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Technology Trends in Pollution-Intensive Industries: A Review of Sectoral Trends

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1. Introduction¹

Since the World Commission on Environment and Development presented the report *Our Common Future*, to the United Nations General Assembly in 1987, the concept of “sustainable development” has been widely used throughout the world. It has been defined as “development which meets the needs of the present generation without compromising the ability of future generations to meet their own needs.” This implies that we need to consider the equity between generations as well as between the industrialised and developing countries. As is addressed in *Agenda 21*, which was adopted at the United Nations Conference on the Environment and Development in Rio de Janeiro, Brazil, in 1992, there is now a growing recognition that it is necessary to take a balanced and integrated approach on environmental protection and economic development in the long run.

The development and adoption of environmentally conscious technologies are under way for both production processes and products in industrial sectors. By using a taxonomy of environmental technologies in chemical process industries, this paper provides some background information on the technological trends in seven pollution-intensive industrial sectors (i.e. pulp and paper, organic chemical, inorganic chemical, iron and steel, petroleum refining, fertiliser, and textile industries) with a particular emphasis on the introduction of cleaner technologies. In addition, economic implications of the introduction of environmental technologies for industrial activities are also discussed.² The focus of this paper is mainly on the supply side, i.e. on environmental technologies in industrialised countries.³

2. Environmental Innovation and Industrial Competitiveness

Given the diversity of industries in terms of production processes, products, and hence pollution sources, the effects of environmental regulation on technological change also vary. Therefore, a general discussion on the implications of environmental technologies for industrial competitiveness is not an easy task. However, Porter (1995a) has recently put forward a hypothesis that environmental regulations can stimulate growth and competitiveness through a dynamic process of innovation. He points out two mechanisms through which this effect comes out. The first is the “first mover” advantage. Strict environmental regulations of a country will induce firms in this country to conduct R&D activity for the purpose of developing technologies designed for compliance (mostly end-of-pipe technologies). If other countries follow this country later in adopting similar strict regulations, firms in the country where strict regulations have been already introduced will have the advantage of exporting abatement technology and control equipment. The so-called “environmental industry” could benefit most from the “first-mover”

¹ Revised version of a paper prepared for the Workshop meeting of the research project on Environmental Regulation, Globalization of Production and Technological Change, UNU/INTECH, Maastricht, 14-15 March, 1997. We are grateful to the participants of the workshop and to Gu Shulin of UNU/INTECH for their comments and suggestions.

² For more general discussion on the interactions between industrial activities and the environment, see literature on “industrial metabolism” or “industrial ecology,” e.g. Allenby and Richards (1994), Ayres and Simonis (1994), Frosch (1995), and Graedel and Allenby (1995). Environmental regulations have only recently begun to be implemented effectively in developing countries and the availability of data on technological and economic aspects of cleaner technologies is limited. However, there exist some studies which deal with the adoption of environmental technologies in developing countries. See Kumar (1995) and van Berkel (1996).

³ This report does not specifically deal with the diffusion of environmental technologies. For those interested in this issue, see, for example, Kemp (1995).

advantage. German equipment for water pollution treatment and Japanese technology for dealing with air emission are well known examples of this kind of benefits.

The second is “innovation offsets.” Environmental regulations would induce firms to conduct more R&D activity for, beyond compliance with the regulations, the re-examination and reconsideration of the products and the whole production process. This might lead to process-integrated innovations (i.e. cleaner technologies), resulting in reduction in pollution and decrease in production costs or increase in output at the same time. Moreover, firms could make product innovations which are better in terms of quality and profitability as well as environmental protection. That is, not only productivity may increase through process innovations, but also product innovations (and patents) may be produced.⁴

There exist several attempts for a detailed study of innovation offsets in line with the economics of technological change literature. Kemp (1993) presents a critical survey of innovation models in pollution control. The main findings of the previous models are: first, that incentive-based instruments provide a greater spur to innovate in pollution control than direct control does; and second, that effluent fees (emission taxes) lead polluting firms to do too much R&D in pollution control and direct regulation too little R&D when the marginal conditions of pollution abatement change as a result of the innovation. However, what distinguishes the more recent contributions from these previous studies is the consideration of strategic behaviour, which is important in deriving firms’ incentives to innovate in industries especially in oligopolistic markets (Ecchia and Mariotti, 1994). Following this new line of research, Biglaiser and Horowitz (1995) study the firm’s incentives to engage in research for pollution-control technologies and to the adoption of new technologies that it discovers or that are being developed by other firms. One of their key findings is that by introducing across the board stricter standards (requiring more firms to adopt “cleaner” technologies”) research activity at the firm level is being reduced. The reason is that with strict adoption rules, firms that were previously considering the feasibility of R&D projects now find it more profitable not to pay the upfront research costs. They prefer to pay the license fee for well established technologies which are becoming available in the market.

As regards the empirical research on the effects of environmental regulation on firms, the debate is still open. On the one hand, Porter and van der Linde (1995b), citing successful cases in firms, claim that many of the innovation offsets produced by an increase in R&D activity are significant and that such cases can be found widely in various industries. They argue that rather than by simply adopting end-of-pipe technologies, which would mostly increase production costs, firms can create innovation offsets by re-examining the production process and product as a whole. According to a survey conducted by the Industrial Research Institute in the U.S. about 246 member companies during 1991, 13 per cent of their R&D was directed at environmental technology. This means that the last two to three years of increase in R&D has been spent on environmental technology. As Rushton (1993) reports based on interviews with several R&D directors around the U.S., firms may be enthusiastic about finding profitable solutions to environmental challenges.

Conceptually, the innovation offsets, besides the first-mover advantage, can be classified into four categories. The first is savings on raw materials and energy through efficient use of them. The second is reduced costs of waste treatment and disposal. The third is improved quality of products by the improvement or elimination of the separation process. The fourth is the development of new products. Porter and van der Linde emphasise the importance of an increase

⁴ Especially in the case of bulk chemicals, the productivity enhancement effect could be large. See, for example, Freeman (1982) and Enos and Park (1988).

in “resource productivity.” However, the extent to which savings on raw materials can contribute to a firm’s economic benefits would be different among industries, depending on the character of the products. For example, the proportion of raw material costs in producing bulk chemicals is quite large (about 60 per cent) whereas that for fine chemicals is relatively small. Therefore, innovation offsets resulting from material savings would be more important to commodity chemicals producers than to fine chemical producers.

On the other hand, based on interviews with managers in firms and macro data on environmental spending and business benefits, Palmer, Oates, and Portney (1995) argue that the importance of innovation offsets is quite limited. According to the Environmental Economics Division of the U.S. Commerce Department’s Bureau of Economic Analysis, the Pollution Abatement and Control (PAC) expenditures, which are used as the measurement of the stringency of environmental regulation in the U.S., came to \$102 billion in 1992 whereas cost offsets, which include both the product and process offsets, amounted to \$1.7 billion, less than 2 per cent of the estimated environmental expenditures.

However, some caveats are necessary in interpreting this estimate. While the costs of capital investment for regulatory compliance are incurred at the beginning of a project, innovation offsets are expected to materialise gradually in the long run. Therefore, by comparing the aggregate data on costs and benefits for one year, the costs of environmental regulation may be overestimated compared with offsets in the long run. In addition, some types of innovation offsets may not be reported in the survey. If a company withdraws from one product area due to stringent environmental regulation and enters a new product field which subsequently becomes profitable, these benefits may not be recognised as “innovation offsets”, because of the environmental regulation by the company.

Apart from the aforementioned points, there are several problems in adopting the PAC expenditures to measure the stringency of environmental regulation⁵. The assumption made here is that high PAC expenditures is a result of large efforts made by industries to reduce pollution and therefore reflect strict environmental regulations. That is, the measurement of PAC expenditures is a type of input-oriented indicators of environmental regulation, which are based on input efforts devoted to environmental protection (Beers and Bergh, 1996). However, regulatory compliance expenditures, as a measure of the environmental burden on industry, fall short of providing a truly exogenous measure of regulatory burden because the level of these costs also depends on the ability of an industry to react to regulations. For example, an innovative, competitive industry may respond to environmental regulations in a more efficient, cheaper way than a less innovative industry, and hence the former may spend less for compliance, independent of the stringency of environmental regulations.

Furthermore, there is no precise definition of PAC expenditures and no simple way to measure it accurately. For example, an investment in energy-saving equipment, which is itself environmentally friendly technology, may have been carried out as part of normal, profit-maximising investment decision. Especially in the case of process-integrated technologies, it is difficult to establish what portion of the total investment expenditures should be allocated to pollution abatement and control. Methodologies of the measurement remain diverse across countries, making international comparisons difficult.

Rather than input-oriented indicators like the PAC expenditures, output-oriented indicators can also be used to measure the stringency of environmental regulations. Output-oriented indicators

⁵ See, for example, Tobey (1990), Low (1992), and Jaffe and Palmer (1996).

are generally based on the concrete data of environmental situations, including pollutant emissions data.⁶ The logic supporting this approach is that better environmental quality has been achieved as a result of stricter environmental regulations. Although these output-oriented indicators, unlike the input-oriented indicators, take into account the results of compensating financial support from the government, they also have some limitations. One of the criticism is that high quality of the environment is not necessarily due to the imposition of strict environmental regulations. Natural environmental conditions or other social factors might have produced the current situation without regulations.

Another research project examined the Porter hypothesis by using an econometric model to analyze the relationship between environmental compliance expenditures (a measure of the stringency of environmental regulation) and R&D expenditures as well as successful patent applications in a cross-section of manufacturing industries (Jaffe and Palmer, 1996). They have found that lagged environmental compliance expenditures have a significant positive effect on R&D expenditures. However, contrary to the results of the study of Lanjouw and Mody (1996), little evidence has been found that industries' inventive outputs (as measured by successful patent applications) are related to compliance costs. This finding might suggest that incremental R&D activity induced by environmental regulations is not productive or produces results that accomplish regulatory compliance only but that do not come out as patentable innovations.

Although different in the analytical approach and the industries under observation, some other studies suggest that firms' response to environmental regulation has impeded productivity growth. Barbera and McConnell (1990) examine the direct and indirect productivity effects of environmental regulations for five polluting industries (i.e. paper; chemical; stone, clay, and glass; iron and steel; and non-ferrous metals). They conclude that the net impact of environmental regulations on total factor productivity growth accounts for about 10 to 30 per cent of the productivity decline of the 1970s in these industries. Gray and Shadbegian (1995) analyse data from 1979 to 1990 on both total factor productivity levels and growth rates. They find that plants with higher abatement cost levels have significantly lower productivity levels. However, they also find that estimates looking at productivity variation within plants over time, or estimates using productivity growth rates show a smaller and insignificant relationship between abatement costs and productivity. By analysing the impact of environmental and occupational health regulation on productivity level and productivity growth rates between 1974 and 1986, Robinson (1995) suggests that regulation diverts economic resources and managerial attention away from productivity-enhancing innovation. The reduction in productivity due to the Environmental Protection Agency (EPA) and the Occupational Safety and Health Agency (OSHA) regulation is estimated to be 28 per cent in the US chemical industry.

There is one caveat which should be mentioned here about the measurement of productivity. The conventional productivity indicator counts only outputs of commercial value but ignores other outputs like emissions which are a nuisance to society and, therefore, unsalable.⁷ If the negatively priced output (i.e. the cost of the environment damages of emissions) is included in the total output, environmental protection measures which seem to reduce productivity in the traditional sense might actually increase "true" productivity. However, it would be extremely difficult, if not impossible, to estimate the cost of the damages imposed on the environment by emissions,

⁶ Xing and Kolstad (1995), for example, adopt sulphur dioxide (SO₂) as a variable to reflect the overall level of environmental regulations.

⁷ As Repetto, Faeth, Rothman, and Austin (1996) put it, "The result is an incomplete and misleading indicator of efficiency - one that misrepresents the underlying process, and that is inconsistent with the law of physics."

including increased illness, reduced recreational opportunities, impairment of materials, and ecological impacts.⁸ In addition, the uncertainty and the measurement error would be significant.

3. Environmental Technologies in Chemical Process Industries

The definition and the classification of environmental technologies, including cleaner technologies, need careful treatment. It is always difficult to provide a clear and precise definition of complex environmental problems and technologies to deal with them.⁹ In terms of production process, most of the pollution-intensive industries can be regarded as “chemical-process industries.” In contrast to “physical-process industries” such as mechanical and automobile industries, in which the assembling process plays an important role, chemical reactions are crucial in the production process of the chemical-process industries, and consequently, by-products are created almost inevitably.

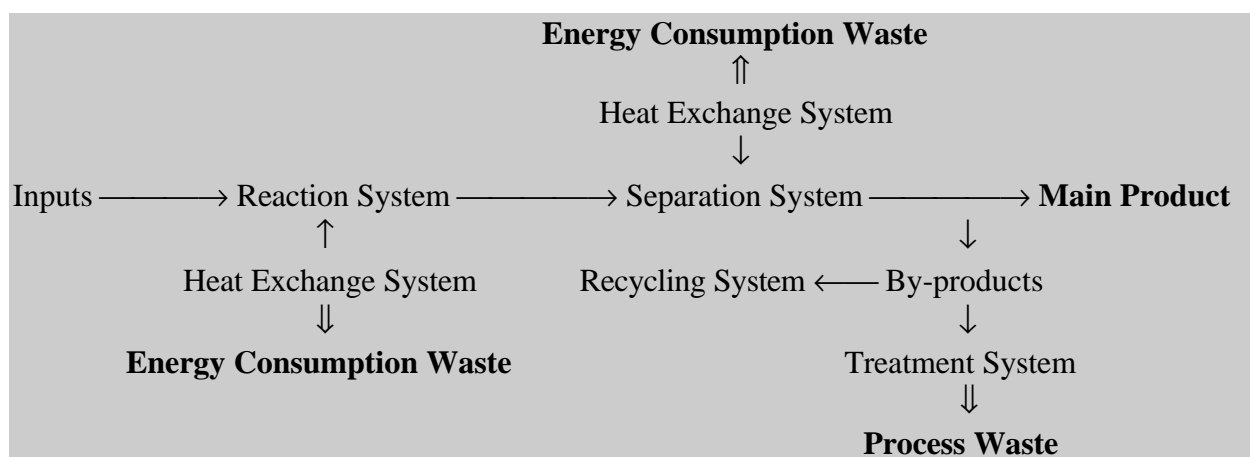
First of all, there exist two levels on which environmental technologies are developed or adopted: the product level and the production process level. When the main product itself is the source of an environmental problem, technological change on the product level is necessary. Among the examples is the chlorofluorocarbons (CFCs), for which substitute products have been developed by chemical companies, following the international agreement on the phase-out of CFCs.

In the chemical-process industries, production processes basically consist of five components: *reaction system*, *separation system*, *recycling system*, *waste treatment system*, and *heat exchange system* (Mizsey, 1994). While *energy-consumption waste* is emitted from the heat exchange system and composed of flue gas and ash from fuel combustion, the first four components produce *process waste*, which includes byproducts and purge streams of the production process.

Overall, the production process of the chemical-process industries, with input materials, main products, and by-products, can be drawn schematically as follows:

⁸ Cropper and Oates (1992), Arrow, et al. (1996), and Hahn (1996) advocate extensive use of benefit-cost analysis for regulatory decisions.

⁹ For example, Kemp (1993) groups environmental technologies into four categories: first, pollution control technologies, which prevent the direct release of environmentally hazardous emissions into the air, surface waters, or soil; second, off-site recycling and waste treatment technologies, including the treatment of effluent in collective waste water treatment plants, the clean-up of polluted soils, and the upgrading of waste material; third, process-integrated changes in production technology, input material changes, and good housekeeping, all of which reduce the amount of pollutants and waste materials generated during production; and fourth, environmentally beneficial products, like zero-emission motor vehicles and low-solvent paints, which are less damaging to the natural environment. Green and Irwin (1996) propose that, on the level of production process, environmental technologies could be divided into four categories: first, end-of-pipe treatment; second, end-of-pipe recovery for use in the same process or for use elsewhere; third, efficiency improvements in the production process (waste minimisation) and substitution of process materials; and fourth, radical redesign of the production process. They also suggest a way of classifying changes in products for environmental protection: first, changes in the material composition of the product; second, redesign of the product for the reduction of environmental impacts in the manufacturing phase, in the use phase, or in the post-use phase; and third, redesign of the product for longer durability.



The types of technological change for environmental protection are classified by identifying the source of environmental problems: energy consumption, by-product, or main product.

1) *Energy Consumption Waste*

Energy is needed in the chemical process industries for various operations: to drive endothermic reactions; to provide optimum reaction conditions of temperature and pressure; and to drive separation processes. When thermal energy is used through combustion process, pollutants are created, such as nitrogen oxides (NO_x),¹⁰ sulphur oxides (SO_x),¹¹ carbon monoxide (CO),¹² hydrocarbons.¹³ To achieve lower emission levels, the sources of energy supply and/or the pattern of its consumption need to be changed. For example, low- NO_x burners are often applied to the various implementation of staged combustion and have the important advantage of being a relatively low cost technology that can be used as a retrofit on existing sources to reduce NO_x

¹⁰ The vast majority of nitrogen oxides are emitted as nitric oxide (NO), although nitrogen dioxide (NO_2) is also produced. Nitric oxide is formed both from atmospheric nitrogen (thermal NO_x) and from nitrogen contained in some fuels (fuel NO_x). The latter source depends on the fuel composition and is not important for fuels with low nitrogen contents but is a major source of NO_x in coal combustion. Nitric oxide can be found, however, when any fuel is burned in air because of the high-temperature oxidation of nitrogen (Flagan and Seinfeld, 1988).

¹¹ Coals and heavy fuel oils contain appreciable amounts of sulphur. In fuel-lean combustion, the vast majority of this sulphur is oxidised to form sulphur dioxide (SO_2). Sulphides, predominantly H_2S and COS, may survive in fuel-rich flames. All of these compounds are considered air pollutants. The sulphides are odoriferous as well. Sulphur removal, either from the fuel or from the combustion products, is required for emission control. A commonly used sorbent for SO_2 is lime (CaO), which reacts with sulphur oxides to form calcium sulphate, or gypsum (CaSO_4). A fraction of the sulphur is further oxidised beyond SO_2 to form sulphur trioxide (SO_3). Sulphur trioxide is a serious concern to boiler operators since it corrodes combustion equipment. Fuel additives such as MgO have been used to control SO_3 formation (Flagan and Seinfeld, 1988).

¹² Carbon monoxide is an intermediate species in the oxidation of hydrocarbon fuels to CO_2 and H_2O . In fuel-rich regions of a flame, the CO levels are necessarily high since there is insufficient oxygen for complete combustion. Only if sufficient air is mixed with such gases at sufficiently high temperature can the CO be oxidised. Thus, imperfect mixing can allow carbon monoxide to escape from combustors that are operated fuel-lean overall. Even in premixed combustion systems, carbon monoxide levels can be relatively high due to the high equilibrium concentrations at the flame temperature. As the combustion products are cooled by heat or work transfer, the equilibrium CO level decreases (Flagan and Seinfeld, 1988).

¹³ Like CO, hydrocarbon emissions from combustion systems result from incomplete combustion. Equilibrium levels of hydrocarbons are low at the equivalence ratios at which practical combustion systems are normally operated, and the oxidation reactions are fast. Hydrocarbons can escape destruction if poor mixing allows very fuel-rich gases to persist to the combustor exhaust or if the oxidation reactions are quenched early in the combustion process. The composition and quantity of hydrocarbons in exhaust gases depend on the nature of the fuel and of the process that limits oxidation. Polycyclic aromatic hydrocarbons (PAH) are a particularly significant class of combustion-generated hydrocarbons since they include a number of known carcinogens or mutagens. These compounds form in extremely fuel-rich regions of the flame, where hydrocarbon polymerisation reactions are favoured over oxidation (Flagan and Seinfeld, 1988).

emissions. Furthermore, in terms of the global warming, technologies for improving the efficiency of energy consumption will be necessary to reduce the emission of carbon dioxide, which is one of the most important greenhouse-effect gases.¹⁴

In new technologies dealing with energy consumption wastes, neither the main product nor the chemical reactions will be changed, limiting the impact of the technological change on the production process. Thus firms would probably consider this option relatively easy. Furthermore, by increasing the efficiency of energy consumption in the production process, energy cost is saved and an increase in productivity is expected. On the other hand, interactions with other technological areas in terms of knowledge and information might be limited, and thus “innovation offsets” might not be large.

