Chapter 14

Green Engineering

Industrial Ecology

14.1 Introduction

The environmental performance of chemical processes is governed not only by the design of the process, but also by how the process integrates with other processes and material flows. Consider a classic example - the manufacture of vinyl chloride.

Billions of pounds of vinyl chloride are produced annually. Approximately half of this production occurs through the direct chlorination of ethylene. Ethylene reacts with molecular chlorine to produce ethylene dichloride (EDC). The EDC is then pyrolyzed, producing vinyl chloride and hydrochloic acid.

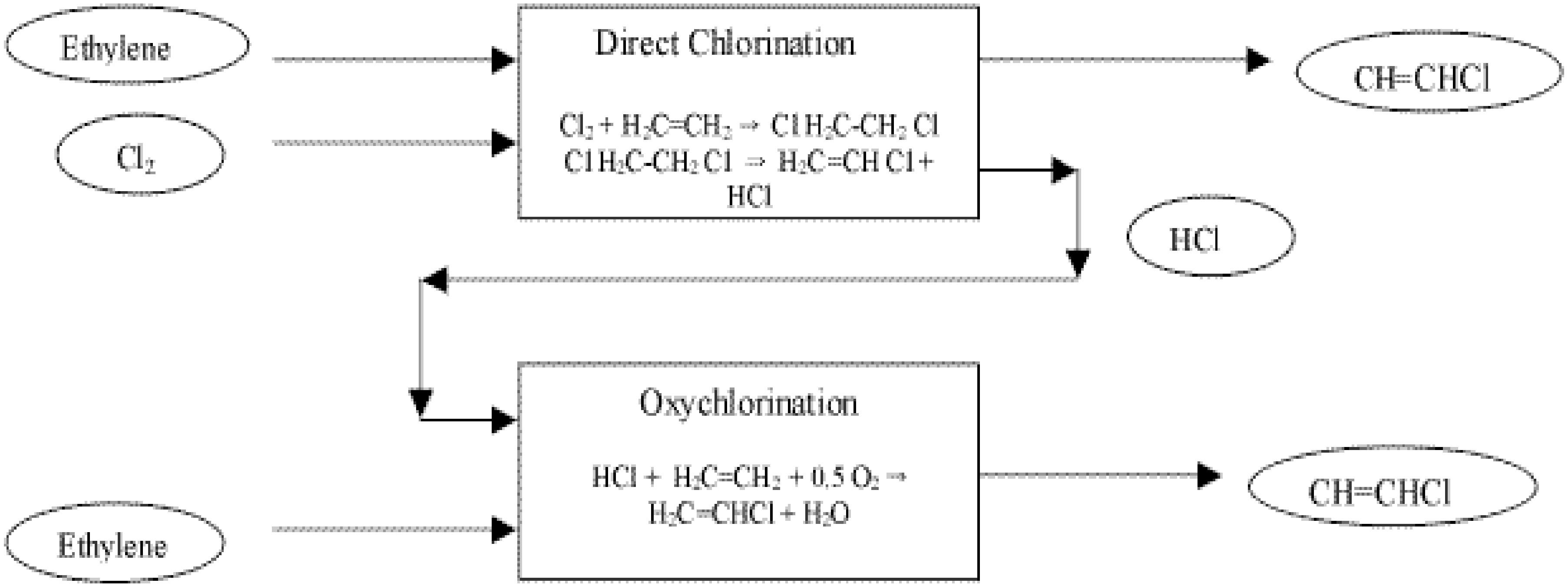
$$Cl_2 + H_2C{=}CH_2 \rightarrow Cl\text{-}H_2C\text{-}CH_2\text{-}Cl$$
$$Cl\text{-}H_2C\text{-}CH_2\text{-}Cl \rightarrow H_2C{=}CHCl + HCl$$

In this synthesis route, one mole of hydrochloric acid is produced for every mole of vinyl chloride. Considered in isolation, this process might be considered wasteful. Half of the original chlorine winds up, not in the desired product, but in a waste acid. But the process is not operated in isolation. The waste hydrochloric acid from the direct chlorination of ethylene can be used as a raw material in the oxychlorination of ethylene. In this process, hydrochloric acid, ethylene and oxygen are used to manufacture vinyl chloride.

$$HCl + H_2C{=}CH_2 + 0.5\ O_2 \rightarrow H_2C{=}CHCl + H_2O$$

By operating both the oxychlorination pathway and the direct chlorination pathway, as shown in Figure 14.1-1, the waste hydrochloric acid can be used as a raw material and essentially all of the molecular chlorine originally reacted with ethylene is incorporated into vinyl chloride. The two processes operate synergistically and an efficient design for the manufacture of vinyl chloride involves both processes.

