, NF and RO), VOCs (PV, MD, contactors), ions (ED, NF, RO, D) organic components (PV, MB, contactors, EM, SLM). Water scarcity on the Earth is less harmful thanks to desalination of brackish waters, seawaters, and mining waters by means of reverse osmosis on a large scale. Energetic uses water recycling systems based on microfiltration, nanofiltration, and electrodialysis. The same processes are used in the small scale in a variety of industrial branches.

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Disposal or recycling of unavoidable waste streams may be achieved by variety of membrane separations, which enable to fractionate the wastewaters onto valuable pure materials that can be subsequently reused as resources or valuable byproducts. The water recovered by such separation can be recycled to the production processes. Membrane processes reduce the consumption of chemicals during the regeneration of ion exchange resins during water softening in power stations that are main consumers of the water but also the main polluters. Membranes enable to avoid the overdosing of fertilizers and all kinds of chemicals used in agriculture, such as herbicides, pesticides by means of controlled release. Insecticides are replaced by pheromones that are also delivered precisely by means of membranes.

The membrane mobile plants are used to prevent major pollution and restoring sites after cessation of activities and to purify the water after flooding. The areas contaminated by industrial activity especially by heavy metals and hydrocarbons are restored by means of ground water and landfill leachates purification with membrane processes. Apart from the environmental issues, the membranes play an important role in direct health protection in many ways, i.e., by the production of pure pharmaceuticals, separation of enantiomers, water, and air cleaning.

Various membrane-based separation methods in different stages of development will be presented in the next chapters as an existing (Part 2) and potential (Part 3) contribution to the clean technologies. The essential feature of these methods is the selectivity of separation, which enables to get pure component of interest. Thus, the membranes are important tools for the recovery of various contaminants that sometimes can be reused or sold as byproducts, but in any case they help us minimize the environmental problems.

The main goal of this book is to reveal new possibilities and to encourage applying them as efficient innovative pathways of reengineering and retrofitting different industrial and environmental technologies. From an energy consumption point of view, the contaminants should be removed at the place where they are emitted from industrial plants. At this location the concentration is high before any dissipation takes place, separation is effective and these contaminants can be easily recovered and recycled for reuse, forming a closed cycle process of clean technology.

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