II) *Byproduct*

When the by-product creates process wastes, broadly speaking, there exist two kinds of technology to deal with them: *end-of-pipe technology* and *process-integrated technology*.

A) *End-of-Pipe Technology*

The end-of-pipe technology, which is basically added to the final stage of a production process, aims at removing or transforming wastes emitted from the production process. The application of this technology requires little change in the production process, and hence the uncertainty about the impact of technological change is limited. These technological applications are available from specialised manufacturers of pollution treatment equipment for air emission, waste water, and solid wastes.

There are a variety of approaches to removing gaseous pollutants from effluent streams, including absorption, adsorption, condensation, chemical reaction, incineration, and selective diffusion through a membrane.¹⁵ For removal of particles from gas streams, there are several different classes of control equipment: settling chamber; cyclone; electrostatic precipitator; filters; and scrubbers. There are several approaches to deal with wastewater: physical process; physico-chemical process; and biochemical process. Depending on the characteristics and chemical composition, various kinds of technologies are used for treating industrial wastes. Generally speaking, there exist two types of treatment of solid wastes: incineration of combustible organic materials and disposal of incombustible inorganic materials.

B) *Process-Integrated Technology*

On the other hand, the purpose of the process-integrated technology is to eliminate or reduce the creation of waste itself within the production process. For process-integrated pollution control, two types of technological change can be implemented.

¹⁴ As the United Nations Framework Convention on Climate Change came into force in March 1994, following ratification by fifty countries, carbon dioxide (CO₂) emissions are now required to be cut to 1990 level by 2000 (Bland and Laird, 1996).

¹⁵ The most common devices used for absorption are columns containing packing or regularly spaced plates, open spray chambers and towers, and combinations of sprayed and packed chambers, which promote intimate contact between the gas and the liquid. Gas adsorption is used industrially for odour control and for the removal of volatile solvents such as benzene, ethanol, trichloroethylene, and so on, from effluent streams. Condensation is carried out in a device that appropriately cools the gas stream and provides a means to remove the layer of condensed liquid. The chemical reaction category refers to those where the key element of the separation is the reaction itself, although many of the separation processes involve chemical reaction. Incineration involves the combustion of the species and is an important process for the treatment of toxic species, where virtually complete removal is necessary. Selective diffusion processes through a membrane have found application in removing gases such as CO₂, H₂S, and H₂ from natural gas streams (Flagan and Seinfeld, 1988).

1) *Physical modification of the production process*

For a given process technology, physical modifications can be taken for the production to be performed in a more efficient and cleaner way.

a) *Good housekeeping and operations*

This includes preventing unnecessary spillages and releases of materials from the production processes. In some cases, it would be possible to achieve a significant environmental return simply through minor improvements in production management at the shop floor level.

b) *Reuse and recycling*

Useful materials in waste streams can be fed back into the production process, reducing process wastes and input material consumption at the same time. Without changing the composition of the main product, the production process is physically modified so that as much material as possible is reused or recycled. In order to achieve this, it is essential to improve technologies and facilities for the separation, collection, and recovery of used material in effective and efficient ways. Available options might include: process-integrated flue-gas purification technologies and filter systems aimed at returning substances to the production process to reduce air emissions; better water removal and internal circulation technologies to increase water reuse; and detection and separation equipment for undesirable substances to increase the reuse of water.

These methods deal with the pollution physically without altering the chemical reaction of the production process. Hence, the chemical composition of the main product is not affected. However, its quality may change. For example, the purity of the main product might increase due to the improvement of the separation system. That would lead to an improved competitiveness of the product. In addition, when the recycling system is improved, and the byproduct can be utilised in another reaction system, whether within the same plant or in a different plant, additional profits would be gained, especially in the case of bulk chemicals, for the production of which material costs occupy a large share of the total costs. These possibilities will generally increase productivity and have positive implications for the company.

2) *Modification of the Reaction System*

In this category, changes in reaction conditions, improved yield/selectivity, and input changes are included.

a) *Changes in Reaction Conditions (temperature, pressure, etc.)*

A new catalyst could alter the conditions at which the chemical reaction takes place from high temperature (e.g. 1000 °C) and/or pressure (e.g. 500 atm) to low temperature (e.g. 300 °C) and/or pressure (e.g. 200 atm). In this case the energy consumption needed to implement the chemical reaction will be reduced, and consequently, its associated waste (NO_x, SO_x, CO₂, etc.) will also decrease. In addition, total cost per production will be reduced.

b) *Improved Yield/Selectivity*

Yield refers to the amount of a specific product formed in a given process per mole of entering reactant, while selectivity is related to the number of moles of desired product formed per mole of undesired product formed.¹⁶ A new catalyst would make it possible to obtain a desired product via a different mechanism, affecting both the yield and the selectivity. Therefore, catalysts are expected to play a key role in energy and material savings by achieving high yield and/or high

¹⁶ For more technical discussion on chemical reactions involving catalysts, see Levenspiel (1972) and Fogler (1992).

selectivity.¹⁷ Here it should be noted that a catalyst changes only the rate of a reaction, but it does not affect the equilibrium. Productivity would increase in this case without changes in the composition of the main product itself.

c) *Input Change*

Input materials (raw materials and auxiliary substances) could be changed so that the impacts of byproducts on the environment would be minimised. By changing the input materials, the byproduct could be changed to another (less environmentally harmful) material. For example, methacrylic acid and its derivatives, which are important monomers in the plastic industry, are usually synthesised from propylene and benzene via acetone. This route, however, uses the hazardous reagents hydrogen cyanide and sulphuric acid, and for every mole of product, half a mole of ammonium sulphate is formed as waste. In contrast, a new, clean route to methacrylates uses ethylene, carbon monoxide, and hydrogen as inputs and produces only water as a byproduct. In some cases the final product will also be changed as a result of using different input materials. Although it would depend on each case whether a newly developed product will be more desirable than the original one, firms might successfully create a new product, less harmful to the environment and more competitive in the market.

III) *Main Product*

When the main product is the source of environmental problems, obviously that product has to be changed to a different one, which will be designed so that its detrimental effects on the environment will be reduced as much as possible. For that purpose, firms might adopt an integrated design approach. Especially, Life Cycle Assessment (LCA) is a useful tool to evaluate the environmental impacts of a product throughout its life cycle from the phase of raw material acquisition via production to consumption.¹⁸

Here the product change is defined as a change in the chemical composition of the final product. Examples include the replacement of compounds of chlorofluorocarbons (CFCs), including CFC-11 and CFC-12, with those of hydrochlorofluorocarbons (HCFCs), or hydrofluoroalkanes (HFAs), including HFC-134a and HFC-32, whose associated Ozone Depletion Potential (ODP) is zero because they don't contain any chlorine and therefore will not be able to attack ozone molecules. In most of the cases in which the chemical composition of the main product is changed, at least one of the input materials has to be changed. It should be noted that in such cases the composition of the byproduct will also be affected as a result and the whole chemical reaction will be changed. In the case of CFCs, as new products are much more complex than those replaced, the change in the route of chemical reactions is also significant.¹⁹ Therefore, although this case can be considered basically as product innovation, process innovation would also be necessary at the same time.

The hierarchy of pollution abatement and control consists of five options: prevention; reduction; recycling; treatment; and disposal at the bottom (Clift and Longley, 1994; Clift, 1995). Using this taxonomy, the end-of-pipe technology deals with treatment and disposal of wastes whereas pollution prevention, reduction, and recycling are implemented with product change or the process-integrated technology. These two methods, namely, product change and the process-integrated technology, compose the so-called *cleaner technology*. The transition from the end-of-pipe to cleaner technologies proceeds along a sliding scale from curative to preventive measures.

¹⁷ For example, Koch, Krause, Manzer, Mehdizadeh, Odom, and Sengupta (1996) emphasise the importance of catalysts for environmental protection.

¹⁸ See Society of Environmental Toxicology and Chemistry (1991) for more information on LCA.

¹⁹ While most CFCs are produced in a single catalytic step, alternatives such as HFC-134a will require 2 to 5 complex catalytic steps (Koch, Krause, Manzer, Mehdizadeh, Odom, and Sengupta, 1996).

4. Technological Trends in Pollution-Intensive Industries

4.1. Pulp and Paper Industry

4.1.1. Introduction to the Pulp and Paper Industry

The pulp and paper industry produces commodity grades of wood pulp, primary paper products, and paper board products. Paper is manufactured by applying a watery suspension of cellulose fibers, which is called pulp, to a screen which allows the water to drain and leaves the fibrous particles behind in a sheet. Only a few paper products for specialised uses are created without the use of water, via dry forming techniques. The production of pulp is the major source of environmental impacts in the pulp and paper industry.

Broadly speaking, there are three types of production facilities in the pulp and paper industry: pulp facilities; integrated pulp and paper facilities; and converting facilities. Pulp facilities are comprised of mills that only produce pulp which is sold to the open market (market pulp) or is transferred to another facility where it is utilised for the production of a final product. Integrated pulp and paper facilities consist of mills that use the bulk of their pulp output in their own primary paper production and sell only the remaining part to the open market and mills that produce only paper products from pulp produced elsewhere. This industry also includes facilities that convert primary paper and paper board products to finished paper products such as packaging, envelopes, and shipping containers. While pulp and paper mills tend to be capital-intensive with large facilities in terms of production, employees, and use of chemical substances, converting facilities tend to be smaller and labour-intensive plants.

Pulp mills are located primarily in regions where pulp trees are harvested from natural stands or tree farms. However, paper mills are more widely distributed, located in proximity to pulping operations and near converting sector markets. The distribution of paperboard mills follows the location of manufacturing in general because such operations are the primary market for paperboards products. There exists a tendency for pulp mills in the industrialised countries to move into higher-value added products. On the other hand, the centres of market pulp supply is moving to the South, and some countries, including Brazil and Indonesia, are also moving toward local integration of pulp and paper production (United Nations Industrial Development Organization, 1993).

Since converting facilities are different in the production process, in terms of the size of facilities, and use of chemical substances, environmental regulations often make a distinction between primary product mills and converting facilities. In this chapter, environmental issues in the primary product mills are mainly considered.

4.1.2. Production Processes and Pollution Sources in the Pulp and Paper Industry

The description of the production processes in the pulp and paper industry is based on the Commission of the European Communities (1993, 1996c) and the United States Environmental Protection Agency (1995e).

The production of paper and paperboard takes place into four stages:

- pulp making
- pulp processing
- bleaching; and
- paper/paperboard production.

Most of the fibre used for paper production comes from long-fibered softwood and shorter-fibered hardwood trees, and pulp mills usually use a mixture of hardwood and softwood fibre in the form of wood chips. Preparing the wood stem for pulp making consists of a number of operations, including debarking, chipping, and chip screening. In recent years, mill waste fibers, newsprint, and corrugated boxes have gained increasing acceptance as secondary fibre sources.

Stock pulp mixture is produced by digesting raw materials into its fibrous constituents via chemical (e.g. Kraft chemical), semi-chemical, mechanical, or secondary fibre pulping. When fibre is obtained from wood, the most common pulping material, chemical pulping is usually adopted. Chemical pulping releases cellulose fibers by selectively destroying the chemical bonds in the glue-like substance (lignin) that binds the fibers together. Therefore, chemical pulps are stronger and can be bleached easier. One of the disadvantages of chemical pulps is that the yields are relatively low (about 50 per cent). On the other hand, mechanical pulps give higher yields (more than 90 per cent) and good quality of printing. However, they are much weaker and darker than bleached chemical pulps because they still contain large amounts of lignin and are difficult to bleach.

After pulp is produced, impurities such as uncooked chips are removed by pulp processing, including screening, defibering, and deknottting. Pulp screening removes remaining oversized particles such as bark fragments and uncooked chips. In open screen rooms, on the one hand, wastewater from the screening process goes to wastewater treatment prior to discharge. In the closed-loop screen rooms, wastewater from the process is reused in other pulping operations and ultimately enters the mill's chemical recovery system. During the pulp processing, residual spend cooking liquor from chemical pulping is also washed from the pulp using brown stock washers. Efficient washing is critical to maximise return of cooking liquor to chemical recovery and to minimise carry-over of cooking liquor, which is known as brown stock washing loss, into the bleach plant because excess cooking liquor increases consumption of bleaching chemicals.

Then the pulp stock needs to be bleached to improve its brightness. The lignin content of a pulp is the major determinant of its bleaching potential. While chemical pulps can be bleached to a greater extent due to their low (about 10 per cent) lignin content, pulps with high lignin content (e.g. mechanical or semi-chemical) are difficult to bleach fully and require heavy chemical inputs. However, excessive bleaching of mechanical and semi-chemical pulps results in loss of pulp yield due to fibre destruction. After bleaching, the pulp is processed into a form suitable for paper-making equipment.

At the paper-making stage, the pulp can be combined with dyes, strength building resins, or texture adding filler materials, depending on its intended end product. Afterwards, the mixture is dewatered, leaving the fibrous constituents and pulp additives on a wire or wire-mesh conveyer.

Additional additives may be applied to the fibers after the sheet-making step as they are carried through a series of presses and heated rollers. The final paper product is usually spooled on large rolls for storage.

While papermaking activities have not been associated with significant environmental problems, the processes used to manufacture pulp, which is later converted into paper, are the major sources of environmental concerns for this industry. Overall, most of the pollutant releases associated with pulp and paper mills occur at the pulp making and bleaching stages, where the majority of chemical inputs occur. Pulp-making processes are the sources of air and water pollutant outputs. Among the various pulping processes, i.e. chemical, mechanical, and semi-chemical pulping, the chemical pulping process releases nuisance odours and particulate to the air. Bleaching processes, primarily used to whiten and brighten pulps for paper manufacture, produces wastewater containing chlorinated compounds such as dioxins.

General water pollution concerns for pulp and paper mills are effluent solids, biochemical oxygen demand, toxicity, and colour. Toxicity problems arise from the presence of chlorinated organic compounds such as dioxin, furans, and others, which are collectively referred to as adsorbable organic halides (AOX), in wastewater after the chlorination/extraction sequence. Screening and cleaning operations during the pulp processing stage are usually sources of large volumes of wastewater. In addition, power boilers and chip digesters are generic pulp and paper mill sources of air pollutants such as particulates and nitrogen oxides. Chip digesters and chemical recovery evaporators are the most concentrated sources of volatile organic compounds (VOCs). The chemical recovery furnace is a source of fine particulate emissions and sulphur oxides.

4.1.3. Environmental Technologies in the Pulp and Paper Industry

The pulp and paper industry has focused its efforts on reducing the releases of toxics, in particular chlorinated compounds. Many of the cleaner technologies proposed for the control of toxic releases consist of process changes that will substitute chlorine dioxide for elemental chlorine and that totally eliminate chlorine in bleaching processes. Furthermore, in some cases, cleaner technologies primarily aimed at reducing toxics releases also lead to reductions in the conventional pollutants such as organic compounds, including biochemical oxygen demand (BOD) and chemical oxygen demand (COD), total suspended solids (TSS), and AOX, and contribute to reduced water use, sludge volumes generated, and air emissions, resulting in a reduction in waste treatment costs. However, because the pulp and paper industry is highly capital-intensive and uses long-established technologies with long equipment lifetimes, cleaner technologies which involve process-integrated modifications will be expensive and require long time periods to implement. Although it is difficult to draw a definite conclusion about the cost impacts of the introduction of cleaner technologies, depending on various factors including the age of equipment and the price of substitute materials, probably the production cost will increase as dioxins and other chlorine-related pollutants are reduced further.

End-of-Pipe Technologies

Overall the pulp and paper making process is water-intensive; pulp and paper mills usually need to operate primary wastewater treatment plants to remove organic and inorganic materials, including BOD, TSS, and other pollutants, before discharging wastewater to a receiving waterway. The two main waste treatment processes in use in the pulp and paper industry are primary sedimentation systems featuring clarifiers, and organic oxidation systems that feature either aerated stabilisation basins or activated sludge processes (Harrison, 1994).

Primary (Physical) Treatment²⁰

Mechanical treatment for removing suspended solids fibers which will settle in a reasonable time from pulp and paper mill effluents is commonly the first external treatment unit operation. Modern primary treatment design to remove suspended solids largely employs units with thickener type mechanically cleaned clarifiers mostly of circular design. The clarifier is the primary piece of equipment in the sedimentation system, followed by subsequent dewatering of sludge handled by such dewatering units as twin wire or screw presses. When properly designed, the mechanically cleaned clarifier gives dependable, settleable solids reduction. Currently, these are the basis of conventional primary treatment applied world-wide in the pulp and paper industry. Other processes for removing suspending solids are fine screening and granular media filtration methods.

Secondary (Biological) Treatment²¹

Biological treatment systems are used extensively by pulp and paper mills, especially for BOD reduction. Typical biological treatment systems presently used are: aerated stabilisation basins; aerated or oxygen activated sludge systems; oxidation ponds; trickling filters; spray irrigation; and land treatment systems. Among them, aerated stabilisation basins and aerated or oxygen activated sludge are the most common secondary treatment systems used by the pulp and paper industry, and both methods are based on accelerating nature's process of reducing wastes to carbon dioxide and water by using oxygen-consuming micro-organisms. There are methods to optimise this process through system designs and selective mill programs such as bioaugmentation, which is the use of naturally occurring hybrid micro-organisms including specifically adapted strains of bacteria and fungi together with enzymes and surfactants (Harrison, 1994).

Tertiary (Physico-Chemical) Treatment²²

In many cases, non-biological tertiary treatment systems are chemical associated coagulation, sometimes followed by sand filtration. They may then be regarded as an add-on option in cases when the treatment plants need to meet the demand for lower levels of pollutants from mills, especially the bleached pulp mill effluent. These systems may also be an integrated part of a greenfield primary and/or secondary treatment plant. Tertiary treatment is normally considered expensive and only a few mills apply it today. Chemicals for tertiary treatment include aluminum oxide, ferric oxide, polyelectrolytes and others.

Cleaner Technologies

Although widely adopted, most of the conventional, end-of-pipe treatment technologies are not effective in destroying many chlorinated compounds and often merely transfer the pollutants by settlement or absorption onto treatment sludge or volatilisation to the air. Therefore, efforts to prevent chlorinated releases have focused on source reduction and material substitution

²⁰ Physical treatment in general eliminate solid particles which exist in water with physical methods such as gravitational force and screening and, broadly speaking, include sedimentation, float separation, and filtration. Sedimentation is a type of methods with which particles in water are separated by settling in gravitational, centrifugal, or electromagnetic fields. Float separation is used for things whose specific weight is larger such as oils and fats. Filtration is a method to separate impurities in water with layers of sand and active carbon, screens made of metal, fibre, or perforated materials, or slit (Ichikawa, 1981).

²¹ Biological treatment processes generally remove impurities in water by utilising synthesis, oxidation, and respiration of organisms. Activated sludge, trickling filter, oxidation pond, and anaerobic decomposition are used for biological processes. However, it is necessary to separate and treat the organics generated (Ichikawa, 1981).

²² Among the methods commonly used for physico-chemical treatment are flocculation and combustion. Flocculation is sedimentation of stable colloid particles dispersed in water by aggregating them with coagulating agent. Some of the physico-chemical processes are considered as preparation for physical processes (Ichikawa, 1981).

technologies such as defoamers, bleaching chemical or wood chip substitution to reduce the industry's use and release of chlorinated compounds. Such source reduction efforts and material substitutions usually require substantial changes in the production process. In addition to the major process changes aimed at reducing toxics releases, the industry is implementing a number of cleaner technologies to reduce water use and pollutant releases (BOD, COD, and TSS) such as: dry debarking, recycling of log flume water, improved spill control, bleach filtrate recycle, closed screen rooms, and improved storm water management.

The industry has also worked to increase the amount of secondary and recycled fibers used for the pulping process. One problem in using recycled fibers is the presence of sticky contaminants, called stickies. Stickies in recycled paper fibers reduce paper quality and cause paper machine downtime. Another problem associated with wastepaper reuse is the probable presence of small quantities of dioxins and other chlorinated organic compounds. In addition, as potentially pathogenic organisms may exist in the feedstock, cleanliness and sanitation issues arise. Although some new technologies have been developed for the de-inking and bleaching processes, there has not been so many promising technologies which effectively and efficiently address the problems of stickies, dioxins, and microbes in the wastepaper feedstock.²³

Good Housekeeping and Operations

Black Liquor Spill Control and Prevention

The mixture of dissolved lignin and cooking liquor effluent from the pulping reactor and washed pulp is known as black liquor. Raw black liquor contains high levels of BOD, COD, and organic compounds. Spills of black liquor can result from overflows, leaks from process equipment, or from deliberate dumping by operators to avoid a more serious accident. Spills of black liquor have impacts on receiving waters, and they are also a source of air emissions and can shock the microbial action of wastewater treatment systems. Black liquor losses also result in the loss of the chemical and heat value of the material. Systems needed to control black liquor spills are a combination of good design, engineering, and most importantly, accurate operator's training.