Figure 14.1-1 Byproduct hydrochloric acid from the direct chlorination of ethylene is used as a raw material in the oxychlorination process; by operating the two processes in tandem, chlorine is used efficiently.



Additional efficiencies in the use of chlorine can be obtained by expanding the number of processes included in the network. In the network involving direct chlorination and oxychlorination processes, both processes incorporate chlorine into the final product. Recently, more extensive chlorine networks have emerged linking several isocyanate producers into vinyl chloride manufacturing networks (McCoy, 1998). In isocyanate manufacturing, chlorine is reacted with carbon monoxide to produce phosgene:

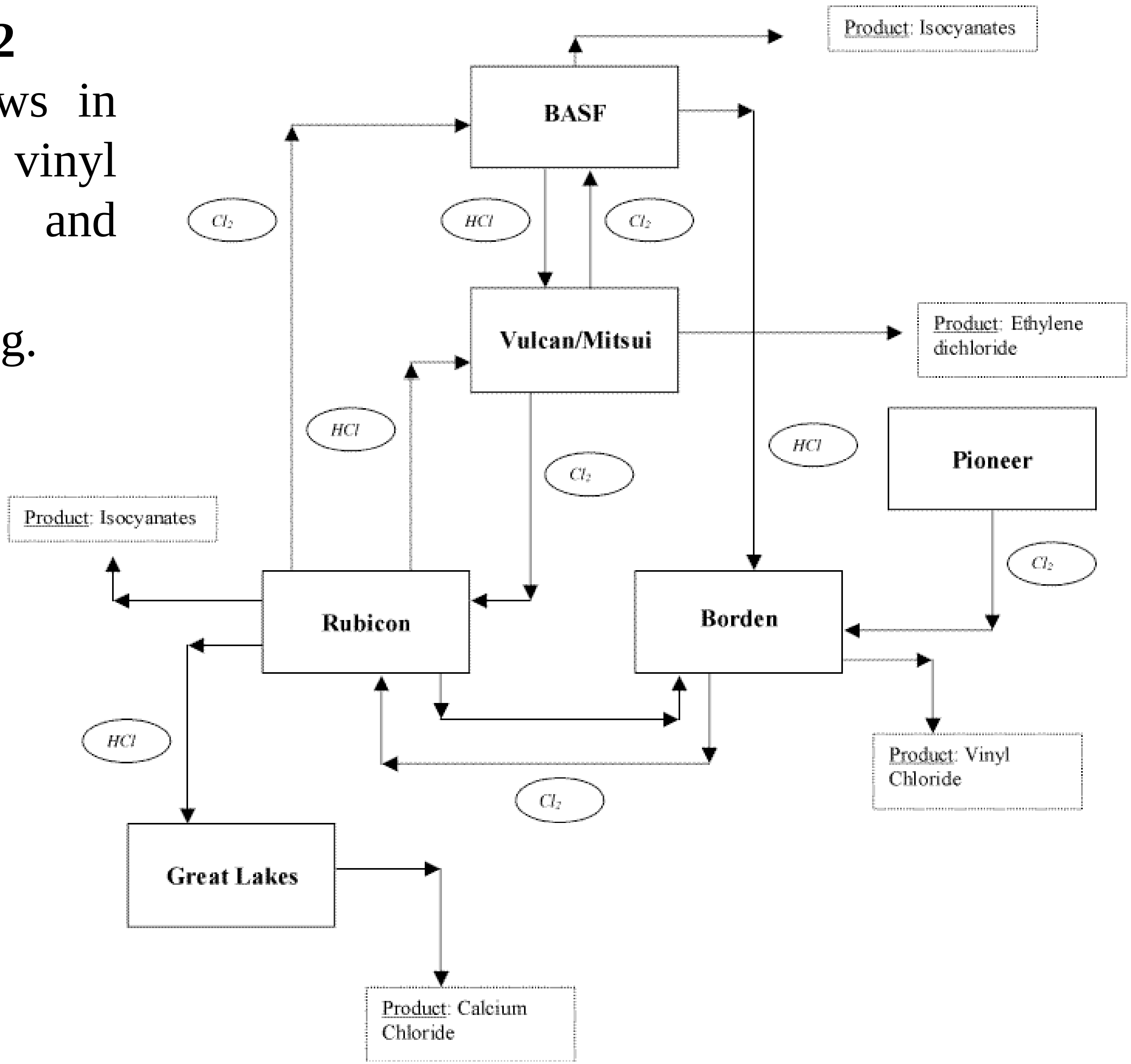
$$CO + Cl_2 \rightarrow COCl_2$$

The phosgene is then reacted with an amine to produce an isocyanate and byproduct hydrochloric acid:

$$RNH_2 + COCl_2 \rightarrow RNCO + 2\ HCl$$

The isocyanate is subsequently used in urethane production, and the hydrochloric acid is recycled. The key feature of the isocyanate process chemistry is that chlorine does not appear in the final product. Thus, chlorine can be processed through the system without being consumed. It may be transformed from molecular chlorine to hydrochloric acid, but the chlorine is still available for incorporation into final products, such as vinyl chloride, that contain chlorine. A chlorine-hydrogen chloride network incorporating both isocyanate and vinyl chloride has developed in the Gulf Coast of the United States. The network is shown in Figure 14.1-2. Molecular chlorine is manufactured by Pioneer and Vulcan Mitsui. The molecular chlorine is sent to both direct chlorination processes and to isocyanate manufacturing. The byproduct hydrochloric acid is sent to oxychlorination processes or calcium chloride manufacturing. The network has redundancy in chlorine flows, such that most processes could rely on either molecular chlorine or hydrogen chloride.

Figure 14.1-2
Chlorine flows in combined vinyl chloride and isocyanate manufacturing.



Consider the advantages of this network to the various companies (Francis, 2000). Vulcan/Mitsui effectively rents chlorine to BASF and Rubicon for their isocyanate manufacturing; the chlorine is then returned in the form of hydrochloric acid for ethylene dichloride/vinyl chloride manufacturing. BASF and Rubicon have guaranteed supplies of chlorine and guaranteed markets for their byproduct HCl.

Even more complex networks could, in principle be constructed. As shown in Table 14.1-1, chlorine is used in manufacturing a number of non-chlorinated products. Table 14.1-1 lists, for selected reaction pathways, the pounds of chlorinated intermediates used along the supply chain, per pound of finished product. This ranking provides one indication of the potential for networking these processes with processes for manufacturing chlorinated products (see Rudd, et al., or Chang, 1996).

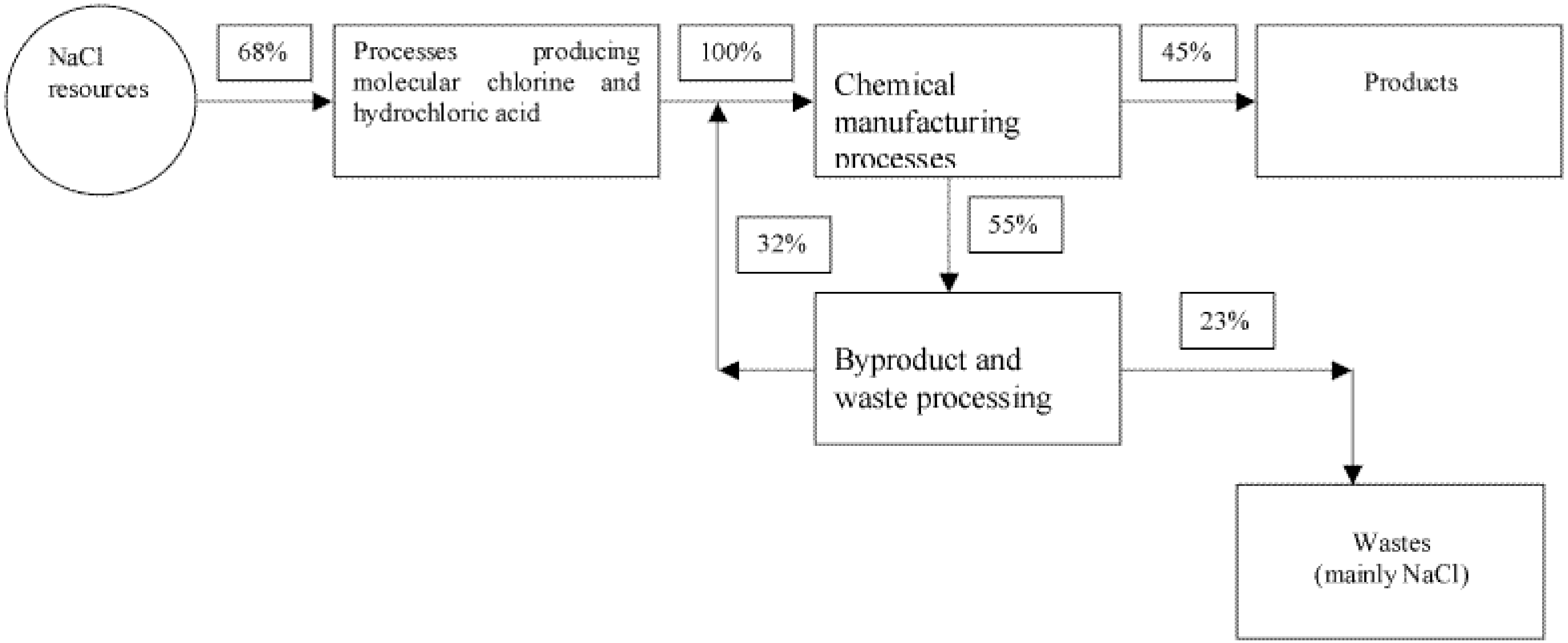
Table 14.1-1 Partial listing of non-chlorinated chemical products that utilize chlorine in their manufacturing processes (Chang, 1996).