Improved Brownstock and Bleaching Stage Washing

Liquor solids remaining in the brownstock pulp are carried over to the bleach plant and then compete with the remaining lignin in the pulp for reaction with the bleaching chemicals. Improved washing, therefore, can reduce the required amount of bleaching chemicals and the subsequent reductions in chlorinated compounds as well as conventional pollutants. Modern washing systems with improved solids removal capacity and energy efficiency are beginning to replace the conventional rotary vacuum washers. Technologies for reduced effluent flows and water use are also used in the bleaching plant.

Improved Chipping and Screening

The size and thickness of wood chips is critical for proper circulation and penetration of the pulping chemicals. Chip uniformity is controlled by the chipper and screens that remove under and oversized pieces. As chip thickness is extremely important in determining the lignin content of pulp, improper chip thickness can therefore result in increased use of bleaching chemicals and the associated chlorinated compounds and conventional pollutants. Equipment is being introduced to separate chips according to their thickness as well as by length and width.

²³ Recently it has been reported that supercritical CO₂ and propane can remove substantial quantities of dioxins and stickies from recycled paper fibers, and supercritical CO₂ can inactivate microbes (Blaney and Hossain, 1997).

Improved Chemical Controls and Mixing

The formation of chlorinated organics can be minimised by avoiding excess concentrations of chlorine-based bleaching chemicals within reactor vessels. This can be accomplished by carefully controlling the chemical application control and monitoring systems. In addition, the introduction of high shear mixers will decrease formation of chlorinated organic compounds.

Reuse and Recycling

The chemical recovery system is a crucial component of the chemical pulping process. It recovers process chemicals from the spent cooking liquor for reuse. The chemical recovery system significantly reduces pollutant outputs while providing substantial economic return due to the recovery of process chemicals. Economic benefits include savings on chemical purchase costs due to high regeneration rates of process chemicals, and energy regeneration from pulp residue burned in a recovery furnace.

Changes in Reaction Conditions

Extended Delignification

Extended delignification further reduces the lignin content of the pulp before it moves to the bleach plant. Because the amount of bleaching chemicals required to achieve a certain paper brightness is proportional to the amount of lignin remaining in the pulp after the pulping process, extended delignification can reduce the amounts of bleaching chemicals needed. The lignin content of the brownstock pulp has been reduced by between 20 and 50 per cent with no losses in pulp yield or strength using such processes. In consequence, chlorinated compounds generated during bleaching are reduced in approximate proportion to reductions in the brownstock lignin process. Facility energy requirements have increased slightly with extended delignification.

Split Addition of Chlorine/Improved pH Control

Reducing the chlorine concentration during the bleaching process by adding elemental chlorine in incremental charges has been shown to reduce the formation of unwanted chlorinated organic compounds. A high pH in the chlorination stages is also known to reduce the formation of chlorinated organic compounds, normally with a decreased pulp yield. However, in combination with split chlorine addition, a high pH has been observed to reduce the formation of chlorinated compounds without a loss of yield.

Improved yield/selectivity with catalysts

Anthraquinone Catalysis

The addition of anthraquinone (a chemical catalyst produced from coal tar) to the pulping liquor has been shown to speed up the Kraft pulping reaction and increase yield by protecting cellulose fibers from degradation. The anthraquinone accelerates the fragmentation of lignin, allowing it to be broken down more quickly by the pulping chemicals. This lowers the amount of lignin in the pre-chlorination pulp, and, thus, reduces the amount of bleaching chemicals needed. Anthraquinone catalysts are increasingly used in combination with oxygen delignification and extended delignification to overcome boiler capacity bottlenecks arising from these delignification processes.

Input Change

Oxygen Delignification

Oxydelignification also reduces the lignin content in the pulp. The process involves the addition of an oxygen reactor between the Kraft pulping stages and the bleach plant. Oxygen delignification can reduce the lignin content in the pulp by as much as 50 per cent resulting in a potentially similar reduction in the use of chlorinated bleaching chemicals and chlorinated compound

pollutants. The process can be used in combination with other process modifications that can completely eliminate the need for chlorine-based bleaching agents. In addition, unlike bleach plant filtrate, the effluent from the oxygen reactor can be recycled through the pulp mill recovery cycle, further reducing the non-pulp solids going to the bleaching plant and the effluent load from the bleach plant. The net effect is reduced effluent flows and less sludge generation. The recovered energy and reduced chemical use offset the cost.

Ozone Delignification

As a result of a considerable research effort, ozone delignification (ozone bleaching) is now being used in the pulp and paper industry. The technology has the potential to eliminate the need for chlorine in the bleaching process. Ozone delignification is performed using processes and equipment similar to that of oxygen delignification. Oxygen delignification and /or extended delignification processes are considered a prerequisite for successful ozone bleaching. When used in combination, the two processes can result in a high quality bright pulp that requires little or no chlorine or chlorine dioxide bleaching. Overall emissions from the combination of the oxygen and ozone processes are substantially lower than conventional processes because effluents from each stage can be recycled. Ozone generation systems are complex and account for a high percentage of the total costs.

Enzyme Treatment of Pulp

Biotechnology research has resulted in the identification of a number of micro-organisms that produce enzymes capable of breaking down lignin in pulp. These organisms are called xylanases. Since enzymes are used as a substitute for chemicals in bleaching pulp, their use will result in a decrease in chlorinated compounds released somewhat proportional to the reduction in bleaching chemicals used. Enzymes are also being used to assist in the deinking of secondary fibre. Use of enzymes may also reduce the energy costs and chemical use in retrieving ink sludge from deinking effluent.

Chlorine Dioxide Substitution

The substitution of chlorine dioxide for elemental chlorine as a bleaching agent is gaining widespread use due to its beneficial impacts on pulp and effluent quality. The use of chlorine dioxide in place of chlorine increases the proportion of oxidative reactions, thereby reducing the formation of residual chlorinated organic pollutants. Chlorine dioxide bleaching produces about 20 percent of the chlorinated compounds produced by using elemental chlorine. Chlorine dioxide substitutions approaching 100 per cent have been shown to increase pulp yields and quality. However, the use of chlorine dioxide is two to four times more expensive than the equivalent oxidising power using elemental chlorine. The processes used to manufacture chlorine dioxide generate a number of by-products that may have environmental impacts, including spent acids, chlorine gas, salt cakes, and acid cakes.

Oxygen-Reinforced/Peroxide Extraction

Oxygen-reinforced extraction (or oxidative extraction) and peroxide-reinforced extraction processes used separately or together have been shown to reduce the amount of elemental chlorine and chlorine dioxide needed in the bleaching process while increasing the pulp brightness. Gaseous elemental oxygen (in the case of oxygen-reinforced extraction) and aqueous hydrogen peroxide (in the case of peroxide extraction) are used as a part of the first alkaline extraction stage to facilitate the solubilization and removal of chlorinated and oxidised lignin molecules.

4.2. Organic Chemical Industry

4.2.1. Introduction to the Organic Chemical Industry

An exact definition of the organic chemical industry is very difficult. The industrial organic chemical sector produces mainly organic chemicals, which contain carbon (C), used as either chemical intermediates or end-products. This means that it is separated from the petroleum (oil and gas) refining sectors, which are primarily engaged in selling hydrocarbons as fuels. By this definition, this industry does not include plastics, drugs, soaps and detergents, agricultural chemicals, paints, and allied products which are typically end-products manufactured from industrial organic chemicals.

The basic hydrocarbon sector processes petroleum refinery feedstocks derived from petroleum and natural gas and from recovered coal tar condensates generated by coke production. The purpose of this large-scale process is to convert the feedstocks into more reactive types of hydrocarbons, that is, olefins (alkenes, e.g. ethylene, propylene, etc.) and aromatics (e.g. benzene, toluene, xylene, etc.). The industrial organic chemical market has two broadly defined categories, commodity and specialty. Commodity organic chemicals are usually intermediates. Most of them are produced in large volumes, using dedicated equipment with continuous and efficient processing, and the manufacturers generally compete on price. As is distinct from the commodity chemicals, specialty chemicals include several thousand distinct products, and they are usually made on a small tonnage scale by using batch processes with two or three different reaction steps to produce a product, often in plants which use multi-purpose equipment. The manufacturers follow market demands and compete on technological expertise, which adds value to their products.

Organic chemical products from oil-producing countries like Saudi Arabia and Mexico and the East Asian countries, including South Korea and China, are beginning to compete with products from industrialised countries in the commodity markets. In an attempt to avoid the fierce price competition, many organic chemical firms in the industrialised countries are switching resources from basic organic chemicals to specialty chemicals and high value-added products.

4.2.2. Production Processes and Pollution Sources in the Organic Chemical Industry

As the industrial organic chemical industry includes thousands of chemicals and hundreds of processes, it is not possible to discuss in detail here all of the production processes adopted in this sector. In this section, the description on the production processes is based on the United States Environmental Protection Agency (1995c) and the Commission of the European Communities (1994a, 1996b). In general, a set of building blocks (feedstocks) is combined in a series of reaction steps to produce both intermediates and end-products. Primary building blocks (e.g. ethylene, propylene, and benzene) are typically used in more reactions than the building blocks further down the chain. Most feedstocks can participate in more than one reaction, and there is typically more than one reaction route to an end-product.

The typical chemical synthesis process involves combining multiple feedstocks in a series of unit operations, including chemical reaction and separation processes. The first unit operation is chemical reaction. The type of reaction process used to manufacture organic chemicals depends on the intended product. However, several types of reactions are common, including polymerisation, oxidation, and addition. Polymerisation is a chemical reaction usually carried out with a catalyst, heat, or light (often under high pressure), in which a large number of relatively

simple molecules combine to form a chain-like macromolecule. Oxidation means in the narrow sense that a substance is chemically combined with oxygen.²⁴ Addition covers a wide range of reactions where a double or triple bond is broken and a component is added to the structure. Alkylation can be considered an addition, as can some oxidation reactions.

Commodity chemicals tend to be synthesised in a continuous reactor while specialty chemicals are usually produced in batches. Most reactions take place at high temperatures, involve metal catalysts, and include one or two additional reaction components. The yield of the reaction will partially determine the kind and quantity of byproducts and releases. Many specialty chemicals require a series of two or three reaction steps.

Once the reaction is complete, the desired product must be separated from the byproducts by a second unit operation. The separation technology employed depends on many factors, including the phases of the substances being separated, the number of components in the mixture, and whether the recovery of byproducts is important. Numerous techniques such as distillation, extraction, filtration, and settling can be used singly or in combination to accomplish separations. The final product may be further processed, for example by spray drying or palletising, to produce the saleable item. Frequently byproducts are also sold in a market, and their value affects the cost of the production process.

Relatively few organic chemical manufacturing facilities are single product/process plants. In addition, many process units are designed so that production levels of related products can be varied over wide ranges. This flexibility is required to accommodate variations in feedstock and product prices which can change the production rate and processes used, even on a short-term (less than a year) basis.

As industrial organic chemical manufacturers use and generate large numbers and quantities of chemicals, the industry produces emissions of chemicals to all media, including air (through both fugitive and direct emissions), water (direct discharge and runoff), and land. The types of pollutants which a single facility releases depend on the feedstocks, processes, equipment in use, and maintenance practices. These can vary from hour to hour and can also vary with the part of the process that is underway.

Among the chemicals released by organic chemical facilities are hydrocarbon feedstocks (e.g. methanol, ethylene glycol, acetone, etc.) and reaction feedstocks (e.g. ammonia, nitric acid, ammonium sulphate, and sulphic acid), reflecting their volume of usage. Hydrocarbons may be released to the atmosphere from storage tank leakage, vents and loading operations. In cases where products are volatile liquids stored and/or transported in bulk or in drums, as much as 50 per cent of the losses to air may occur in transport and storage, rather than in processing. Fugitive emissions are generally defined as volatile organic compound (VOC) emission sources, not associated with a specific piece of equipment but scattered throughout the plant. Such emissions from organic chemical plants mainly originate, for example, from valves, gaskets, or during wastewater treatment. Because of their mobility, VOCs may be significant water as well as atmospheric pollutants. Vapours (either chemically unchanged or modified) are later condensed and absorbed into surface waters, or they may be lost from water solution or suspension and later precipitated.²⁵ Emissions to air also arise from furnace flue gases and incineration waste gases. Liquid wastes (organic or aqueous) include surface run-off, cooling water, and equipment wash

²⁴ In the broad sense, oxidation means reactions in which electrons are transferred from one substance to another.

²⁵ Around 80 per cent of all organic pollutants in air will be estimated to end up in the sea. Most of this occurs either from direct absorption to the sea from the air or via rivers (Commission of the European Communities, 1994a).

solvent/water. Spillage of tar and oil, which can lead to contaminated surface run-off from surrounding areas, may result from storage and loading operations. Spent catalysts and residue sludge are examples of the emissions of solid waste from the organic chemical industry.

4.2.3. Environmental Technologies in the Organic Chemical Industry

In the organic chemical industry, as is mentioned above, production processes, pollution sources, and hence environmental technologies to deal with them are process-specific and often constrained by site-specific considerations. Thus, it is difficult to generalise about the relative merits of different environmental technologies. The age, size, and purpose of the plant will influence the choice of the most effective environmental technology.

In the case of end-of-pipe technologies, the cost of retrofitting (i.e. installation on an existing system) will depend on the available space and the ease of access to the point of installation. Where major changes to the process currently in operation are required, the investment costs may reach up to five times as much as the cost of incorporation of the same technologies into a new plant.

Because of the large scale investment in existing production capacity, and the lifetime of capital equipment, the implementation of cleaner technologies at the earliest stages is unlikely unless a company undertakes the design of a new production line. There are, however, more numerous opportunities for cleaner technologies that can be realised by improving and modifying current processes and equipment without significant cost implications. Commodity chemical manufacturers redesign their processes infrequently so that the redesign of the reaction process or equipment is unlikely in the short term. In this case, good housekeeping and operational measures, including changes in storage and loading, monitoring and maintenance, and process control operations, are the most feasible responses, especially in the case of fugitive VOC emissions. Specialty chemical manufacturers are making a greater variety of chemicals and have more process and design flexibility. Incorporating changes in chemical reaction phases might be possible for them, although it would be difficult and takes time to develop them.

Improvements in Heat Exchange System

Flue gas from furnaces, which includes SO_x and NO_x , needs to be closely controlled.²⁶ To deal with NO_x from cracker furnace stacks, low- NO_x burners are often adopted on gas-fired furnaces.²⁷ New plants are also equipped with catalytic de- NO_x equipment on stacks. However, catalytic de- NO_x equipment is relatively expensive, and the use of it may give rise to increased ammonia emissions. In some cracker plants, the fuel used to fire the cracker is sulfur-free because the mixture of hydrogen and methane is produced internally as part of the cracking process, and virtually no SO_2 is emitted.

²⁶ Modifications of the combustion process that reduce the peak temperatures in the flame, including flue gas recycle steam injection, can be used to reduce thermal NO_x emissions, although the penalty in reduced combustion efficiency may be high. On the other hand, temperature reduction, which is effective for thermal- NO_x , has little influence on fuel- NO_x . What is required for the control of fuel- NO_x is to divide the combustion process into separate fuel-rich and fuel-lean stages (Flagan and Seinfeld, 1988).

²⁷ Some furnaces use low- NO_x technology that keeps NO_x emissions down to less than 20 per cent of permitted levels (Baker, 1993).

End-of-Pipe Technologies

As regards discharges to water, because of the highly integrated character of the organic chemical industry, especially petrochemical industry, with sites comprising of many plants producing a variety of substances, each process is dependent on several others, and as a result of this, most producers treat aqueous effluent in central treatment plants which receive effluent from many processes. The nature of any treatment of effluent prior to central treatment is therefore largely plant specific and is designed such that the composition of the final waste stream achieves an optimum level of treatment at a central works.

Cleaner Technologies

Using cleaner technologies which prevent the release or generation of pollution in the first place have several advantages over end-of-pipe waste treatment technologies. Cleaner technologies can be implemented at any stage of the development of a process. Although changes made at the research and development stage would have the greatest impact, in general changes in the process design and operating practices could yield significant results.

Good Housekeeping and Operations

Improved storage and loading of materials

Changes in storage and loading practices would yield the most immediate gains with small amounts of investment. For example, for batch reactions in a closed vessel, the chemicals are more likely to be emitted at the beginning and the end of a reaction step (associated with vessel loading and product transfer operations), than during the reaction process. Emissions from storage can be minimised by using double skinned tanks, floating roofs, and connecting vents to vapour recovery units or the flare system. Vapour recovery units for loading/unloading operations can reduce atmospheric emissions. Also, operational procedures of storage and loading can be optimised to minimise the spillage of tar and oil.

Improved monitoring and maintenance

Due to the large number of potential sources of fugitive VOC emissions and possible difficulties in accessibility, monitoring and maintenance programmes are laborious. However, it has been proven that such measures significantly reduce fugitive emissions. Many companies are now in the process of replacing pumps, seals and gaskets with no-leak or low-leak alternatives.

Improved process control

Another area that can yield significant benefits is improved process control so that less off-specification product is produced (that must be discarded) and the plant operates closer to the optimal (fewer by-products). A company is using continuous process optimisation to reduce the generation of acid coke - a process residue - with savings in treatment costs. New in-line process controls are under development that may allow better process optimisation through tighter process control.

Improved Cleaning of Equipment

Chemical substitution, particularly of water for non-aqueous solvents, can also prevent pollution. For example, a company is using a high-pressure water-jet system to clean polymer reaction vessels. This replaces organic solvent cleaning that produces solvent waste. The saving from the installation of the new system is larger than the initial investment cost.

Improved Separation Process

Improved separations design also offers an opportunity for cleaner technology since separation account for about 20 per cent of energy use in the chemical process industry. For example, a solvent can be replaced by an excess of a reaction component, thus eliminating the need to separate the solvent from the waste stream while reducing separation costs.

Reuse and Recycling

Reuse of hydrocarbons

The most important measures for controlling emissions to air are based on reuse and recycling technologies. Many hydrocarbon waste streams, which would otherwise be emitted to air, may either be used as fuel for heat and steam generation or reprocessed although this might result in a higher level of NO_x and SO_x emission.

Reuse and recycling of wastewater

In the case of aqueous emissions, some process-integrated measures are utilised in the organic chemical industry to minimise waste. Where possible, all streams are recycled or further processed to maximise recovery. In some steam crackers, a dilution steam generation system is adopted to allow recycling of furnace steam, cutting down the amount of water sent to effluent treatment by a factor of ten. Oils and hydrocarbons in the steam are concentrated and recovered at a later stage, by using a corrugated plate interceptor and dissolved air flotation (Baker, 1993).²⁸

Regeneration of spent catalysts

Spent catalysts may be regenerated and reused for many times, and, consequently, solid wastes will be reduced. However, catalysts must be eventually disposed of at landfills.

Improved yield/selectivity

The importance of catalysis is not only to generate and control the chemistry of carbocations but also to initiate the synthetic sequence by providing suitably activated high tonnage building blocks for elaboration into larger compounds. Together with the invention of increasingly sophisticated and selective non-biological catalysts, there has been the development of biological catalysts. New catalysts have found application, especially in the fine chemical industry. However, even a good catalyst with respect to the selectivity of the reaction it catalyses is not necessarily clean. There are always problems associated with poisoning and regeneration or of leakage of the catalyst itself into the environment, especially where homogeneous catalysts are used. For these reasons, a major recent field of development has been in supported catalysts (Suckling, 1994). Such advances are built upon the chemistry of organic and inorganic polymers (especially zeolites) and have already provided ways to avoid the halogen (e.g. bromine) problem outlined above.