Product	Synthesis pathway	Pounds of chlorinated intermediates per pound of product
Glycerine	Hydrolysis of epichlorohydrin	4.3
Epoxy resin	Epichlorohydrin via chlorohydrination of Allyl chloride, followed by reaction of epichlorohydrin with bisphenol-A	2.3
Toluene diisocyanate	Phosgene reaction with toluenediamine	2.2
Aniline	Chlorobenzene via chlorination of benzene, followed by reaction of chlorobenzene with ammonia	2.2
Phenol	Chlorobenzene via chlorination of benzene, followed by dehydrochlorination of chlorobenzene	2.1
Methylene diphenylene diisocyanate	Phosgene reaction with aniline (also produced with chlorinated intermediates)	1.5
Propylene oxide	Chlorohydration of propylene	1.46

An examination of individual processes, such as those listed in Table 14.1-1, can be useful in building process networks, but the individual process data do not reveal whether efficient use of chlorine is a major or a minor issue in chemical manufacturing. To determine the overall importance of these flows, it is useful to consider an overall chlorine balance for the chemical industry. The overall flows of chlorine into products and wastes, as well as the recycling of chlorine in the chemical manufacturing sector, is shown in Figure 14.1-3.

The data indicate that roughly a third of the total chlorine, eventually winds up in wastes. By employing the types of networks shown in Figures 14.1-1 and 14.1-2, the total consumption of chlorine could be reduced.

Figure 14.1-3 A summary of flows of chlorine in the European chemical manufacturing industry (Francis, 2000).



Identifying which processes could be most efficiently integrated is not simple and the design of the ideal network depends on available markets, what suppliers and markets for materials are nearby, and other factors. What is clear, however, is that the chemical process designers must understand not only their process, but also processes that could supply materials, and processes that could use their byproducts. And, the analysis should not be limited to chemical manufacturing.

Continuing with our example of waste hydrochloric acid and the manufacture of vinyl chloride, by-product hydrochloric acid could be used in steel making or by-product hydrochloric acid from semiconductor manufacturing might be used in manufacturing chemicals.

Finding productive uses for byproducts is a principle that has been used for decades in chemical manufacturing. What is relatively new, however, is the search for chemical byproduct uses in industries that extend far beyond chemical manufacturing. This chapter will examine both of these topics - the overall flows of raw materials, products and by-products in chemical manufacturing industries - as well as the potential for combining material and energy flows in chemical manufacturing with material and energy flows in other industrial sectors. Variously called by-product synergy, zero waste systems, or even industrial ecology, the goal of this design activity is to create industrial systems that are as mass efficient as possible.

Section 14.2 provides an overview of material flows in chemical manufacturing and describes analysis methods that can be used to optimize flows of materials.

Section 14.3 examines case studies of exchanges of materials and energy across industrial sectors and the emerging concept of eco-industrial parks.

Finally, section 14.4 briefly attempts to assess the potential benefits of by-product synergies.