Input Change

In the research and development stage, all possible reaction pathways for producing the desired product can be examined. These can be evaluated in light of yield, undesirable byproducts, and their health and environmental impacts. "Clean synthesis" or "green synthesis" is one of the areas of considerable research focus. One of the examples is the production of methacrylic acid and its derivatives, which are important monomers in the plastic industry. They are usually synthesised from propylene and benzene via acetone. This route, however, uses the hazardous reagents hydrogen cyanide and sulphuric acid, and for every mole of product, half a mole of ammonium sulphate is formed as waste. In contrast, a new process produces methacrylates with ethylene, carbon monoxide, and hydrogen as inputs and emits only water as a byproduct. Given a range of

²⁸ Among other examples, a company has collected and isolated its waste water in a trench coming from the phenol rail car unloading area and reused the water in resin batches. This eliminated the entire waste stream with savings in treatment costs. Another company is now sending all quality control and raw material samples back to be reused in the production process, saving money and reducing wastes at the same time (USEPA, 1995c).

feedstocks with reasonable chemical reactivity such as alkenes (e.g. ethylene) or alkynes, the principal task of chemistry is to construct larger chains and rings bearing the appropriate substituents of carbon, oxygen, nitrogen or other elements for the product to cause the desired effect when sold to and used by the customer. Traditional chemistry relies on the introduction of oxygen or of halogens (e.g. chlorine, bromine) in particular to activate the hydrocarbon fragment to enable new bonds to be formed. However, as is shown in many industrial sites, all of the bromine used during production processes does not end up in the product sold. For clean synthesis, ideally only those atoms required in the main product to create its effect should appear in the production process. As it will probably be impossible to accomplish that, however, an asymptotic approach to such ideality would be to make every input material leave the production process as water or perhaps as a lower alcohol, and every activating group as a carbonyl group, which could be removed by reduction and elimination or by decarboxylation. More research will be necessary until many of the possibilities which have been proposed become feasible and economical (Suckling, 1994).

4.3. Inorganic Chemical Industry

4.3.1. Introduction to the Inorganic Chemical Industry

The inorganic chemical industry manufactures chemicals which are often of a mineral origin, but not of a basic carbon molecular. These include sulphur, nitrogen, phosphorus, and chlor-alkali products. Inorganic chemicals are used at some stage in the manufacture of a great variety of other products. The industry's products are used as basic chemicals for industrial processes (i.e. acids, alkalis, salts, oxidising agents, industrial gases, and halogens); chemical products to be used in manufacturing products (i.e. pigments, dry colours, and alkali metals); and finished products for ultimate consumption (i.e. mineral fertilizers, glass, and construction materials). As the greatest use of inorganic chemicals is as processing acids in the manufacture of chemical and non-chemical products, inorganic chemicals often do not appear in the market for final products.

Within the industry, the chlor-alkali sector produces mainly chlorine, caustic soda (sodium hydroxide), soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate. The production of chlorine and caustic soda, co-products produced in about equal amounts primarily through the electrolysis of salt (brine), is the one of the largest single processes. Since economic and environmental characteristics vary depending on the specific type of inorganic chemical process, the production of chlorine and caustic soda is mainly dealt with in this chapter as an example of the inorganic chemical industry.

The majority of chlorine production is used in the manufacturing of organic chemicals such as vinyl chloride monomer, ethylene dichloride, glycerine, glycols, chlorinated solvents, and chlorinated methanes. Vinyl chloride is used in the production of polyvinyl chloride (PVC) and many other organic chemicals. The pulp and paper industry also consumes chlorine production. Other major uses are disinfection treatment of water, and the production of hypochlorites. Much of the chlorine is consumed in the same manufacturing plant in the production of chemical intermediates.

The largest users of caustic soda are the organic chemicals industry and the inorganic chemicals industry. The primary uses of caustic soda are in industrial processes, neutralisation, and off-gas scrubbing; as a catalyst; and in the production of alumina, propylene oxide, polycarbonate resin, epoxies, synthetic fibers, soaps, detergents, rayon, and cellophane. The pulp and paper industry

uses caustic soda for pulping wood chips, and other processes. Caustic soda is also used in the production of soaps and cleaning products, and in the petroleum and natural gas extraction industry as a drilling fluid.

Since chlorine and caustic soda are co-products produced in almost equal amounts, the distribution of the caustic soda manufacturing industry is essentially the same as the chlorine manufacturing industry. As chlorine is difficult to store and transport economically, chlorine and caustic soda are produced near the chlorine consumers which are primarily chemical manufacturers and pulping operations. Consequently, chlor-alkali facilities are concentrated near the chemical industries. In addition, as the production of one product can depend on the demand of the other, the market pull switches between caustic soda and chlorine. Therefore, increased demand for chlorine must be met immediately by increased chlorine production via electrolysis of brine and, consequently, caustic soda.

Recently, regulatory restrictions on the production or disposal of some products which require large amounts of chlorine to manufacture (i.e. chlorofluorocarbons, PVC, and chlorinated solvents) have adversely affected the market. Chlorine's commercial appeal has recently been further reduced by a number of environmental groups which call for a gradual phaseout or an immediate ban of chlorine and chlorinated compounds as industrial feedstocks.²⁹ Also some industries have begun switching from caustic soda to soda ash, where possible, to avoid caustic soda shortages. Soda ash is obtained almost entirely from natural sources of trona ore. Demand for caustic soda may also decrease as pulp mills increase their reclamation of caustic soda from spent pulping liquor.

4.3.2. Production Processes and Pollution Sources in the Inorganic Chemical Industry

As an example of the production processes in the inorganic chemical industry, the chlorine and caustic soda production process is described in this section, based on the United States Environmental Protection Agency (1995a), the Commission of the European Communities (1995a) and Kelham (1996). Chlorine and caustic soda are co-products of electrolysis of saturated aqueous solution of sodium chloride, NaCl (salt water or brine). In addition, relatively small amounts (by weight) of hydrogen gas are produced at the same time in the production process. Energy, in the form of direct current electricity, is supplied to drive the reaction. The amount of electrical energy required depends on the design of the electrolytic cell, the voltage used, and the concentration of brine used. For each ton of chlorine produced, 1.1 tons of sodium hydroxide and 28 kilograms of hydrogen are produced. Three types of electrolysis processes are used for the manufacture of chlorine, caustic soda, and hydrogen from brine:

- 1) mercury cell process;
- 2) diaphragm cell process; and
- 3) membrane cell process.

Each electrolytic cell consists of an anode and cathode in contact with the brine solution. The distinguishing feature of each cell type is the method employed to separate and prevent the mixing of the chlorine gas and sodium hydroxide. Consequently, each process produces a different purity of chlorine gas and a different concentration of sodium hydroxide. In 1992, around 28 per cent of the world-wide chlorine capacity was based on the mercury cell technology, and the share of the newer membrane method in total world capacity rose from zero to 20 per cent over the period 1975 to 1992. The mercury process still dominates in Europe, accounting for some 65 per cent,

²⁹ See Hileman (1993), Moghissi (1995), and Yosie (1996) on recent developments of the chlorine debate.

and the membrane process is used only in 10 per cent of the European plants whereas in the United States 85 per cent of the plants are already using the membrane process (Economic Commission for Europe, 1994b). In Japan, the mercury technology was phased out in the 1970s after the Minamata accident, and currently 87 per cent of the plants are using the membrane cells with improvements. Capacity using the membrane method has increased considerably in Asian and African countries and in Canada and Brazil (Economic Commission for Europe, 1994a).³⁰ Both economic and environmental concerns favour the conversion of chlor-alkali plants from the mercury and diaphragm cells to the use of membrane cells. Membrane cells are a relatively recent development, which has fewer adverse effects on the environment and produces a higher quality product at a lower cost than the other methods. The major pollutant outputs from all three electrolytic processes are chlorine gas emissions (both fugitive and point source), spend acids, freon (both fugitive and point source), impurities removed from the input salt or brine, and pollutants originating from electrolytic cell materials and other system parts.

The advantage of the mercury process over the diaphragm and membrane cell technologies is that it produces a pure chlorine gas without oxygen, and a pure 50 per cent caustic soda solution without having to further concentrate a more dilute solution. However, mercury cells operate at a higher voltage than diaphragm and membrane cells and, therefore, use more energy. The process also requires a very pure brine solution with little or no metal contamination. Elaborate precautions must be taken to avoid releases of mercury to the environment. Small amounts of mercury are found in the brine purge and miscellaneous sources which include floor sumps and cell wash water. Air emissions consist of mercury vapour and chlorine gas released in relatively small amounts as fugitive emissions from the cells and in the tail gases of the chlorine processing, caustic soda processing, and hydrogen processing. Solid wastes containing mercury include mercury cell butters, which are semisolid amalgams of mercury with barium or iron formed when an excess of barium is used during salt purification.

Diaphragm cells have the advantage of operating at a lower voltage than mercury cells and, therefore, use less electricity. In addition, the brine entering a diaphragm cell can be less pure than that required by mercury and membrane cells. The chlorine gas produced by the diaphragm process, however, is not pure and must be processed to remove oxygen, water, salt, and sodium hydroxide. Another disadvantage of the process is that the caustic soda produced contains chlorides and requires evaporation to bring it to a usable concentration. The use of lead and graphite anodes and asbestos diaphragms generates lead, asbestos, and chlorinated hydrocarbons in the caustic soda and chlorine processing waste streams.

Membrane cells have the advantages of producing a very pure caustic soda solution and of using less electricity than the mercury and diaphragm processes. In addition, the membrane process does not use highly toxic materials such as mercury and asbestos. Disadvantages of the membrane process are that the chlorine gas produced must be evaporated to increase the concentration. Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly additional purification steps prior to electrolysis. Wastewater from the membrane cell process originates from the ion exchange wash water, which consists of dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminum chloride.

Brine solutions are typically treated with a number of chemicals to remove impurities prior to input to the electrolytic cells. Pollutant outputs from this process include fugitive chlorine emissions and brine muds. Brine muds primarily consist of magnesium hydroxide, calcium carbonate, and barium sulphate. Removal of impurities account for a significant portion of the

³⁰ For example, the Taiwanese industry has not adopted the mercury cells in any plant (Nakanishi, 1993).

overall costs of chlor-alkali production, especially in the membrane process. Depending on the amount of impurities in the salt and the electrolysis process, different purification steps are required.

The chlorine gas recovered from electrolytic cells is cooled to remove water vapour. The remaining water vapour is removed by scrubbing the chlorine gas with concentrated sulphuric acid. The process of purifying and liquefying impure chlorine gas involves the absorption of the chlorine in a stream of carbon tetrachloride. The chlorine is subsequently removed in a stripping process in which the carbon tetrachloride is either recovered and reused, or is vented to the atmosphere.

Caustic soda solution generated from chlor-alkali processes is typically processed to remove impurities. When sodium sulphate is not removed during the brine purification process, salt recovered from the evaporators is recrystallized, and consequently, the wastewater from the caustic soda processing contains sodium sulphates. Significant levels of copper may also be present in the wastewater due to corrosion of pipes and other equipment. Wastewater from the membrane process contains caustic soda solution and virtually no salt or sodium sulphates.

The hydrogen produced in all of the electrolytic processes contains small amounts of water vapour, sodium hydroxide, and salt, which is removed through cooling. The hydrogen produced during the mercury cell process also contains small amounts of mercury, which must be removed by cooling the hydrogen gas to condense the mercury and treating with activated carbon.

4.3.3. Environmental Technologies in the Inorganic Chemical Industry

There have been some cases where the chemical industry has simultaneously reduced pollutant outputs and operating costs through cleaner technologies. In the inorganic chemicals manufacturing sector, however, cleaner technologies which are also economically feasible are not as easily found as in other sectors. Since the inorganic chemicals industry's products are primarily commodity chemicals, the manufacturing processes have been developed over many years, and the technological opportunities are relatively limited. Therefore, the manufacturers redesign their processes infrequently so that the prospect for the redesign of the reaction process or equipment is unlikely at least in the short term. Moreover, the constraint on financial resources in the industry makes even more difficult the adoption of cleaner technologies that require significant capital expenditures such as process-integrated modifications. In addition, the industry's process equipment has been amortised over long periods of time, making new, cost-effective process equipment improvements scarce. As a result, cleaner technologies in the inorganic chemicals industry are generally restricted to less costly options such as good housekeeping and operational changes, and reuse and recycling. Many of the technological changes discussed below, aiming at reducing wastes as well as materials use, have been carried out by the industry primarily as the means of improving process efficiency and reducing production costs.

In chlor-alkali production, cleaner technologies have been demonstrated for both the mercury cell and diaphragm cell processes. However, the best opportunity to reduce pollutant outputs, conserve energy, and reduce costs is in the conversion to the membrane cell process. In terms of energy consumption, the membrane cell process uses only about 77 per cent of that of the mercury cell process and about 90 per cent of that of the diaphragm cell process. The membrane cell technology uses no mercury in the production process and also generates significantly less airborne and waterborne pollutants and solid wastes.

Improvement in Heat Exchange System

Heat exchangers are often the source of significant byproduct wastes generated by overheating the main product closest to the tube walls. The best way to reduce these undesirable byproducts from overheating is to reduce the heat exchanger tube wall temperature. This can be accomplished through a number of techniques which do not reduce the overall heat transferred.

End-of-Pipe Technologies

A large portion of the inorganic chemical industry's pollutants leave the facilities as wastewater or wastewater treatment system sludge. Improved treatment and minimisation of wastewater are effective measures that often do not require significant changes to the industrial processes. Modern wastewater treatment technologies such as ion exchange, electrolytic cells, reverse osmosis, and improved distillation, evaporation, and dewatering can often be added to existing treatment systems.

Cleaner Technologies

Good Housekeeping and Operations

Prevention of leaks and spills

The elimination of sources of leaks and spills can be a very cost effective pollution prevention opportunity. Leaks and spills can be prevented by installing seamless pumps and other "leakless" components, maintaining a preventative maintenance program, and maintaining a leak detection program.

Improvement of inventory management and storage

Good inventory management can reduce the generation of wastes by preventing materials from exceeding their shelf life, preventing materials from being left over or not needed, and reducing the likelihood of accidental releases of stored materials. Designing a materials storage area, limiting traffic through the area, and giving one person the responsibility to maintain and distribute materials can reduce materials use, and the contamination and dispersal of materials.

Optimisation of processes

Process changes that optimise reactions and raw materials use can reduce waste generation and releases. Many larger facilities are using computer process control systems which analyse the process and products continuously and respond more quickly and accurately than manual control systems (Ashayeri, 1996). These systems are often capable of automatic start-ups, shutdowns, and product changeover which can bring the process to stable conditions quickly, minimising the generation of wastes.

Reuse and Recycling

Wastewater streams containing acids or metals can be concentrated enough to be sold commercially as a product by slightly altering the manufacturing process, adding process steps, and segregating wastewater streams. Moreover, many wastewater streams could be reused within the same or different processes, significantly reducing discharges to the wastewater treatment system.

Changes in reaction conditions

Improvement in reactor efficiencies

Since the chemical products are primarily created inside the process reactor, it can be the primary source for waste (off-site) materials. One of the most important parameters dictating the reactor

efficiency is the quality of mixing. A number of techniques can be used to improve mixing such as installing buffers in the reactor, a higher rpm motor for the agitator, a different mixing blade design, multiple impellers, and pump recirculation. The method used to introduce feed to the reactor can also have an effect on the quality of mixing. A feed distributor can be added to equalise residence time through the reactor, and feed streams can be added at a point in time closer to the ideal concentration. This will avoid secondary reactions which form unwanted by-products.

Improved yield/selectivity

Improvement in catalysts

The catalyst plays a critical role in the effectiveness of chemical conversion in the reactor. Alternative chemical makeups and physical characteristics can lead to substantial improvements in the effectiveness and life of a catalyst. Different catalysts can also eliminate byproducts formation. Noble metal catalysts can replace heavy metal catalysts to eliminate wastewater contaminated with heavy metals. The consumption of catalysts can be reduced by using a more active form, and emissions and effluents generated during catalyst activation can be eliminated by obtaining the catalyst in the active form.

Input change

The substitution or elimination of some of the raw materials used in the manufacturing of inorganic chemicals can result in substantial waste reductions and cost savings. Because impurities in the feed stream can be a major contributor to waste generation, one of the most common substitutions is to use a higher purity feedstock. This can be accomplished either by working with suppliers to get a higher quality feed or by installing purification equipment. Raw materials can also be substituted with less toxic and less water-soluble materials to reduce water contamination, and with less volatile materials to reduce fugitive emissions. Sometimes certain raw materials can be eliminated all together. The need for raw materials that end up as wastes should be re-examined to determine if raw materials can be eliminated by modifying the process and improving control.

4.4. Iron and Steel Industry

4.4.1. Introduction to the Iron and Steel Industry

The iron and steel industry produces iron and steel mill products such as bars, strips, and sheets as well as formed products such as steel nails, spikes, wire, rods, pipes, and non-steel electrometallurgical products such as ferroalloys. Broadly speaking, there are two types of steel production facilities, namely, integrated steel mills and minimills. While the integrated steel industry is contracting in the industrialised countries, the minimill companies continue to expand their capacity and enter new markets. Minimills use electric arc furnaces (EAFs) to melt scrap and other materials to make steel products, instead of using coke, iron ore, and scrap as the integrated producers do. In addition to the fundamental differences in production technologies, minimills have narrow product lines and produce much less product per facility (less than 1 million tons of steel per year). The automotive and construction sectors have been the two largest steel consuming industries. Consequently, fluctuations in sales and choice of materials in these industries have a significant impact on the iron and steel industry.

Traditionally, the mill sites were selected for their proximity to water, a large amount of which is used for cooling, processing, and transportation, and the sources of their raw materials, namely iron ore and coal. However, over the last two decades the structure of the steelmaking industry

has changed dramatically and the geographical distribution of the industry will continue to change because minimills are built anywhere electricity and scrap are available at a reasonable cost together with a local market for steel products. Lower scrap prices in the 1960s and 1970s created opportunities for the minimill segment of the market to grow rapidly.

Initially, the EAF technology could only be used in the production of low quality long products such as concrete reinforcing bars. However, over the years minimill producers have improved in quality and have overcome technological limitations to diversify their product lines. Consequently, many of the large, fully-integrated facilities have closed, and those that are still operating have reduced their workforce, increased the automation of the production processes, and invested in new technologies to remain competitive. More than half of the market for quality steel producers still remains beyond minimill capability, although minimills have recently entered new markets such as flat-rolled products. The EAF producers also face the problems of fluctuating scrap prices which are more volatile than the prices of raw materials used by the integrated producers.

4.4.2. Production Processes and Pollution Sources in the Iron and Steel Industry

In this section, the description of the production processes in the iron and steel industry is based on the United States Environmental Protection Agency (1995b) and the Commission of the European Communities (1996a). Steel is an alloy of iron usually containing less than one percent carbon. The process of steel production occurs in several sequential steps. The two types of steelmaking technology in use today are the basic oxygen furnace (BOF) and the electric arc furnace (EAF). Although these two technologies use different input materials, the output for both furnace types is molten steel, which is subsequently formed into steel mill products. The BOF input materials are molten iron, scrap, and oxygen. In the case of EAF, electricity and scrap are the input materials used. BOFs are typically used for high tonnage production of carbon steels, while EAFs are used to produce carbon steels and low tonnage alloy and specialty steels. The processes leading up to steelmaking in a BOF are very different from the steps preceding steelmaking in an EAF. However, the steps after each of these processes producing molten steel are the same.

When a BOF is used, cokemaking and ironmaking precede the steelmaking process. These steps are not needed for steelmaking with an EAF. Coke, which is the fuel and carbon source, is produced by heating coal in the absence of oxygen at high temperatures in coke ovens. Pig iron is then produced by heating the coke, iron ore, and limestone in a blast furnace. In the BOF, molten iron from the blast furnace is combined with flux and scrap steel where high-purity oxygen is injected. This process, with cokemaking, ironmaking, steelmaking, and subsequent forming and finishing operations is referred to as fully integrated production.

Alternatively, in an EAF the input material is primarily scrap steel, which is melted and refined by passing an electric current from the electrodes through the scrap. The molten steel from either process is formed into ingots or slabs that are rolled into finished products. Rolling operations may require reheating, rolling, cleaning, and coating the steel. Since obsolete scrap contains high percentage of impurities, it is difficult to manufacture high-quality steels to satisfy ever-increasing quality requirements with existing steelmaking technologies. On the other hand, increased use of scrap has a desirable effect on the reduction of carbon dioxide emission as the melting scrap consumes only approximately one third of the energy consumed in the preparation of molten iron from iron ores (Nakajima, 1993).

The coke-making process is regarded as one of the industry's areas of the greatest environmental concern, with air emissions and quench water as major problems. The slag produced during the ironmaking process contains unwanted impurities in the iron ore such as sulfur from the fuels. The waste products from the basic oxygen steelmaking process include slag, carbon monoxide, and oxides of iron emitted as dust. In addition, when the hot iron is poured into ladles or in the furnace, iron oxide fumes are released and some of the carbon in the iron is precipitated as graphite (kish). The steelmaking process using EAF produces metal dusts, slag, and gaseous products. The particulate matter³¹ that is removed as emissions in the dry system is EAF dust, and the two primary hazardous constituents of EAF emission control dust are lead and cadmium.

During the finishing process, mill scale, rust, oxides, oil, grease, and soil are chemically removed from the surface of steel. Inorganic acids such as hydrochloric or sulphuric acid are most commonly used for the pickling process, and spent pickle liquor may contain considerable residual acidity and high concentrations of dissolved iron salts. Steel products are often given a coating to inhibit oxidation and extend the life of the product. A common coating process is galvanising, where a thin layer of zinc is deposited on the steel surface. Significant zinc contamination of soil might be seen in the vicinity of the facilities.

4.4.3. Environmental Technologies in the Iron and Steel Industry

Most of the environmental technologies in the iron and steel industry have concentrated on reducing cokemaking emissions, electric arc furnace (EAF) dust, and spent acids used in finishing operations. Mainly for economic reasons, reuse and recycling measures are used extensively in the iron and steel industry. Solid wastes such as filter dusts and sludges are recycled in the processes. However, due to the complexity, size, and age of the equipment used in steel manufacturing, process-integrated technological changes that have the highest potential of pollution reduction, such as cokeless technologies, would require significant capital investments.

End-of-Pipe Technologies

Removal of blast furnace dust emissions

Blast furnace flue gas contains dust emissions. To remove coarse particulates, the flue gas is cleaned with a settling chamber or a cyclone. Mechanical collectors such as settling chambers or cyclones are typically much less expensive than the others, but are generally only moderately efficient in particle removal. Since they are much better for large particles than for small ones, they often are used as precleaners for the more efficient final control devices, especially at high particulate loading (Flagan and Seinfeld, 1988). The dust collected may be reused in the sintering plant or landfilled. For fine dust removal, the flue gas is further treated, either by dry (e.g. electroprecipitation) or wet (e.g. scrubber) technologies. Electrostatic precipitation can treat large volumetric flow rates of gas at relatively low pressure drops with very high removal efficiencies. However, they are expensive and relatively inflexible to changes in process operating conditions. Fabric filters tend to have very high efficiencies but are expensive and are generally limited to dry, low-temperature conditions. Scrubber can also achieve high efficiencies and offers the auxiliary advantage that gaseous pollutants can be removed simultaneously with particles. However, scrubbers can be expensive to operate, owing to their high pressure drop and to the fact that they produce a wet sludge that must be treated or disposed of (Flagan and Seinfeld, 1988). The

³¹ Particulate matter refers to everything emitted in the form of a condensed (liquid or solid) phase (Flagan and Seinfeld, 1988).

wastewater from the scrubbing process, which contains zinc, lead, cadmium and cyanide, nitrogen compounds, and COD, is recirculated and passes a sedimentation unit. A blow-down, which is necessary to prevent contamination build-up, is subjected to a sandfiltration, followed by an (optional) biological treatment.

Removal of EAF dust

EAF dust contains molten steel and high concentrations of lead and cadmium. Most of the dust emissions from melting in EAF are collected and cleaned by a hole in the furnace roof. Fugitive emissions through skylights, doors, etc. are reduced by local hoods, total building evacuation or doghouses (encapsulation).

Cleaner Technologies

Reuse and Recycling

Recycling of coke by-products

Improvements in the in-process recycling of tar decanter sludge are common practice. Sludge can either be injected into the ovens to contribute to coke yield, or converted into a fuel that is suitable for the blast furnace. Volatile components of the coke oven gas stream are recovered including the coke oven gas itself, which is used as a fuel for the coke oven, naphthalene, ammonium compounds, crude light oil, sulfur compounds, and coke breeze (coke fine). The coke breeze, which is produced during the coke quenching, handling, and screening operation, is reused in other manufacturing processes on-site (e.g. sintering) or sold off-site as a byproduct.

Recycling of EAF dust

Facilities producing specially steels such as stainless steel with a lower zinc content, still have opportunities to recover chromium and nickel from the EAF dust. In-process recycling of EAF dust involves palletising and then reusing the pellets in the furnace. With an average zinc concentration of 19 per cent, much of the EAF dust is shipped off-site for zinc reclamation. Most of the EAF dust recovery options are only economically viable for dust with a zinc content of at least 15 to 20 per cent. However, recycling EAF dust on-site has not proven to be technically or economically competitive for all mills. Improvements in technologies have made off-site recovery a cost effective alternative to thermal treatment or secure landfill disposal.

Recovery of hydrochloric acid

Large-scale steel manufacturers commonly recover hydrochloric acid in their finishing operations. However, the techniques used are not suitable for small- to medium-sized steel plants. Currently, a recovery technique for smaller steel manufacturers and galvanising plants is in pilot scale testing. The system under development removes iron chloride (a saleable product) from the hydrochloric acid, reconcentrates the acid for reuse, and recondenses the water to be used as a rinse water in the pickling process. Because the only byproduct of the hydrochloric acid recovery process is a non-hazardous, marketable metal chloride, this technology generates no hazardous wastes. This technology is less expensive than transporting and disposing of waste acid and eliminates the associated long-term liability.

Recovering of fluoride

To reduce spent pickling liquor and simultaneously reduce fluoride in the plant effluent, one facility modified their existing treatment process to recover the fluoride ion from rinse water and spent pickling acid raw water waste streams. The fluoride is recovered as calcium fluoride (fluorspar), an input product for steelmaking. Although the process is still under development, the recovered calcium fluoride is expected to be a better grade than the purchased fluorspar, which would reduce the amount of flux used by approximately ten per cent. Not only would the

generation rate of sludge from spent pickling liquor treatment be reduced (resulting in a savings in off-site sludge disposal costs), but a saving in chemical purchases would be realised.

Recycling of wastewater

Quenching waste water is seen as one of the major problems in the cokemaking process. Replacing single-pass wastewater systems with closed-loop systems minimises chemical use in wastewater treatment and reduces water use.³²

Recycling of scrap and other materials

Scrap and other materials are recycled extensively in the iron and steel industry to reduce the raw materials required and the associated pollutants. For example, oils and greases are recycled or reused.

Changes in Reaction Conditions

Continuous casting

The continuous casting process bypasses several steps of the conventional ingot teeming process by casting steel directly into semifinished shapes and offers great improvements in process efficiency. This increased efficiency also results in a considerable savings in energy and some reduction in the volume of mill wastewater.

Input Change

Elimination of coke

Cokeless technologies substitute coal for coke in the blast furnace, eliminating the need for cokemaking, and have enormous potential to reduce pollution generated during the steelmaking process. Among the cokeless technologies in use or under development are the Japanese Direct Iron Ore Smelting (DIOS) process, HIs melt process, and Corex process. The capital investment required is significant.

Reduction of coke

Several technologies are available or are under development to reduce the quantity of coke needed by changing the method by which coke is added to the blast furnace or by substituting a portion of the coke with other fuels. The reduction in the amount of coke produced proportionally reduces the coking emissions. For example, use of pulverised coal injection technology can replace about 25 to 40 per cent of coke in the blast furnace and substantially reduce emissions associated with the cokemaking process. Some steel makers also inject other fuels such as natural gas, oil, and tar/pitch, instead of coke into the blast furnace, although these fuels replace coke only in limited amounts.

Use of scrap with low lead and cadmium content

As the two primary hazardous constituents of EAF emission control dust are lead and cadmium, it is desirable to use scrap steel with low lead and cadmium content as a raw material.

³² Some European plants have implemented technology to shift from water quenching to dry quenching, which eliminates suspected carcinogenic particles and VOCs and at the same time reduces energy costs (USEPA, 1995b).

4.5. Petroleum Refining Industry

4.5.1. Introduction to the Petroleum Refining Industry

Petroleum refining is the physical, thermal, and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. The primary products of the industry fall into three major categories: fuels (motor gasoline, diesel and distillate fuel oil, liquefied petroleum gas, jet fuel, residual fuel oil, kerosene, and coke); finished non-fuel products (solvents, lubricating oils, greases, petroleum wax, petroleum jelly, asphalt, and coke); and chemical industry feedstocks (naphtha, ethane, propane, butane, ethylene, propylene, butylene, butadiene, benzene, toluene, and xylene). Generally, the petroleum refining industry can be characterised by a relatively small number of large facilities. Since the efficiency in transporting crude oil feed stocks and finished products is important, petroleum refineries typically are located near crude oil sources (on-shore petroleum terminals, oil and gas extraction areas) or consumers (heavily industrialised areas).

4.5.2. Production Processes and Pollution Sources in the Petroleum Refining Industry

In the following, the production processes in the petroleum refining industry are described based on the United States Environmental Protection Agency (1995d), the Commission of the European Union (1994b), and United Nations Industrial Development Organization (1994). Crude oil is a mixture of many different hydrocarbons and small amounts of impurities, and its composition can vary significantly depending on its source. Petroleum refineries are a complex system of multiple operations, and the operations used at a given refinery depend on the properties of the crude oil to be refined and the desired products. Portions of the outputs from some processes are re-fed back into the same process, fed to new processes, fed back to a previous process, or blended with other outputs to form finished products.

Refining crude oil into useful petroleum products can be separated into two phases and a number of supporting operations. The first phase, which is one of the most important operations in a refinery, is desalting of crude oil and the subsequent distillation into its various boiling point components or fractions. Distillation involves the heating, vaporisation, fractionation, condensation, and cooling of feedstocks. The atmospheric and vacuum distillation processes, when used in sequence, result in lower costs and higher efficiencies. A potential source of emissions from distillation of crude oil are the combustion of fuels in the furnace and some light gases leaving the top of the condensers on the vacuum distillation column. A certain amount of non-condensable light hydrocarbons and hydrogen sulphide pass through the condenser to a hot well, and then are discharged to the refinery sour fuel system or are vented to a process heater, flare or another control device to destroy hydrogen sulphide. The quantity of these emissions depends on the size of the unit, the type of feedstock, and the cooling water temperature.

The second phase is made up of three different types of downstream processes: combining, breaking, and reshaping. Certain fractions from the distillation of crude oil are further refined in thermal cracking (visbreaking), coking, catalytic cracking, catalytic hydrocracking, hydrotreating, alkylation, isomeration, polymerisation, catalytic reforming, solvent extraction, merox, dewaxing, propane deasphalting, and other operations. These downstream processes change the molecular structure of hydrocarbon molecules either by breaking them into smaller molecules, joining them to form larger molecules, or reshaping them into higher quality molecules. For many operations, a

number of different techniques are used in the industry. Supporting operations may include wastewater treatment, sulphur recovery, additive production, heat exchanger cleaning, blowdown systems, blending of products, and storage of products.

While the raw material input is primarily crude oil, petroleum refineries also use and generate an enormous number of chemicals, many of which leave the facilities as discharges of air emissions, wastewater, or solid waste. Pollutants generated typically include volatile organic chemicals (VOCs), carbon monoxide (CO), sulphur oxides (SO_x), nitrogen oxides (NO_x), particulates, ammonia (NH₃), hydrogen sulphide (H₂S), metals, spent acids, and numerous toxic organic compounds.³³

The principal sources of emissions from a refinery are of two types. The first type consists of emissions which are specific to units/functions of the refinery, namely, sulphur removal units, catalytic cracking units, coke plants, and storage and loading operations. Process off-gas streams, or sour gas, from the coker, catalytic cracking unit, hydrotreating units, and hydroprocessing units can contain high concentrations of hydrogen sulphide mixed with light refinery fuel gases. Sulfur is removed from them to recover saleable elemental sulfur.

Air emissions from catalytic cracking operations include the process heater flue gas emissions, fugitive emissions, and emissions generated during regeneration of the catalyst, including carbon monoxide. Fine catalyst dust, which is produced in the fluidized-bed catalytic cracking units (FCCUs), is also emitted. The coking process produces air emissions, including the process heat flue gas emissions, fugitive emissions, and emissions that may arise from the removal of the coke from the coke drum. Wastewater is generated from the coke removal and cooling operations and from the steam injection. In addition, the removal of coke from the drum can release particulate emissions and any remaining hydrocarbons to the atmosphere.

Storage tanks are used throughout the refining process to store crude oil and intermediate process feeds for cooling and further processing. Even when equipped with floating tops, storage tanks account for considerable VOC emissions at petroleum refineries.³⁴ Tank bottoms from crude oil storage tanks, which are comprised of heavy hydrocarbons, solids, water, rust, and scale, constitute a large percentage of refinery solid waste and pose a particularly difficult disposal problem due to the presence of heavy metals. Also, substantial amounts of acid are spent during the alkylation process, in which an olefin and an isoparaffin compound are joined using either a sulphuric acid or hydrofluoric acid catalyst.

The second type comprises emissions which are not specific to particular installations, and can be analysed as interfunctional aspects, including combustion emissions, emissions from regenerations of catalysts, and diffuse emissions. The design and management of the fuel system and the fuel composition of the refinery have an important impact on the environmental effects of the refinery. In a modern refinery, up to 80 per cent, in some cases even 90 per cent of all SO₂ emissions and also a major part of the NO_x and particulate emissions of the refinery are dependent on or directly related to the type of fuels used and their respective share in the total fuel consumption of the refinery. CO emissions are also produced when combustion processes are poorly regulated.

³³ However, it should be noted that the pollutant outputs from the refining facilities are modest in comparison to the pollutant outputs realised from the consumption of petroleum products by the transportation sector, electric utilities, chemical manufacturers, and other industrial and commercial users.

³⁴ A study of petroleum refinery emissions found that the majority of tank losses occurs through tank seals on gasoline storage tanks (USEPA, 1995d).

Many of spent catalysts contain heavy metals such as cobalt, nickel, and vanadium, and during use, they become contaminated with carbon residue and heavy metal oxides and sulphides. This contamination can pose a fire hazard during handling and storage. In addition, toxic components can be leached in landfill sites. Therefore, catalysts are regenerated continuously or periodically by burning the coke off the catalyst at high temperatures, producing SO_x, NO_x, and particulates.

Fugitive emissions occur throughout the refinery processes and arise from the thousands of potential fugitive emission sources such as valves, pumps, tanks, pressure relief valves, flanges, and so on. While individual leaks are typically small, the sum of all fugitive leaks at a refinery can be one of its largest emission sources. Also, many refineries unintentionally release liquid hydrocarbons, although their quantity is relatively small, to ground water and surface waters. At some refineries contaminated ground water has migrated off-site and resulted in continuous seeps to surface waters.

4.5.3. Environmental Technologies in the Petroleum Refining Industry

The petroleum refiners are currently facing difficult environmental challenges: reduced emissions to air, water, and land; reduced lead, benzene, sulfur, and vapour pressure in gasoline; and reduced sulfur and increased cetane number for diesel fuels. As government regulations become more stringent and waste disposal costs rise, environmental technologies in the petroleum refining industry are becoming increasingly important. Since the industry currently spends a significant amount of money on environmental quality and protection, a strong incentive is provided to the industry to find ways to reduce the generation of waste and to lessen the burden of environmental compliance investments. For the petroleum refining industry, cleaner technologies have been primarily realised through improved housekeeping and operating procedures and increased reuse and recycling of materials.

Although there have been some cases where petroleum refineries have reduced pollution outputs and operating costs simultaneously through cleaner technologies, these process-integrated technologies have not yet been fully implemented. Cost is the primary barrier to most of the cleaner technology projects; that is, many cleaner technologies are simply not cost-effective. Since corporate investment decisions depend on the value of the return on invested capital, firms find it difficult to adopt cleaner technologies which would not meet the profit rate requirements set by corporate management. In addition, the equipment used in the petroleum refining industry is very capital-intensive and has very long lifetimes.³⁵ This reduces the incentive to undertake process-integrated modifications to existing, expensive facilities.

Improvement in Heat Exchange System

Heaters fired with low-sulfur fuels such as natural gas or desulfurized gas emit negligible quantities of sulfur oxides and particulates, and less nitrogen oxides than heaters fired with heavier sulfur-bearing fuels. The use of low-NO_x burners and low-nitrogen gaseous fuels is a method of reducing NO_x emissions. Recently, a novel technology for removing NO_x from flue gases and other streams has been developed.³⁶

End-of-Pipe Technologies

³⁵ The average refinery or chemical plant unit is generally designed to last 15 years (Kirschner, 1995).

³⁶ This add-on process can remove NO_x at lower temperatures, as compared to conventional NO_x-removal technologies (120-350°C vs. 300-400°C) (Rhodes, 1993).

Treatment of hydrocarbon emissions with flares

Flares deal with small, low-concentration exhaust streams from vents and leakage from pressure relief valves to eliminate hydrocarbons emitted during shutdowns for maintenance turnaround or emergency conditions. However, flares may emit nitrogen oxides and sulfur oxides as well as unburned hydrocarbons and soot, which result from incomplete combustion.

Treatment of wastewater

Process wastewater arises from desalting crude oil, steam stripping operations, pump gland cooling, product fractionator reflux drum drains and boiler blowdown. Petroleum refineries typically utilize primary and secondary wastewater treatment. Primary wastewater treatment consists of the separation of oil, water, and solid in two stages. Some wastes associated with the primary treatment of wastewater at petroleum refineries may be considered as hazardous. In secondary treatment, dissolved oil and other organic pollutants may be consumed biologically by micro-organisms. Secondary treatment generates biomass waste, which is typically treated anaerobically, and then dewatered.

Treatment of FCCU dust

A significant amount of fine catalyst dust is produced in FCCU as a result of the constant movement of the catalyst grains against each other. The catalyst dust is separated from the carbon monoxide stream via cyclones and/or electrostatic precipitators and is sent off-site for disposal or treatment.

Cleaner Technologies

Good Housekeeping and Operations

Reduction in fugitive emissions

One of the largest sources of fugitive emissions from refineries is storage tanks containing gasoline and other volatile products. These losses can be significantly reduced by installing secondary seals, double bottoms, or grooved concrete foundations on storage tanks. A leak detection and repair (LDAR) program consists of using a portable VOC detecting instrument to detect leaks during regularly scheduled inspections of valves, flanges, and pump seals. Leaks are then repaired immediately or are scheduled for repair as quickly as possible. Barge loading is also an important source of VOC emissions. By installing a marine vapour loss control system, which would consist of vapour recovery or VOC destruction in a flare, these emissions could be reduced significantly.

Reuse and Recycling

Recycling and regeneration of spent caustics

Caustics used to absorb and remove hydrogen sulphide and phenol contaminants from intermediate and final product streams can often be recycled. Spent caustics may be saleable to chemical recovery companies if concentrations of phenol or hydrogen sulphide are high enough. Process changes in the refinery may be needed to raise the concentration of phenols in the caustic to make the recovery of the contaminants economical. Caustic containing phenols can also be recycled on-site by reducing pH of the caustic until the phenol become insoluble, thereby allowing physical separation. The caustic can then be treated in the refinery wastewater system.

Reuse of oil sludges as feedstock

Many oil sludges can be sent to a coking unit or the crude distillation unit where it becomes part of the refinery products. Sludge sent to the coker can be injected into the coke drum with quench water, injected directly into the delayed coker, or injected into the coker blowdown contactor used in separating the quenching products. Use of sludge as a feedstock has increased

significantly in recent years and is currently carried out by most refineries. The quantity of sludge that can be sent to the coker is restricted by coke quality specifications which may limit the amount of sludge solids in the coke.

Reuse of spent catalysts and coke fines

Significant amounts of catalyst fine are often present around the FCCU catalyst hoppers and reactor and regeneration vessels. Coke fines exist around the coker unit and coke storage areas. The fines can be collected and recycled before being washed to the sewers or migrating off-site via the wind. Collection techniques include dry sweeping the catalyst and coke fines and sending the solids to be recycled or disposed of as non-hazardous waste. Coke fines can also be recycled for fuel use. Another collection technique involves the use of vacuum ducts in dusty areas (and vacuum hoses for manual collection) which run to a small baghouse for collection. In a new process, the waste is smelted with a reductant (coke) in the presence of a collector metal (scrap iron) and lime (Rhodes, 1993). The coke reduces the metal oxides, and the metals, which are collected as an iron alloy, are suitable for resale as steel alloy or as scrap. The ceramic carrier contained in the catalyst combines with lime to produce a cement-like slag, which can be used as building material.