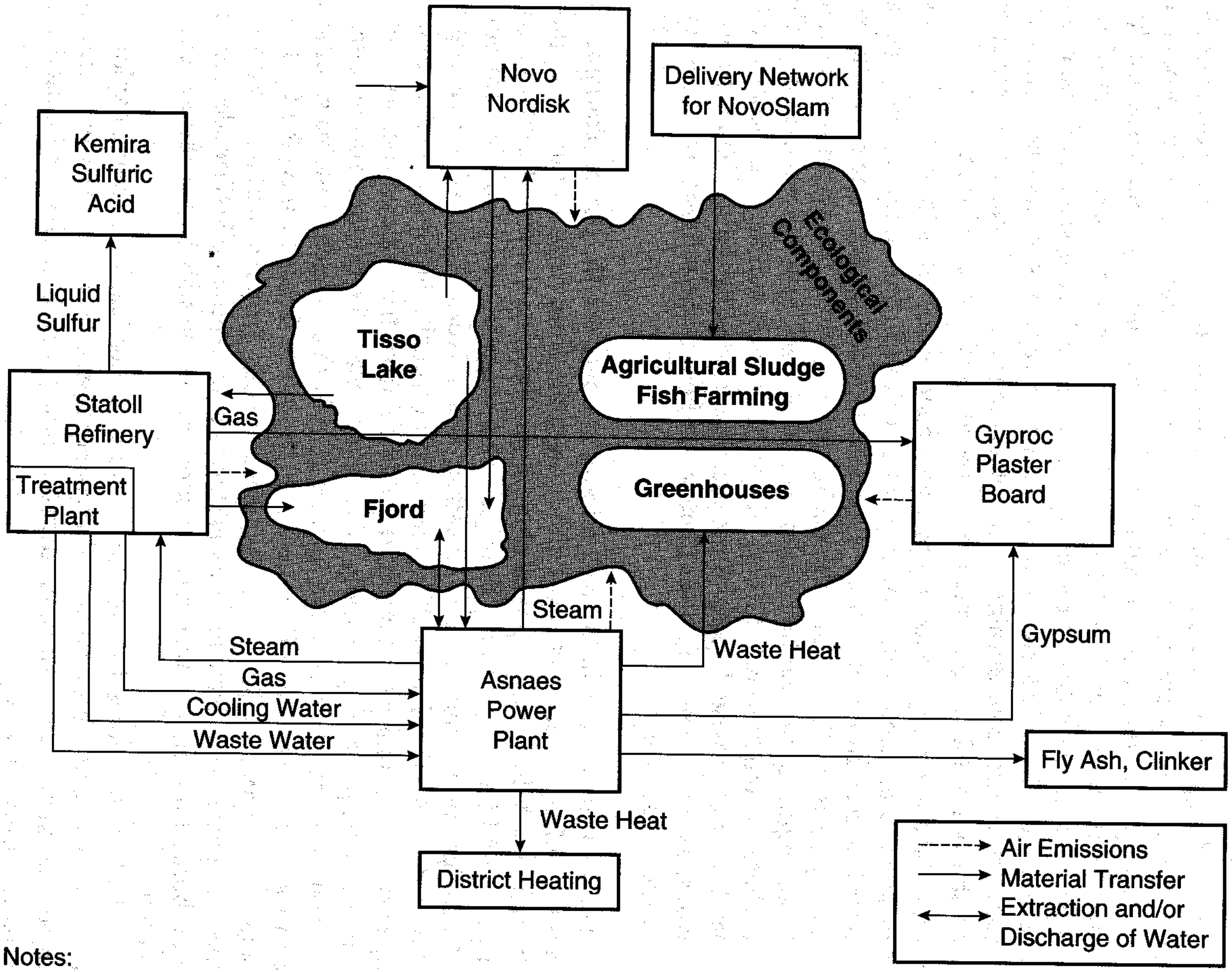
What is Industrial Ecology?

The phrase Industrial Ecology evokes powerful images and strong reactions, both positive and negative. To some, the phrase conjures images of industrial systems that mimic the mass conservation properties of natural ecosystems. Powerful analogies can be drawn between the evolution of natural ecosystems and the potential evolution of industrial systems. Billions of years ago, the Earth's life forms consumed the planet's stocks of materials and changed the composition of the atmosphere. Our natural ecosystems evolved slowly to the intricately balanced, mass conserving networks that exist today. Can our industrial systems evolve in the same way, but much more quickly? These are interesting visions and thought provoking concepts. But, is Industrial Ecology merely a metaphor for these concepts? Is there any engineering substance to the emerging field of Industrial Ecology? As demonstrated in this Chapter, Industrial Ecology is much more than a metaphor and it is a field where engineers can make significant contributions. At the heart of Industrial Ecology is the knowledge of how to reuse or chemically modify and recycle wastes - making wastes into raw materials. Chemical engineers have practiced this art for decades.