Improved Yields/Selectivity

Use of high quality catalysts

By using catalysts of higher quality, process efficiencies can be increased while the required frequency of catalyst replacement can be reduced. Modification of FCCU catalysts could provide a new source of olefin for the production of methyl tertiary butyl ether (MTBE), which is an unleaded fuel additive considered non-toxic³⁷ (Bell, Manzer, Chen, Weekman, Hegedus and Pereira, 1995).

Input Changes

Use of non-hazardous degreasers

Spent conventional degreaser solvents can be reduced or eliminated through substitution with less toxic and/or biodegradable products.

4.6. Fertiliser Industry

4.6.1. Introduction to the Fertiliser Industry

Broadly speaking, three different types of fertilisers are produced. The first type is straight fertilisers, containing only one of the main fertiliser components, namely, nitrogen (N), phosphorus (P), and potassium (K). Ammonia, ammonium nitrate, nitric acid, and urea are among the examples. The second type is compound fertilisers, produced by reaction of a straight fertiliser with a chemical or with another fertiliser (e.g. mono ammonium phosphate, nitro phosphate). The third type is blend fertilisers, produced by blending two or more straight or compound fertilisers (NPK-fertilisers, PK-fertilisers, NK-fertilisers).

The fertiliser industry is relatively capital intensive in production with a long lead time for the installation of new plants. Fertiliser plants are often large integrated operations that produce many important products, including fertilisers, for other industries. While the components of finished

³⁷ However, MTBE has already been banned in Alaska because gas station staff have been affected by headaches and nausea (Porteous, 1996).

fertiliser products are relatively simple chemicals, the production technologies used are highly developed. While ammonia nitrogen fertiliser is produced in almost all the main consuming areas of the world, phosphate and potassium fertilisers are produced near regions which are rich in minerals. As natural gas constitutes a large part of the input costs, fertiliser manufacturers in countries such as Eastern Europe and the former Soviet Union have a cost advantage vis-à-vis their foreign competitors because they can obtain natural gas for a lower price. Consequently, the fertiliser industry is currently undergoing a restructuring and rationalisation process. Plants have been shut down and production has been concentrated in the most favourably located sites in terms of raw materials and outlets. Large investments have been made to improve efficiency and productivity, particularly in the use of energy, to produce fertilisers of the highest quality and to distribute them in the most efficient way.

4.6.2. Production Processes and Pollution Sources in the Fertiliser Industry

Technological requirements vary substantially in their complexity and maturity between the different branches of the fertiliser industry. The following description of the manufacturing processes in the fertiliser industry is based on the Commission of the European Communities (1994c, 1995b) and United Nations Industrial Development Organization (1993). The fertiliser industry causes pollution of air and surface waters. Air pollution is mainly caused by emission of nitrogen compounds, including nitrogen oxides (NO_x) and ammonia (NH_3), and fluorides, including hydrogen fluoride (HF) and silicon fluoride (SiF_4). NO_x contributes to the formation of smog and acid rain. NH_3 in the air is poisonous and also contributes to the formation of acid rain and odour problems. Fluoride in the air is extremely poisonous. The discharge of phosphogypsum to surface waters is the most important cause of water pollution.

Nitrogen fertilisers

Nitric acid is mainly used for manufacture of straight and compound fertilisers. At a smaller scale it is used in chemical industry and for manufacture of explosives. Nitric acid is produced by oxidation of ammonia gas. The nitric acid production process may cause air pollution. First, off-gas is emitted from the absorption columns, which may contain nitrogen monoxide (NO) and nitrogen dioxide (NO_2). Second, emission of NO, NO_2 , NH_3 , and nitric acid (HNO_3) may be caused by leakages. In addition, during maintenance and repairs of equipment, some amount of gases may be lost. The NO_x concentration in the off-gas depends on the pressure in the absorption columns. Solid and water pollution may be caused by discharge of condensate and cooling water, which may be polluted by leaks of cooling equipment.

Most of urea is used directly as fertiliser, but it is also used for manufacture of cattlefeed and synthetic resins. Urea is produced by mixing liquid ammonia (NH_3) and carbon dioxide (CO_2) in a reactor under high pressure. The urea production process may cause air pollution by emissions from the gas scrubber and from the granulator to prilling tower. After urea is separated from the reaction products, the remaining gaseous mixture, containing NH_3 and CO_2 , is led into a condenser and recycled to the reactor. Some of the gas is wasted from the condenser. This off-gas is treated in a scrubber to remove NH_3 . The off-gas from the granulator or prilling tower may contain NH_3 , formaldehyde, and dust. Water pollution may be caused by discharge of wastewater, containing NH_3 , from the gas scrubber. This water can be treated in an ammonia strip installation or utilised in a nitric acid factory.

Ammonium nitrate (AN) is mainly used for production of straight and compound fertilisers and also for production of explosives. A solution of AN is formed by reaction of gaseous NH_3 and HNO_3 . Calcium ammonium nitrate (CAN) is manufactured by mixing AN melt with limestone.

Production processes for AN and CAN may cause air pollution by emission of dust and ammonia. Dust emission may result from grinding limestone and from the prilling or granulation installation. Ammonia may be emitted from the gas scrubber, from the reaction of AN with lime and from the prilling or granulation installation. It is difficult to reduce or treat this emission because of the large amount of air used in this process step.

Phosphorus fertilisers

Phosphoric acid (H_3PO_4) is manufactured by two different production processes: the wet process; and the thermic process. The wet process is the most commonly used method for production of phosphoric acid (95 per cent of the world production). In the wet process, phosphate rock reacts with sulphuric acid. Phosphate rock contains generally phosphorus in the form of $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6$ (apatite) and a great variety of other elements such as silicon, aluminium, iron, heavy metals, and radio active elements. Phosphoric acid may cause air pollution by emission of dust, sulphur dioxide (SO_2), and fluorides. Dust emission is caused by handling and grinding of phosphate rock. SO_2 is emitted from the reaction of phosphate rock with sulphuric acid. Fluorides (HF and SiF_4) are emitted from the reactors and the evaporators. Disposal of phosphogypsum creates serious problems for the phosphoric acid industries. Discharge of phosphogypsum into surface water may cause serious water pollution due to the large quantities of phosphorus (P), fluorine (F), cadmium (Cd), other heavy metals, including chromium (Cr), and radio active elements which are discharged with the phosphogypsum. Soil pollution may also be caused by on land disposal of phosphogypsum. In the thermic process, phosphate rock is heated in a furnace, at which pure phosphorus and a slag are formed. The slag contains all impurities from the rock. The phosphorus may be converted into phosphoric acid, which is used in detergent and food industries, but not in fertilisers. The energy demand of the thermic process is extremely high, whereby this process is much more expensive than the wet process.

Single superphosphate (SSP) is a mixture of mono calciumphosphate and gypsum. SSP may be used for production of compound fertilisers or applied directly as a fertiliser. It is produced by reaction of phosphate rock with diluted sulphuric acid. Triple superphosphate (TSP) is relatively pure mono-calciumphosphate, containing no gypsum. It is used directly as a fertiliser or for production of compound fertilisers. TSP is produced by reaction of phosphate rock with phosphoric acid. The production of SSP and TSP may cause air pollution by emission of fluoride and dust. Water pollution may be caused by discharge of waste water containing phosphorus, fluorine, and suspended solids.

Potassium fertilisers

Potassium chloride (KCl) is the most commonly used straight potassium fertiliser. However, it is never directly applied as a single fertiliser in agriculture, but it is used for production of compound fertilisers. No significant improvements have been reported recently in potash processing.

Compound fertilisers

Compound fertilisers contain at least two of the three elements, nitrogen, phosphorous, and potassium. The composition of various types of compound fertilisers may differ considerably. They are produced by chemical reactions between straight fertilisers with other fertilisers or chemicals. Compounds used frequently in these reactions are mono-ammonium phosphate (MAP) and di-ammonium phosphate (DAP). They are produced by reaction of phosphoric acid with gaseous ammonia, and their production processes may cause air pollution by emissions of ammonia, fluorine, and dust. Water pollution may be caused by discharge of process condensates

and waste water, which may contain suspended solids (product) and fluorides if phosphoric acid is used in the production process.

Blend fertilisers

Blend fertilisers are produced by mixing two or more granulated fertiliser types. Since the production process does not involve any chemical reactions, emissions may be caused only by washing and dust generation.

4.6.3. Environmental Technologies in the Fertiliser Industry

In the fertiliser industry, most of the measures for environmental protection are aimed at reducing emissions going to the atmosphere and groundwater from the production processes. For that purpose, end-of-pipe technologies such as gas scrubbers and dust collectors, good housekeeping methods, and reuse and recycling systems of process waters are used extensively in the industry. Except for new technologies for the production of phosphoric acid, the extent to which process-integrated technological changes involving modifications of chemical reactions are adopted has been relatively limited in the fertiliser industry.

Among the typical examples of additional investments required to deal with effluents are the introduction of double absorption in the design of sulphuric acid plants, and of units to remove fluoride compounds and to dispose of phosphogypsum in the design of phosphoric acid plants, as well as the addition of specialised equipment to remove nitric oxide emissions during the nitric acid process are

Reuse and recycling measures have also been widely adopted in the industry. Process streams, however, usually have to be concentrated before actual recycling to the production process. This aspect may cause an increase of the production costs. Accidental or point source emissions should be separated from other streams such as cooling water and storm water, and be treated or recycled. Cooling water may be contaminated by accidents in the production process. If the cooling water is recirculated, which is the case in most factories, it is possible to treat or recycle the accidentally contaminated cooling water.

End-of-Pipe Technologies

Nitric acid

The off-gas from the absorber columns can be treated for further removal of nitrogen dioxide (NO_2) with three approaches, namely, non-selective catalytic reduction, selective catalytic reduction, and alkaline absorption. In non-selective catalytic reduction, the off-gas is mixed with methane and a catalyst, and the reaction produces hydrogen (H_2), carbon dioxide (CO_2), and nitrogen (N_2). A disadvantage of this process is that ammonia (NH_3) and carbon monoxide (CO) may be formed as byproducts of the reaction. In the selective catalytic reduction, the off-gas is mixed with ammonia gas and a catalyst. Products of the reaction of nitrogen monoxide (NO) with ammonia are nitrogen and water (H_2O). When temperatures are too high or too low, nitrogen monoxide (NO), ammonium nitrate (NH_4NO_3), and ammonium nitrite (NH_4NO_2) may be formed as byproducts of the reaction. In the alkaline absorption process, the off-gas is scrubbed with an alkaline solution such as sodium hydroxide (NaOH), and as a result, nitrite is formed, which can be removed by a reaction with nitric acid (HNO_3) or sulphuric acid (H_2SO_4). The alkaline absorption process is possible only when the off-gas contains equal quantities of NO and nitrogen dioxide (NO_2) and the process control is complicated.

Urea and ammonium nitrate

Dust emission from prilling and granulation is reduced by application of cloth filters, cyclones, and wet dust collectors. While cyclones remove only large particles, cloth filters can also remove much smaller particles. Wet dust collectors are generally applied if gases or vapours have to be removed as well. Gaseous ammonia is generally removed by scrubbing. The scrubber is often preceded by a condenser, and water is mostly used as a scrubbing liquid. The removal efficiency may be increased by addition of acid to the scrubbing liquid.

Phosphoric acid

Dust emissions are reduced by treating the off-gas from rock handling and rock grinding in several types of dust filters. Formation of dust may be prevented by grinding the phosphate rock under wet conditions. Fluoride emissions are reduced by scrubbing all off-gases containing fluorides. As waste disposal of byproduct phosphogypsum has increasingly come under scrutiny in recent years, the industry needs to find ways to deal with it. One possibility is to purify the phosphogypsum by removing radium, cadmium, and other impurities and to generate phosphogypsum with relatively low concentrations of pollutants. If the discharge of the pollutants, of which cadmium and phosphorus are the most important, is reduced further, the phosphogypsum can be reused, for example, for production of sulphuric acid, or be disposed of in controlled dumping sites. However, no feasible method for gypsum purification has been developed so far.

Cleaner Technologies

Good Housekeeping and Operations

Storage and handling of nitrogen fertiliser

The operating conditions in nitrogenous fertilizer plants are severe in terms of pressure and temperature and involve handling of hazardous, inflammable and corrosive fluids. With the advent of modern technology, plants have grown in size having large number of sophisticated equipment, piping, etc., thus making it more complex. All these factors have increased potential hazard of fire, explosion or toxic release, and the affected areas are on increase (Saxena and Mehra, 1994). Good housekeeping measures could avoid problems associated with the storage and handling of fertilizer materials. For example, ammonia is a extremely toxic product which can, when stored in large quantities as a liquid either under pressure or at low temperatures, present a major safety hazard. Ammonium nitrate, a major fertilizer in Europe and the U.S., is now produced, stored, and transported under controlled conditions to avoid explosive decomposition.

Reuse and Recycling

Reuse and recycling of spillage, waste water, and condensate

Nitric acid

In the production of nitric acid, by recovering NaNO_2 scrub solution from alkaline adsorption, the discharge of waste water and pollutants (nitrites) from the scrubbing process can be eliminated. Recovery of spilled HNO_3 solution by using it for calcium ammonium nitrate production can eliminate the discharge of waste water and pollutants (nitrites) from the spilling. The waste water discharge from the degasification process and the pollutants (HNO_3) discharge can be reduced by the recycling of HNO_3 to absorption columns. The recycle of condensed off-gas to ammonium nitrate production can almost eliminate the discharge of waste water and pollutants (HNO_3). However, the costs of installation of emission reduction systems in old nitric acid plants are high and often not feasible. Most liquid wastes can be recycled in the production process of urea. By recycling of condensate, most of the discharge of water from the condenser can be eliminated.

Ammonium nitrate

The discharge of waste water and pollutants from the ammonium nitrate (AN) production process can be reduced by the recovery of spillage and the recycling of condensate and wash water. Minimum waste water discharges from the production process of calcium ammonium nitrate (CAN) can be achieved by recycling of wash water, scrubbing water, and condensates.

Phosphoric acid

The condensate from the evaporators of the phosphoric acid production process may have a high concentration of fluoride, which may be recovered as H_2SiF_6 with a commercial value. In the production process of superphosphates, by applying the recovery of fluoride (H_2SiF_6) and the total recycling of all off-gas and scrubbing water, the discharges of pollutants from superphosphate production can be reduced to almost zero.

Reuse of phosphogypsum

In most of the cases that phosphogypsum is used as a substitute of natural gypsum, some treatment of the phosphogypsum is required. This increases the costs of reuse of phosphogypsum, and it may become uneconomical in comparison with the use of natural gypsum. In countries without indigenous gypsum deposits, nevertheless, the treatment of phosphogypsum might be more economical than importation of natural gypsum. The reuse of phosphogypsum may be decreased by the availability of other suppliers of waste gypsum, which may be of a much purer quality than phosphogypsum. Presently very little phosphogypsum is reused in the EU countries, due to the low costs of the current disposal methods and the high costs for purification of phosphogypsum.³⁸

Changes in Reaction Conditions

Improved production efficiency of nitric acid

Waste emissions may be reduced by improving the production efficiency. There are several measures to achieve it: higher pressure in absorption columns; lower temperature in absorption columns; and excess oxygen supply to the reactor and cooler. Implementation of these measures will result in a better oxidation of NO to NO_2 and a better absorption of NO_2 , resulting in a higher output of nitric acid.

Input Changes

Use of pure inputs for the production of phosphoric acid

Due to the gradually stricter standards, the industry needs to reduce the cadmium content of fertilisers. Magmatic phosphate rock with a low cadmium content could be used for the production of phosphoric acid, and the cadmium concentration of the waste gypsum would be low. However, since the world reserves of magmatic phosphate rock are very limited, this might not be a realistic possibility. Alternatively, the cadmium content of phosphate rock can be reduced by calcination of the rock in a fluidized bed at a high temperature. Although the efficiency of cadmium removal is relatively high, the cost of this method is high.

Nitrophosphate process as an alternative method of making compound fertilisers

Nitrophosphate process can produce phosphoric acid without generating phosphogypsum. The nitrophosphate production process may be carried out in one or two stages. In the first stage, phosphate rock is acidulated by reaction with nitric acid. In the second stage, gaseous ammonia is added to the resulting mixture of phosphoric acid and calcium nitrate. This reaction results in the formation of the mixture of CaHPO_4 , NH_4NO_3 , and $\text{Ca}(\text{NO}_3)_2$, which can be used directly as a

³⁸ A new method developed in the U.S. can convert phosphogypsum into sulphuric acid and an inert aggregate more economically than systems applied in the past (Commission of the European Communities, 1994c).

fertiliser or be mixed with other fertilisers. There are several advantages of the nitrophosphate technology. First, being independent from sulphur and sulphuric acid, no part of the process generates sulphur oxide pollution. Second, it consumes the byproduct, carbon dioxide, rather than natural lime in the production of straight N products such as CAN. Third, it produces neither a problematic high-volume solid waste such as gypsum nor the large volume of contaminated water needed to transport it as a slurry (Fertilizer International, 1994).

4.7. Textile Industry

4.7.1. Introduction to the Textile Industry

The textile industry is a group of related industries which uses a variety of natural (cotton, wool, etc.) and various synthetic fibers (nylon, polyesters, and rayon) and is thus diverse in terms of manufacturing methods and finished products such as thread, yarn, bolt fabric, sheets, and carpets. The textile industry is chemical-intensive and uses a large number of various chemical substances, including dyestuffs, mineral salts, acid, base, and chemicals for functional finishing. As the textile industry is influenced by the trends in fashion, continuous changes in chemicals used in the production processes are necessary in terms of colouring and functional finishing (Commission of the European Communities, 1994d). The textile industry is also water-intensive, and environmental problems in the industry are typically associated with waster pollution. Natural impurities extracted from the fibre processed and the chemicals used for processing are the two main sources of pollution. Effluents are generally hot, alkaline, strong smelling and coloured by chemicals used in dyeing processes. Some of the chemicals are toxic substances. Other environmental issues now considered equally important and relevant to the textile industry include air emissions, especially volatile organic compounds (VOCs).

4.7.2. Production Processes and Pollution Sources in the Textile Industry

Although various types of raw materials (e.g. cotton, wool, synthetic fibre) are processed in different ways, it is possible to categorise production processes in the textile industry based on similarities between various types of fibre. In this section, a typical categorisation is described following United Nations Environment Programme Industry and Environment (1993): wool scouring; wool finishing; dry processing; woven fabric finishing; knit fabric finishing; carpet manufacture; and stock and yarn dyeing and finishing.

Wool scouring includes processes such as top making, and general raw wool cleaning. Scouring is employed to remove natural and acquired impurities from fibers and fabric. Raw wool must be cleaned by wet processes before the fibre can be dry processed to produce fibre, yarn, or fabric. Neither cotton nor synthetic fibers require this initial wet cleaning before processing. Since raw sheep wool contains a significant amount of impurities, the scouring process contributes to more than half of pollution load in terms of biochemical oxygen demand (BOD).

Along with wool finishing, processes such as carbonising, fulling, dyeing, bleaching, rinsing, and fire proofing are included. Wastes generated by the three distinct finishing processes (i.e. stock, yarn, and fabric finishing) are similar. This category uses a wide variety of chemicals, making it different from other fabric finishing categories, and generate a high effluent load, including toxic pollutants such as chromium and phenols.

Among the processes included in dry processing are: yarn manufacturing; yarn texturing; unfinished fabric manufacturing; fabric coating; fabric laminating; tire cord and fabric dipping; carpet tufting; and carpet backing. Although mills within the dry processing category typically carry out dry-type operations, some waste is produced by spillage and vessels or floor cleaning.