The history of the chemical manufacturing industries provides numerous examples of waste streams finding productive uses. Nonetheless, even though the chemical manufacturing industries now provide excellent case studies of Industrial Ecology in practice - networked and mass efficient processes - there is much left to be done. While the chemical manufacturing industries are internally integrated, there is relatively little integration between chemical manufacturing and other industrial sectors and between chemical manufacturers and their customers.

Engineers could take on design tasks such as managing the heat integration between a power plant and an oil refinery or integrating water use between semiconductor and commodity material manufacturing. The goal is to create even more intricately networked and efficient industrial processes - an industrial ecology. Not all of the tools needed to accomplish these goals are available yet, but this Chapter begins to describe the basic concepts and suggests the types of tools that the next generation of process engineers will require.

Figure 14.3-1 The industrial network at Kalundborg, Denmark. (Ehrenfeld and Gertler, 1997)



Notes:
(1) This figure is not drawn to scale, nor is it an accurate geographic depiction.
(2) Unused residuals resulting from all activities in the industrial ecopark are eventually released into the biosphere.

Industrial Symbiosis

EXCHANGE OF RESOURCES

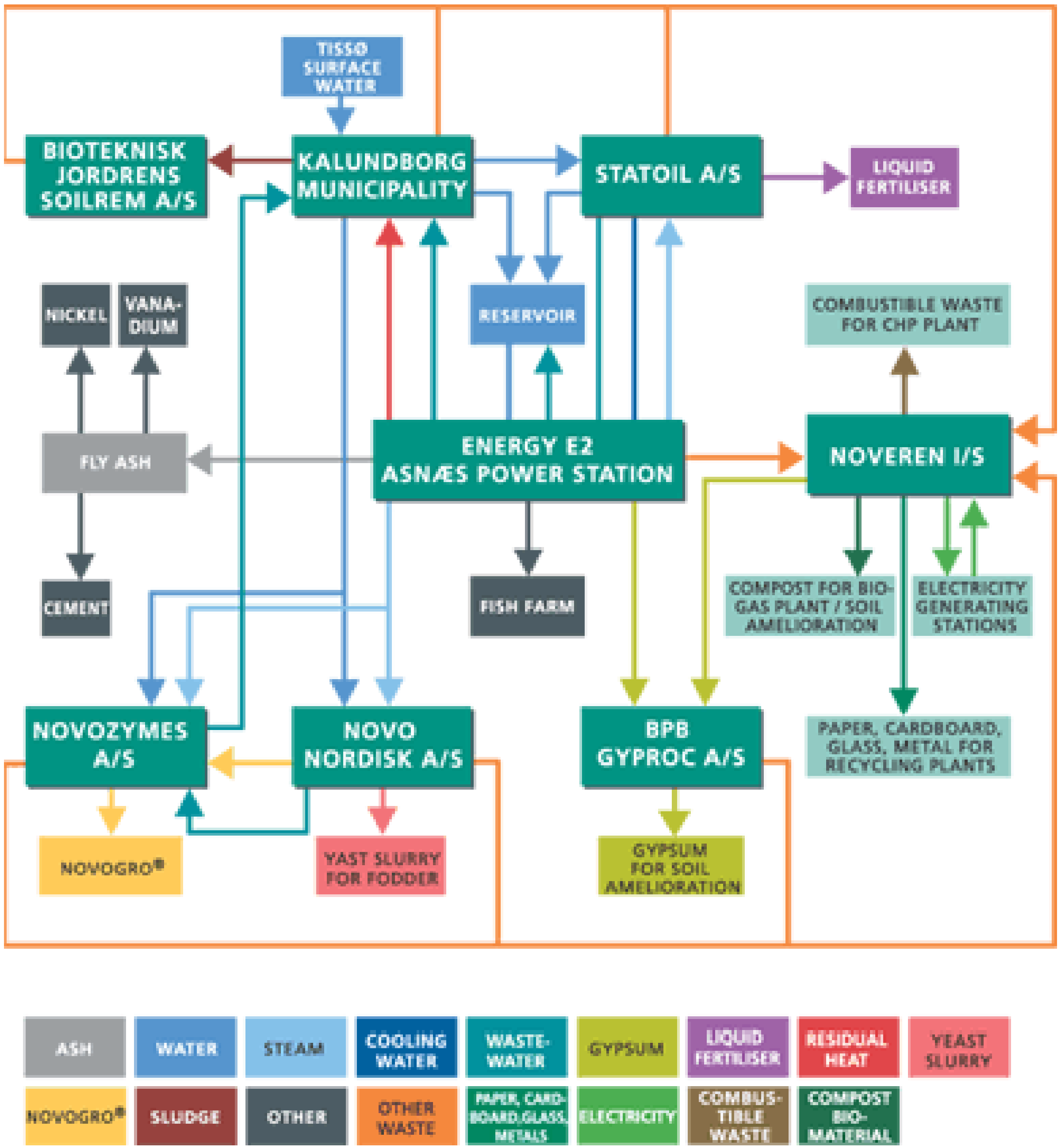
http://www.symbiosis.dk/

Industrial Symbiosis

Symbiosis means co-existence between diverse organisms in which each may benefit from the other. In this context, the term is applied about the industrial co-operation taking place in Kalundborg between a number of companies and Kalundborg Municipality, all of which exploit each otherís residual or by-products mutually.

The Symbiosis co-operation has developed spontaneously over a number of decades and today comprises some 20 projects. The exchange of residual products between the companies is laid out in the diagram.

All projects are environmentally and financially sustainable.



TISSØ SURFACE WATER
BIOTEKNISK JORDRENS SOILREM A/S
KALUNDBORG MUNICIPALITY
STATOIL A/S
LIQUID FERTILISER
NICKEL
VANA-DIUM
RESERVOIR
COMBUSTIBLE WASTE FOR CHP PLANT
FLY ASH
ENERGY E2 ASNÆS POWER STATION
NOVEREN I/S
CEMENT
FISH FARM
COMPOST FOR BIO-GAS PLANT / SOIL AMELIORATION
ELECTRICITY GENERATING STATIONS
NOVOZYMES A/S
NOVO NORDISK A/S
BPB GYPROC A/S
PAPER, CARDBOARD, GLASS, METAL FOR RECYCLING PLANTS
NOVOGRO®
YAST SLURRY FOR FODDER
GYPSUM FOR SOIL AMELIORATION
ASH
WATER
STEAM
COOLING WATER
WASTE-WATER
GYPSUM
LIQUID FERTILISER
RESIDUAL HEAT
YEAST SLURRY
NOVOGRO®
SLUDGE
OTHER
OTHER WASTE
PAPER, CARD-BOARD,GLASS, METALS
ELECTRICITY
COMBUS-TIBLE WASTE
COMPOST BIO-MATERIAL

Networking

The Industrial Symbiosis of Kalundborg is built as a network co-operation between six processing companies, one waste handling company and the Municipality of Kalundborg.

The philosophy behind the Symbiosis is that the six companies: **Energy E2** Asnæs Power Station, the plasterboard factory **BPB Gyproc A/S**, the pharmaceutical plant **Novo Nordisk A/S**, the enzyme producer **Novozymes A/S**, the oil refinery **Statoil A/S, Bioteknisk Jordrens Soilrem A/S** as well as the waste company **Noveren I/S** and **Kalundborg Municipality** - exploit each other's residual or by-products on a commercial basis.

One company's by-product becomes an important resource to one or several of the other companies. The outcome is reduced consumption of resources and a significant reduction in environmental strain. The collaborating partners also benefit financially from the co-operation because the individual agreement within the Symbiosis is based on commercial principles.

Steam and Heat

Asnæs Power Station produces heat for the city of Kalundborg and process steam for the Statoil Refinery, Novo Nordisk A/S and for Novozymes A/S. The combination of heat and power production results in a 30% improvement of fuel utilisation compared to a separate production of heat and power.

Approximately 4,500 households in Kalundborg receive district heat from Asnæs Power Station. District heat has replaced approx. 3,500 small oil-fired units.

Statoil Refinery receives process steam and water from Asnæs Power Station. The steam covers about 15% of the refinery's total consumption of steam. The refinery uses the steam for heating oil tanks, pipelines etc. Novozymes A/S and Novo Nordisk A/S use steam from Asnæs Power Station for the heating and sterilisation of the processing plants.