Woven fabric finishing is divided into two groups. The first removes impurities, cleans or modifies the cloth (desizing, scouring, bleaching, mercerising). While the natural fibers (cotton and wool) contain substantial impurities and require special treatment to convert them to the completely white, uniformly absorbent form essential for dyeing and resin treatment, synthetic fibers contain only those impurities that were necessary for manufacture of the fibre and spinning to obtain the yarn. The second group involves dyeing, printing, resin treatment, water or flame proofing, soil repellency and a few special finishes. Since a significant amount of effluent is generated from the removal of foreign matter during cleaning and from various chemicals additives used in finishing, this is one of the most important categories in the textile industry.

Knit fabric finishing is characterised by operational units such as bleaching, dyeing, printing, resin treatment, water proofing, flame proofing, and the application of soil repellency or special finishes. Since the knit yarn is treated with lubricants, rather than with the starch or polymeric sizes used for woven goods, the sizing/desizing and mercerising operations are not required for the knit, and the generation of effluent load is relatively low.

Carpet manufacturing uses mostly synthetic fibers, including nylon, acrylic, and polyesters), although some wool and cotton is also processed, and forms a distinct part of the textile industry. This category is characterised by the following processes: bleaching; scouring; carbonising; dyeing; printing resin treatment; water proofing; flame proofing; soil repellency; and backing with formed and unformed latex or jute. The effluents from this category are similar in many ways to those of the knit fabric finishing mills.

Typical products in stock and yarn dyeing and finishing are sewing thread, textile, and carpet yarn. This category is typically characterised by operational units such as cleaning, scouring, bleaching, mercerising, dyeing, and special finishing, and includes plants which clean, dye, and finish fibre stock of yarn. Yarn dyeing and finishing are different from woven fabric finishing because there are no sizing and desizing operations and from knit fabric finishing because of their mercerising operations and waste use.

Broadly speaking, there are two types of pollution source in the textile industry. The major part of pollution in the textile processing arises from natural impurities, including grease and dirt. The second pollution source is waste chemicals emitted from the process or washed from finished textiles. Generally, the waste water produced in the textile processing originates from bath dumps, washing and rinsing cycles, and equipment clean-up, and have a high BOD, a high concentration of total dissolved solids, and a high temperature. The conventional source of air pollution from a textile mill is the boiler stack, and these emissions normally consist of pollutants such as suspended particles and sulphur dioxide.

4.7.3. Environmental Technologies in the Textile Industry

In the textile industry, implementation of cleaner technologies has been considered mainly for economic reasons. Therefore, when the costs of water, energy, and chemicals can be reduced, there is a strong incentive for the textile industry to implement the practice of saving, reuse and recycling. As environmental problems in the textile industry are typically associated with waste

water, the reduction, reuse, and recycling of water is particularly emphasised in the industry. However, the extent to which the practice of water use reduction and reuse is implemented would depend on the cost effectiveness of the technologies and the technological feasibility, i.e. the quantity and variety of chemical substances in the water. There is a tendency that by increasing the size of mills, the incentives towards water reduction rise, especially waste water is discharged directly onto the surface water. As the stringency of environmental regulations is increasing, cleaner technologies, for example, input changes for a reduction or elimination of the use of chemicals, are being developed in the industry.

End-of-Pipe Technologies

Methods used for waste water effluent treatment in the textile industry can be classified into three categories: primary or mechanical processes; biological processes; and advanced physico-chemical processes.

Primary treatment,³⁹ which includes screening, neutralisation, equalisation, and gravity sedimentation, is used to remove suspended matter such as oil and grease and to achieve uniform flows and concentrations. Coarse and fine mesh screening is provided to remove the fibers and devices such as fine mesh vibrating screens have proved excellent wool fibre removers. An equalisation tank or basin is generally necessary to blend waste batch dumps and the surges or other flow variations, which would upset downstream treatment processes, and equipped with an aeration and mixing mechanisms that is adequate to prevent the deposition of solids and septicity. Neutralisation is necessary when effluents exhibit a widely fluctuating pH due to changing yarn types and can be effectively achieved by using alkalis such as lime and caustic or acids like hydrochloric and sulphuric acid. Substantial amount of oil and grease remaining after in-plant recovery processes are removed by flotation.

Biological treatment⁴⁰ involves the development and cultivation of micro-organisms to achieve a major reduction in the soluble effluent load, which is measured in terms of BOD/COD, to meet effluent limits. This process can be achieved either in the presence of oxygen (i.e. aerobically) or in the absence of oxygen (i.e. anaerobically).

Advanced physico-chemical treatment⁴¹ processes, including chemically assisted sedimentation, mixed media filtration, adsorption, and ozonation, are used to remove suspended matter that cannot be stabilised easily (e.g. chromium and phenol). When chromium needs to be removed, the soluble hexavalent chromium must be reduced to insoluble chromic form, and then the trivalent chrome can be precipitated as hydroxide and removed as a sludge.

Small amounts of wasted sludge from activated sludge system can be treated in lagoons. When waste sludge is more substantial, aerobic digestion is more suitable. Other residues from textile processes, including solid wastes such as cans, rejected fabric, and willow dust, are generally carted away to a landfill or incinerated off- or on-site. In the latter case, adequate air pollution control measures need to be taken to control particulates and scrub flue gas.

End-of-pipe control methods for air emissions from the boiler stack (e.g. suspended particle and sulphur dioxide) include cyclone separators, bag filters and wet scrubbers. Oil mist and VOC emissions to air are less conventional and more difficult to control. Proper air ducting system and

³⁹ See also footnote 15 on physical treatment.

⁴⁰ See also footnote 16 on biological treatment.

⁴¹ See also footnote 17 on physico-chemical treatment.

the installation of mist eliminators are an important technique for controlling oil mists. Another source of air emission, VOCs released during and after drying, finishing, and solvent processing operations, may be solved by using activated carbon for vapour adsorption and solvent recovery. Incineration is expensive and emissions from incineration also need to be handled separately.

Cleaner Technologies

Good Housekeeping and Operations

Reduction in water use

Poor housekeeping measures, including broken or missing valves, unattended leaks from pipes and hoses, and instances when cooling waters are left running when machinery is shut down, is a major source of excessive water use. By simply implementing strict housekeeping measures, a significant amount of water can be conserved, consequently reducing effluent volume.

Automated chemical dispensing systems

Automation of chemical dispensing and optimisation of processing sequence and recipes can be used for effective uses of chemicals. An automated chemical dosing system offers some important advantages over the manual method. First of all, flexibility can be gained by running smaller lots. Also, automation offers faster delivery times, better laboratory-to-dye house correlation, a wider variety of styles and higher quality. Moreover, the handling of some chemicals is hazardous so an automated system can minimise the chances of worker injury.

Improved Washing

Use of hot water instead of conventional cold water can in some cases halve water consumption for a comparable rate of washing efficiency. Also, horizontal washing configurations have demonstrated performance comparable to two conventional vertical configurations. By dropping the dye bath and avoiding overflow during rinsing and soaking, water consumption can be reduced.

Pad-Batch Dyeing

One potential improved process for dyeing is pad-batch dyeing. This method is one of the most reliable and controllable available today and has been used quite successfully in a wide variety of applications. Benefits include the elimination of the need for salt or chemical specialities from the dye bath, with associated cost savings, simplicity, speed, and waste reduction. In general, the quality of pad-batch dyeing is equal to or better than dyeing systems.

Reuse and Recycling

Reuse of cooling water

By segregating water used for cooling purposes and setting up an independent closed loop system, it becomes possible to use cooling water directly and repeatedly.

Reuse of washing water

Most of the effluent volumes arising from a textile mill come from washing operations, primarily the preparation of fibre and dyeing operations. Since most of the washing cycles are in a series, used water in the previous washing stages can be potentially reused. New textile mills now adopt the counter-current method, with which the least contaminated water from the final stage of washing is reused for the next-to-last washing stage and so on until the water reaches the first washing stage, where the water is finally discharged.

Recovery of sizes

Size represents the largest single group of chemicals in the textile industry which, in most cases, does not become a permanent part of the product. Therefore, size recovery presents one of the greatest opportunities for savings. Starch is the most commonly used size material, especially in developing countries such as India and Thailand. However, since starch is degraded in the desizing process with dilute acids or enzymes, recovery is not possible. Sizes which are recoverable are more expensive than starch, so it is difficult for a non-vertical textile mill to use them because another independent processor must recover them at a later stage. For example, ultra-filtration technology is used to recover sizes from desizing effluents.

Recovery of caustic soda

Caustic soda can be recovered from mercerising wash waters using membrane technology or by effective evaporation.

Recovery of grease

Wool grease can be recovered from wool scouring effluents either by acid cracking, by centrifuging, or by solvent extraction.

Input Changes

Substitution of Chemicals

Substitution of low BOD process chemicals for those having high BOD values can reduce BOD. When the starch is degraded by oxidation using hydrogen peroxide (H₂O₂) instead of enzymes, the BOD is much lower in the effluent because the starch is degraded fully to carbon dioxide and water. Using enzymes that degrade the starch size to ethanol instead of anhydroglucose, the ethanol can be recovered by distillation for use as a solvent or fuel, thereby reducing the BOD load in the desized effluent considerably.

Solvent Systems for Processing

Solvent systems for preparation, dyeing, finishing, and drying of textile have some advantages over the conventional water system, including elimination of a pre-scour; smaller, less costly equipment; flexibility of making short, continuous runs; low utility requirements; considerable water usage reduction; and better levelling and uniformity. However, two caveats are necessary for the implementation of solvent technology. First, chemical systems, dyes, specialities, etc. appropriate to solvent use need to be available at a commercially competitive cost. Secondly, environmental regulations for airborne emissions from solvent processing equipment, storage facilities, and hazardous waste regulations on recovery by-products (still bottoms, etc.) may make many solvent processes uneconomic.

5. Concluding Remarks

What follows is a preliminary discussion on the emerging patterns of the introduction of environmental technologies in pollution-intensive industries. In most of the industrial branches examined in this review, the introduction of end-of-pipe technologies is widely found. However, it seems that cleaner technologies have not yet been fully utilised in production processes in various industrial sectors. When cleaner technologies are introduced, they are mainly measures for reuse and recycling and they are selected on the basis of the rate of return calculations. That is, the extent to which cleaner technologies are adopted is limited mostly in cases where reuse and recycling of energy, water, and raw materials can contribute to a reduction in production costs. With some exceptions, process-integrated modifications involving chemical reactions have not yet been realised.

Generally speaking, the impact of end-of-pipe technologies on the whole production process is limited, compared with that of cleaner technologies. This implies that firms will face less uncertainty and irreversibility when they make a decision on investment in end-of-pipe technologies. Therefore, most of the firms would prefer to adopt end-of-pipe technologies, which include additions to existing facilities, rather than altering the whole production process or the main product. However, there will be limits in the extent to which the adoption of end-of-pipe technologies is appropriate when we are dealing with environmental problems in the long run. That is because it will be very costly to reduce pollution emissions further at the end of the production process with small concentration levels, but not necessarily small enough to be safe for the environment. In order to achieve drastic reductions in emissions, more fundamental changes will be necessary in the production process and/or the composition of the product itself. Furthermore, with the application of end-of-pipe technologies the benefits of raw material and energy savings will not occur, and technological spillovers to the main production process will be limited.

Eventually, firms would need to develop cleaner technologies by introducing an integrated assessment of their production processes and products. In this context, modifications of the chemical reaction system will be particularly desirable, although they might introduce complicated and uncertain impacts on the main product. That will require industries, including the chemical industry, which are generally classified as science-based industries, to conduct more research on basic sciences. Traditionally, the focus of the R&D activity for environmental protection has been on process engineering, in which how to design chemical reactors and equipment is studied with three main tools, i.e. transport phenomena, thermodynamics, and chemical reaction engineering. Now research on basic sciences for the development of new chemical synthesis and catalysis, including advanced oxidation and reduction methods, biosynthesis, and use of alternative feedstocks, needs to be emphasised.⁴²

This changing character of innovations for environmental protection would suggest that the role played by capital goods suppliers might change. Traditionally equipment suppliers have provided manufacturers with process innovation embodied in capital goods. In the case of environmental technologies, end-of-pipe technologies, including settling chambers, cyclone separators, filters, and scrubbers, have been mostly developed by equipment suppliers. However, as is shown above, when dealing with byproducts, by modifying the chemical reaction, the main product will also be affected. Therefore, exclusive attention to byproducts is not sufficient, nor appropriate. In other words, modifications of the chemical reaction system will involve both process and product developments, making the separation between them very difficult.

The implication of this trend for the relationship between equipment suppliers and product manufacturers is not clear. Modifications of the chemical reaction system may increase the scope for product manufacturers to invest more on R&D because detailed knowledge on product characteristics would be crucial for innovation. In this case, in-house R&D activities and capabilities will become important, having significant effects on productivity and patents and implications for the long-term competitiveness of firms. Even in a mature industry like the paper and pulp industry (an example of the chemical-process industries), in which technological opportunities are considered to be limited, when confronted with environmental regulation for reducing water pollutants, there is scope for the development of radical innovations for pulp bleaching (e.g. oxygen delignification and ozone delignification) by conducting in-house R&D. In

⁴² For more discussion on basic research needs for future environmental technologies, see Eisenberger (1996) and Hileman (1996).

this case, environmental regulation will work as a stimulus for “waking up” the industry and induce firms to conduct more R&D activities to find new technological solutions.

Alternatively, the suppliers may play a more important role in technological development because new chemical reactions and catalysts would require more expertise on the design of process equipment. In this case, a close cooperation on innovative activity between suppliers and product manufacturers will be necessary.⁴³ In analysing this issue, it would be useful to make a distinction in terms of technological characteristics between the chemical-process industries and the “physical-process” industries (e.g. the machinery and automobile industries). In the physical-process industries, the manufacturing process consists mostly of the assembly of parts by using mechanical methods. Physical modifications are usually adopted on specified points of the production process, and their effects on other parts of the production process and product quality would be limited and thus predictable. Therefore, capital goods suppliers could play a larger role for environmental protection in these industries than in the chemical-process industries.

In order to understand companies’ shift from treatment-oriented, end-of-pipe technologies towards prevention-oriented, cleaner technologies, it is necessary to identify the factors which will influence the introduction of cleaner technologies. Researchers of the economics of technological change have come to understand innovation process by focusing on three explanatory variables: market demand, technological opportunity, and appropriability conditions. It is often emphasised that market demand, i.e. environmental regulation in this case, is the crucial factor in promoting innovative activities of firms. However, the supply factor of innovation, i.e. technological opportunities, also needs careful analysis. In particular, technological opportunities may be expanded under the influence of environmental regulation. One of the potential mechanisms for the exploitation of technological opportunities would be to increase knowledge spillovers from other scientific and technological fields. As is discussed in the section of the organic chemical industry, environmental regulation actually enhanced the interactions between various research areas and, as a result, a new, clean-synthetic method of methacrylates was developed by a chemical firm. Prior to the development of this process, this company was not involved in the methacrylates business. However, by taking advantage of the knowledge accumulated with the technology of the oxo-process for hydroformylation, that company could succeed in producing an innovation in a new field. Another example is the case of chlorine and caustic soda production; the development of membrane cell technology was realised through the merger of chlorine and caustic soda technology with material technology (i.e. ion exchange membrane).

As is discussed in the evolutionary economics literature, the cognitive ability and computational ability of economic agents (e.g. firms) is limited, and the frame of the search process for new technologies is constrained by the history, experience, and expectation of each company.⁴⁴ Therefore, environmental regulation could create an environment in which researchers in firms are encouraged to pay more attention to research findings in different disciplines, increasing knowledge spillovers via interactions from other fields which have been ignored previously. In other words, environmental regulation may promote an inter- and trans-disciplinary approach,⁴⁵ technology fusion,⁴⁶ or knowledge spillovers between different areas.⁴⁷ In addition, during the

⁴³ Based on a questionnaire survey to a sample of eight hundred firms from all manufacturing sectors in the U.K., Green, McMeekin, and Irwin (1994) suggest that collaboration with suppliers is an important factor for environmental innovation projects.

⁴⁴ For evolutionary learning, see Nelson and Winter (1982) and Dosi, Marengo, and Fagiolo (1996).

⁴⁵ Gibbons, Limoges, Nowotny, Schwartzman, Scott, and Trow (1994) argue that the new mode of knowledge production is increasingly characterised by transdisciplinary approaches in application-oriented contexts.

⁴⁶ Based on his observation of the innovations of the Japanese firms, Kodama (1995) emphasises the importance of technology fusion in contrast with technical breakthroughs.

process of innovative activities for environmental protection, knowledge feedback to other technological areas might be created through enhanced interactions between different areas.

Another type of knowledge spillovers depends on the distribution of knowledge.⁴⁸ Especially, the transfer of knowledge on environmental issues would be enhanced between firms within the same industry. If a company doesn't take appropriate actions for environmental protection, consumers would consider the industry as a whole, rather than the specific company, not to be environmentally friendly because consumers usually do not have sufficient knowledge on production processes and they tend to think that similar technologies have been adopted by other companies in the same industry. Thus, not only the image of the company but also that of its competitors would be damaged. That is, there exists a negative externality to firms due to "intra-industry information spillovers."⁴⁹ In this case, it is not beneficial for each firm to try to gain advantage (i.e. the improvement of its own image) by showing that other firms' activities are not environmentally desirable because that strategy would risk its own interest. Therefore, firms have an incentive to co-operate and share knowledge among those in the same industry.⁵⁰

In addition, there could exist another factor which promotes knowledge transfer between firms. If accurate information on which technologies are being used in each firm is available, the government may impose environmental regulations based on the state-of-the-art technology in the industry. In this case, although the innovating firm may benefit from licensing the new technology, which is required by a more stringent regulation, that will be a significant financial burden on other firms in the industry. To avoid the ratcheting up of emission standards, which occurs whenever a better technology is developed by any firm, the industry as a whole may choose to have a uniform stance on the feasibility of technological solution and environmental issues. In other words, the information asymmetry between the government and the industry may be utilised by the industry at the sectoral level.⁵¹ As the transaction costs of information sharing and coordination between firms would be high, industrial associations may play an important role in taking the initiative.

To summarise, the transition from end-of-pipe technologies to cleaner technologies would encourage firms to conduct more R&D activities. Innovations would be enhanced not only by the demand factor (i.e. environmental regulation), but also by the supply factor (i.e. expansion of technological opportunities). The mechanism through which technological opportunities expand would be increased knowledge spillovers in terms of disciplinary fields (due to search processes conducted in different, distant disciplines, and interactions among them) and external sources (due to the common interest of firms to improve the image of the industry and to avoid the ratcheting up of environmental regulation). This knowledge-spillover effect would be beneficial

⁴⁷ Henderson and Cockburn (1996) find that research productivity is increased through external and internal knowledge spillovers in drug discovery.

⁴⁸ For more general discussion on the incentives and norms of knowledge production and transfer, see Dasgupta and David (1994).

⁴⁹ Hummels (1997) points out the "international information spillovers," in which a decline of sales of a product may occur not only in the country whose environment is directly affected by the manufacturer's activities, but also in distant markets.

⁵⁰ In the case of the recycling of "lens with film" (i.e. disposable camera) in Japan, as the leading company is worried that other companies in this product market may not take enough actions for environmental protection and that consumers may have a negative image of the lens with film itself, regardless which company actually produced, that company took the initiative in coordination in the industry and decided to offer its own channels for recovering used products from consumers to other companies' products (Baba, Yarime, and Hatashima, 1997).

⁵¹ Lewis (1996) argues, based on recent development in the economics of incentive regulation and agency, that the presence of asymmetric information calls for some important departures from the textbook prescription of market permits and emission taxes for controlling pollution.

not only for environmental protection but also for technological developments in other areas, and that may contribute to creating innovation offsets.

As regards policy implications, it is often argued that environmental policy has the possibility of “locking-in” technology to potentially inferior one, for example, by requiring firms to adopt a static approach and invest in the best available technology at the moment (Soete and Arundel, 1995). In the case of chlorine and caustic soda production, however, it seems, in retrospect, that governmental regulation has picked up the right technology (i.e. membrane cell technology) in Japan whereas the European industry have their technology locked into an inferior one (i.e. mercury cell technology).⁵² After the Minamata accident, the Japanese government forced firms to abandon the mercury cell method and to switch to the membrane cell process. Without regulation, as is shown in the case of the European industry, probably the technological shift from the mercury cells to the membrane cells would not have occurred in the Japanese industry. Overall, environmental regulation in this case stimulated innovative activities of firms in a relatively mature area, and benefits have been achieved in the environmental front as well as in the economic efficiency of firms.⁵³

We should emphasise, however, that regulation would work in either way in terms of lock-in effect, depending on the situation of each technology. That is, regulation may have the lock-in effect of forcing firms to adopt a technology which is currently the best but potentially inferior. Alternatively, governmental regulation may be able to “lock out” technology from the currently dominant, but potentially undesirable one under the working of increasing returns to its adoption to a more favourable alternative.⁵⁴

As this paper has shown, the characteristics and sources of pollution, and consequently, environmental technologies to deal with it vary depending on the specific characteristics of industrial sectors. Also, the data necessary to examine these arguments is very difficult to obtain at the aggregate level. Therefore, it will be necessary to do in-depth sectoral studies to obtain detailed information about what kinds of environmental technologies are actually used and what implications their introduction has for the competitiveness of industry. Future research should seek to find out how “sustainable development” can be achieved by analysing the incentives to introduce cleaner technologies and the behaviour of industry at the micro and sectoral level. By considering the merits and demerits of existing technologies, it will be seen how far we can proceed under this industrial production system and what needs to be modified. In other words, it will be of critical importance to examine the scope and limits of manufacturing processes from within.

⁵² Foray and Grübler (1990) discuss the technological lock-in in the ferrous casting industry, which has had different trajectories in France and Germany.

⁵³ Although originally patented by Du Pont, the new technologies have been improved by the Japanese firms, including Asahi Glass and Tokuyama Soda, which together currently have a large share of the world market (Shiroki, Noaki, Katayose, and Kashiwada, 1995).

⁵⁴ There are several mechanisms through which the effect of increasing returns is created, including technological improvement through intensive learning, technological interrelatedness, and informational increasing returns. For more discussion on increasing returns, see David (1985), Arthur (1988), and Cowan and Gunby (1996).

References

- Allenby, Braden R. and Deanna J. Richards, eds., *The Greening of Industrial Ecosystems*, Washington, D.C.: National Academy Press (1994).
- Arrow, Kenneth J., Maureen L. Cropper, George C. Eads, Robert W. Hahn, Lester B. Lave, Roger G. Noll, Paul R. Portney, Milton Russell, Richard Schmalensee, V. Kerry Smith, and Robert N. Stavins, *Benefit-Cost Analysis in Environmental, Health, and Safety Regulation: A Statement of Principles*, American Enterprise Institute (1996).
- Arthur, W. Brian, "Competing Technologies: An Overview", in Giovanni Dosi, Christopher Freeman, Richard Nelson, Gerald Silverberg, and Luc Soete, eds., *Technical Change and Economic Theory*, London: Pinter Publishers (1988).
- Ashayeri, Jalal, Annelies Teelen, and Willem Selen, "Computer-Integrated Manufacturing in the Chemical Industry," *Production and Inventory Management Journal*, **37** (1), 52-57 (1996).
- Ayres, Robert U. and Udo E. Simonis, eds., *Industrial Metabolism: Restructuring for Sustainable Development*, Tokyo: United Nations University Press (1994).
- Baba, Yasunori, Masaru Yarime, and Hiroyuki Hatashima, "Realising the Shift Towards Closed-Loop Recycling: Strategies of the Japanese Firms," *International Journal of Innovation Management*, **1** (1), 89-110 (1997).
- Baker, John, "Crackers seek lower costs and emissions," *European Chemical News*, **60** (1578), 18-19 (1993).
- Barbera, Anthony J. and Virginia D. McConnell, "The Impact of Environmental Regulations on Industry Productivity: Direct and Indirect Effects," *Journal of Environmental Economics and Management*, **18**, 50-65 (1990).
- Beers, Cees van and Jeroen van den Bergh, *An Empirical Multi-Country Analysis of the Impact of Environmental Regulations on Foreign Trade Flows*, Regional and Environmental Economics, Tinbergen Institute, Working Paper TI 96-57/5 (1996).
- Bell, A. T., L. E. Manzer, N. Y. Chen, V. W. Weekman, L. L. Hegedus, and C. J. Pereira, "Protecting the Environment Through Catalysis," *Chemical Engineering Progress*, **91** (2), 26-34 (1995).
- Berkel, Cornelius Wilhelmus Maria van, *Cleaner Production in Practice: Methodology Development for Environmental Improvement of Industrial Production and Evaluation of Practical Experiences*, Ph.D. Thesis, University of Amsterdam (1996).
- Biglaiser, Gary and John K. Horowitz, "Pollution Regulation and Incentives for Pollution-Control Research," *Journal of Economics & Management Strategy*, **3**, 663-684 (1995).
- Bland, Will and Ted Laird, "Energy," in Alan Heaton, ed., *An Introduction to Industrial Chemistry*, Glasgow: Blackie Academic & Professional (1996).
- Blaney, Carol A. and Shafi U. Hossain, "Cleaning Up Recycled Paper," *CHEMTECH*, **27** (2), 48-51 (1997).
- Clift, Roland, "Clean Technology - An Introduction," *Journal of Chemical Technology and Biotechnology*, **62**, 321-326 (1995).
- Clift, Roland and Anita J. Longley, "Introduction to Clean Technology," in Kirkwood, R. C. and A. J. Longley, eds., *Clean Technology and the Environment*, Glasgow: Blackie Academic & Professional (1994).
- Commission of the European Communities, *The Technical and Economic Aspects of Measures to Reduce Water Pollution Caused by the Discharges from the Pulp and Paper Industry*, Luxembourg: Office for Official Publications of the European Communities (1993).
- Commission of the European Communities, *Identification and Brief Description of the Emissions (Water, Air & Wastes) from the Different Sectors of the Organic Chemical Industry*, Luxembourg: Office for Official Publications of the European Communities (1994a).

- Commission of the European Communities, *Technical Note on the Best Available Technologies to Reduce Emissions of Pollutants into the Air from the Refining Industry*, Luxembourg: Office for Official Publications of the European Communities (1994b).
- Commission of the European Communities, *Descriptive Analysis of the Technical and Economical Aspects of Measures to Reduce Water Pollution Caused by Discharges from the Fertilizer Industry and Other Industries Entailing Nutrient Discharges*, Luxembourg: Office for Official Publications of the European Communities (1994c).
- Commission of the European Communities, *Technical and Economic Aspects of Measures to Reduce Water Pollution from the Textile Finishing Industry*, Luxembourg: Office for Official Publications of the European Communities (1994d).
- Commission of the European Communities, *Identification and Brief Description of the Emissions (Water, Air, Wastes) from the Different Sectors of the Manufacture of Basic Inorganic Chemicals and Non-Metallic Mineral Products*, Luxembourg: Office for Official Publications of the European Communities (1995a).
- Commission of the European Communities, *Panorama of EU Industry 95*, Luxembourg: Office for Official Publications of the European Communities (1995b).
- Commission of the European Communities, *Techno-Economic Study on the Reduction Measures, Based on Best Available Technologies, of Water Discharges and Waste Generation from the Primary and Secondary Iron and Steel Industry*, Luxembourg: Office for Official Publications of the European Communities (1996a).
- Commission of the European Communities, *Techno-Economic Study on the Reduction Measures, Based on Best Available Technology, of Industrial Emissions (Air, Water, Wastes) from the Basic Petrochemical Industry*, Luxembourg: Office for Official Publications of the European Communities (1996b).
- Commission of the European Communities, *Techno-Economic Study on the Reduction Measures, Based on Best Available Techniques of Emissions (Water, Wastes, Air) from the Paper and Board Manufacturing Industry*, Luxembourg: Office for Official Publications of the European Communities (1996c).
- Cowan, Robin and Philip Gunby, "Sprayed to Death: Path Dependence, Lock-in and Pest Control Strategies", *The Economic Journal*, **106** (436), 521-542 (1996).
- Cropper, Maureen L. and Wallace E. Oates, "Environmental Economics: A Survey", *Journal of Economic Literature*, **30**, 675-740 (1992).
- Dasgupta, Partha and Paul A. David, "Toward a new economics of science", *Research Policy*, **23**, 487-521 (1994).
- David, Paul A., "Clio and the Economics of QWERTY", *AEA Papers and Proceedings*, **75** (2), 332-337 (1985).
- Dosi, Giovanni, Luigi Marengo, and Giorgio Fagiolo, *Learning in Evolutionary Environments*, mimeo (1996).
- Ecchia, Giulio and Marco Mariotti, *A Survey on Environmental Policy: Technological Innovation and Strategic Issues*, Fondazione Eni Enrico Mattei, Nota di lavoro 44.94 (1994).
- Economic Commission for Europe, *Market Trends for Selected Chemical Products 1985-1990 and Prospects to 1995*, Geneva: United Nations (1994a).
- Economic Commission for Europe, *The Chemical Industry in 1993: Annual Review (Production and Trade Statistics 1990-1992)*, Geneva: United Nations (1994b).
- Eisenberger, Peter M., ed., *Basic Research Needs for Environmentally Responsive Technologies of the Future: An Integrated Perspective of Academic, Industrial, and Government Researchers*, Princeton Materials Institute, Princeton University (1996).
- Enos, J. L. and W. -H. Park, *The Adoption and Diffusion of Imported Technology: The Case of Korea*, London: Routledge (1988).
- Fertiliser International, "The Environmental Advantages of Nitrophosphates," *Fertiliser International*, 334, June (1994).

- Flagan, Richard C. and John H. Seinfeld, *Fundamentals of Air Pollution Engineering*, Englewood Cliffs, New Jersey: Prentice Hall (1988).
- Fogler, H. Scott, *Elements of Chemical Reaction Engineering, Second Edition*, Englewood Cliffs, New Jersey: Prentice Hall (1992).
- Foray, Dominique and Arnulf Grübler, "Morphological Analysis, Diffusion and Lock-out of Technologies: Ferrous Casting in France and the FRG," *Research Policy*, **19**, 535-550 (1990).
- Freeman, Christopher, *The Economics of Industrial Innovation, Second Edition*. London: Pinter Publishers (1982).
- Frosch, Robert A., "The Industrial Ecology of the 21st Century," *Scientific American*, **273** (3), 144-147 (1995).
- Gibbons, Michael, Camille Limoges, Helga Nowotny, Simon Schwartzman, Peter Scott, and Martin Trow, *The New Production of Knowledge*, London: SAGE Publications (1994).
- Graedel, T. E. and B. R. Allenby, *Industrial Ecology*, Englewood Cliffs, New Jersey: Prentice Hall (1995).
- Gray, Wayen B. and Ronald J. Shadbegian, *Pollution Abatement Costs, Regulation, and Plant-Level Productivity*, National Bureau of Economic Research, Working Paper No. 4994 (1995).
- Green, Kenneth and Alan Irwin, "Clean Technologies," in Peter Groenewegen, Kurt Fischer, Edith G. Jenkins, and Johan Schot, eds., *The Greening of Industry Resource Guide and Bibliography*, Washington, D.C.: Island Press (1996).
- Green, Kenneth, Andrew McMeekin, and Alan Irwin, "Technological Trajectories and R&D for Environmental Innovation in UK Firms," *Futures*, **26** (10), 1047-1059 (1994).
- Hahn, Robert W., ed., *Risks, Costs, and Lives Saved: Getting Better Results from Regulation*, Oxford University Press (1996).
- Harrison, Andy, "Waste Treatment: Legislation Propels New Technologies," *Pulp & Paper*, **68** (7) (1994).
- Henderson, Rebecca and Iain Cockburn, "Scale, Scope, and Spillovers: the Determinants of Research Productivity in Drug Discovery", *RAND Journal of Economics*, **27** (1), 32-59 (1996).
- Hileman, Bette, "Debate Over Phaseout of Chlorine, Chlorinated Organics Continues," *Chemical & Engineering News*, **71** (49), 31-32, December 6 (1993).
- Hileman, Bette, "Basic Research Needs For Future Environmental Technologies Emerge," *Chemical & Engineering News*, **74** (6), 26-27, February 5 (1996).
- Hummels, Henning, *Impending Losses of Sales as a Stimulus to Ecologically Conscious Behaviour of Multinational Corporations*, Discussion Paper 1997/01, Wirtschaftswissenschaftlichen Dokumentation, Technischen Universität Berlin (1997).
- Ichikawa, Shin, "Mizu Kankyo Hozen no Kagaku Gijutsu (Chemical Technologies for the Protection of the Water Environment)," in Tadao Yoshida, ed., *Kankyo Hozen no Kagaku Gijutsu* (Chemical Technologies for Environmental Protection), Tokyo: Maruzen (1981).
- Jaffe, Adam B. and Karen Palmer, *Environmental Regulation and Innovation: A Panel Data Study*, National Bureau of Economic Research, Working Paper No. 5545 (1996).
- Kelham, Steve, "Chlor-alkali Products," in Alan Heaton, ed., *An Introduction to Industrial Chemistry, Third Edition*, Glasgow: Blackie Academic & Professional (1996).
- Kemp, René, "An Economic Analysis of Cleaner Technology: Theory and Evidence," in Kurt Fischer and Johan Schot, eds., *Environmental Strategies for Industry: International Perspectives on Research Needs and Policy Implications*, Washington, D.C.: Island Press (1993).
- Kemp, René, *Environmental Policy and Technical Change: A Comparison of the Technological Impact of Policy Instruments*, Maastricht, The Netherlands: Universitaire Pers Maastricht (1995).

- Kirschner, Elisabeth M., "Chemical Industry Modernizes Aging Plants For Safety And Efficiency," *Chemical & Engineering News*, July 10, 14-18 (1995).
- Koch, T. A., K. R. Krause, L. E. Manzer, M. Mehdizadeh, J. M. Odom, and S. K. Sengupta, "Environmental Challenges Facing the Chemical Industry," *New Journal of Chemistry*, **20**, 163-173 (1996).
- Kodama, Fumio, *Emerging Pattern of Innovation: Sources of Japan's Technological Edge*, Boston: Harvard Business School Press (1995).
- Kumar, Ritu, *Environmental Policies and Industrial Development: Are They Compatible?*, Global Forum on Industry, Vienna: United Nations Industrial Development Organization (1995).
- Lanjouw, Jean Olson and Ashoka Mody, "Innovation and the International Diffusion of Environmentally Responsive Technology," *Research Policy*, **25**, 549-571 (1996).
- Levenspiel, Octave, *Chemical Reaction Engineering, Second Edition*, New York: John & Wiley Sons (1972).
- Lewis, Tracy R., "Protecting the environment when costs and benefits are privately known," *RAND Journal of Economics*, **27** (4), 819-847 (1996).
- Low, Patrick and Alexander Yeats, "Do 'Dirty' Industries Migrate?," in Patrick Low, ed., *International Trade and the Environment*, World Bank, Discussion Paper 159 (1992).
- Mizsey, Peter, "Waste Reduction in the Chemical Industry: A Two Level Problem," *Journal of Hazardous Materials*, **37**, 1-13 (1994).
- Moghissi, A. Alan, "Chlorine: A Clash Between Environmental Science and Environmental Advocacy," *Environment International*, **21** (6), 759-760 (1995).
- Nakajima, Koe, "Recent Trends of Steel Science and Technology for Environmental Strategy," *Journal of Materials Processing Technology*, **59**, 221-232 (1996).
- Nakanishi, Junko, "Gijutsu-ya no Kankyo Seisaku Iron, No. 2: Suigin Kisei to Nihon-teki Taishitsu (A Technologist's Essay on Environmental Policy, No. 2: Mercury Regulation and the Japanese Characteristics)," *Sekai*, **577** (2), 349-357 (1993).
- Nelson, Richard R. and Sidney G. Winter, *An Evolutionary Theory of Economic Change*, The Belknap Press of Harvard University Press (1982).
- Organization for Economic Co-operation and Development, *Pollution Abatement and Control Expenditure in OECD Countries*, Environmental Monograph, Paris: Organization for Economic Co-operation and Development (1996).
- Palmer, Karen, Wallace E. Oates, and Paul R. Portney, "Tightening Environmental Standards: The Benefit-Cost or the No-Cost Paradigm?," *Journal of Economic Perspectives*, **9** (4), 119-132 (1995).
- Porteous, Andrew, *Dictionary of Environmental Science and Technology, Second Edition*, Chichester, UK: John Wiley & Sons (1996).
- Porter, Michael and Claas van der Linde, "Green and Competitive: Ending the Stalemate," *Harvard Business Review*, September-October, 120-134 (1995a).
- Porter, Michael and Claas van der Linde, "Toward a New Conception of the Environment-Competitiveness Relationship," *Journal of Economic Perspectives*, **9** (4), 97-118 (1995b).
- Repetto, Robert, Paul Faeth, Dale Rothman, and Duncan Austin, *Has Environmental Protection Really Reduced Productivity Growth?: We Need Unbiased Measures*, World Resources Institute (1996).
- Rhodes, Anne K., "Technology, efficient operation key elements in environmental strategy," *Oil & Gas Journal Special*, **91** (48), 39-49 (1993).
- Robinson, James C., "The Impact of Environmental and Occupational Health Regulation on Productivity Growth in U.S. Manufacturing," *The Yale Journal of Regulation*, **12**, 387-434 (1995).
- Rushton, Brian M., "How Protecting the Environment Impacts R&D in the United States," *Research • Technology Management*, **36** (3), 13-21 (1993).

- Saxena, S. K. and Kavita Mehra, "Nitrogenous Fertilizer Industries: Safety and Prevention of Environmental Hazards", *Chemical Engineering World*, **29** (11), 77-79 (1994).
- Shiroki, Hiroyuki, Yasuhide Noaki, Mitsuru Katayose, and Akio Kashiwada, "Improvement of Electrolyzer and Ion Exchange Membrane for High-efficiency Chlorine and Caustic Soda Production", *Modern Chlor-Alkali Technology*, **6**, 222-233 (1995).
- Simpson, R. David, *Environmental Policy, Innovation, and Competitiveness Advantage*, Resources for the Future, Discussion Paper 95-12 (1995).
- Society of Environmental Toxicology and Chemistry, *A Technical Framework for Life-Cycle Assessment*, Washington, DC: Society of Environmental Toxicology and Chemistry (1991).
- Soete, Luc and Anthony Arundel, "European Innovation Policy for Environmentally Sustainable Development: Application of a Systems Model of Technical Change", *Journal of European Public Policy*, **2** (2), 285-315 (1995).
- Suckling, C. J., "Clean Synthesis," in Kirkwood, R. C. and A. J. Longley, eds., *Clean Technology and the Environment*, Glasgow: Blackie Academic & Professional (1994).
- Tobey, James A., "The Effects of Domestic Environmental Policies on Patterns of World Trade: An Empirical Test," *Kyklos*, **43** (2), 191-209 (1990).
- United Nations Environment Programme Industry and Environment, *The Textile Industry and the Environment*, Paris: United Nations Environment Programme (1993).
- United Nations Industrial Development Organization, *Industry and Development: Global Report 1993/94*, Vienna: United Nations Industrial Development Organization (1993).
- United Nations Industrial Development Organization, *Pollution Prevention and Abatement Guidelines for the Petroleum Refining Industry*, Vienna: United Nations Industrial Development Organization (1994).
- United Nations Industrial Development Organization, *Pollution Prevention and Abatement Guidelines for the Iron and Steel Industry*, Vienna: United Nations Industrial Development Organization (1995).
- United States Environmental Protection Agency, *Industry Sector Notebook: The Inorganic Chemicals Industry*, Washington, D.C.: United States Environmental Protection Agency (1995a).
- United States Environmental Protection Agency, *Industry Sector Notebook: The Iron and Steel Industry*, Washington, D.C.: United States Environmental Protection Agency (1995b).
- United States Environmental Protection Agency, *Industry Sector Notebook: The Organic Chemicals Industry*, Washington, D.C.: United States Environmental Protection Agency (1995c).
- United States Environmental Protection Agency, *Industry Sector Notebook: The Petroleum Refining Industry*, Washington, D.C.: United States Environmental Protection Agency (1995d).
- United States Environmental Protection Agency, *Industry Sector Notebook: The Pulp and Paper Industry*, Washington, D.C.: United States Environmental Protection Agency (1995e).
- World Commission on Environment and Development, *Our Common Future*, Oxford: Oxford University Press (1987).
- Xing, Yuqing and Charles D. Kolstad, *Do Lax Environmental Regulations Attract Foreign Investment?*, University of California at Santa Barbara, Department of Economics, Working Paper in Economics 6-95 (1995).
- Yosie, Terry F., "The Changing Landscape of the Chlorine Debate", *Environmental Science and Technology*, **30** (11), 498A-501A (1996).