Some of the cooling water from Asnæs Power Station is used by a fish farm producing 200 tonnes of trout and salmon on a yearly basis. The fish have better growth conditions in the heated water.

Profits

Total water consumption

The Symbiosis companies have reduced the overall consumption by 25% by recycling the water and by letting it circulate between the individual Symbiosis partners. A total of 1.9 mio cubic metres of ground water and 1 mio cubic metres of surface water are saved on a yearly basis.

Oil

The Symbiosis partners have reduced their oil consumption by 20,000 tonnes per year, corresponding to a 380-tonne reduction of sulphur dioxide outlet on a yearly basis. The major reductions have been achieved by Novozymes A/S, Novo Nordisk A/S and Statoil that have used process steam from the production at Asnæs Power Station.

Ash

The combustion of coal and orimulsion at Asnæs Power Station results in approx. 80,000 tonnes of ash, which are used in the construction and cement industries for the manufacturing of cement or the extraction of nickel and vanadium.

Profits

Gypsum
Every year BPB Gyproc A/S receives up to 200,000 tonnes of gypsum from Asnæs Power Station. This figure corresponds to the large majority of the companyís annual consumption. The gypsum substitutes the natural gypsum used in the production of plasterboards.

NovoGro®
NovoGro® from Novozymes A/S substitutes the use of lime and part of the commercial fertiliser on approximately 20,000 hectares of farmland.

Wastewater
The collaboration of Novozymes A/S, Asnæs Power Station and Kalundborg Municipality, in the area of wastewater treatment, reduces the environmental impact on Jammerland Bugt considerably.

Sludge
The recycling of sludge stemming from the treatment plant brings about a reduction in production time at A/S Bio-teknisk Jordrens Soilrem, synonymous with expenditure cuts and improved economy.

Other Waste:

On a yearly basis, Noveren I/S receives:

- 13,000 tonnes of newspaper / cardboard which after a quality check are sold to cardboard and paper consuming industries in Denmark, Sweden and Germany producing new paper, new cardboard, egg boxes and trays for e.g. the health sector.

- 7,000 tonnes of rubble and concrete that are used for different surfaces after crushing and sorting.

- 15,000 tonnes of garden / park refuse delivered as soil amelioration in the area.

- 4,000 tonnes of bio waste from households and company canteens. The bio waste is used in the compost and biogas production.

- 4,000 tonnes of iron and metal, which is resold after cleaning for recycling.

- 1,800 tonnes of glass and bottles that are sold to producers of new glass.

Advantages of the Symbiosis

The exchange of resources between industrial companies provides a number of advantages:

- Recycling of by-products. The by-product of one company becomes an important resource for another company.

- Reduced consumption of resources, e.g. water, coal, oil, gypsum, fertiliser, etc.

- Reduced environmental strain: reduced CO_2 and SO_2 emissions, reduced discharges of wastewater and less pollution of watercourses etc.

- Improved utilisation of the energy resources. Waste gases are used in the energy production.

Criteria for Symbiosis

The philosophy behind the Industrial Symbiosis can be used to advantage in other areas of industry. The Kalundborg experience, however, demonstrates that a number of conditions must be fulfilled:

The companies must fit each other

An industrial symbiosis can only work, given the right composition of industries in one area. One companyís residual products must take the place of another companyís raw material. Diversity within the local industrial structure is therefore an important must in an industrial symbiosis.

The companies must be located near each other

The physical distance between the individual companies is of great importance. The transport of residual products over large distances is seldom profitable which means that the distance must be as short as possible. Experience from Kalundborg demonstrates that the geographical distance is the most important parameter when energy is exchanged between the companies. Other by-products can be transported to advantage over larger distances.

There must be openness between the companies

Today the basis of the Symbiosis co-operation of Kalundborg is openness, communication and mutual trust between the partners. The Kalundborg companies are located in a small community that has helped establish fine conditions for open and intimate working relations.

SYMBIOSIS PARTNERS

KALUNDBORG KOMMUNE

ENERGI E2

Bioteknisk Jordrens
SOILREM
- iordens bedste valg

STATOIL

novo nordisk®

BPB Gyproc

Noveren I/S

novozymes®

Final Examination

Date: June 13, 2011 (Mon)

Time: 9:30-11:30 am

Place: 302-720

Open book, notebook,

Take a calculator